Dipyridocatecholate-Bridged Complexes of Platinum and Ruthenium Diimine Chromophores

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Received November 18, 1997

New Ru−Pt heterometallic complexes have been prepared and their electrochemical and luminescence properties characterized. One series of complexes contains a tris diimine-chelated Ru(II) center linked to one, two, or three Pt(II) diimine moieties via a dipyridocatecholate (dpcat; 1,10-phenanthroline-5,6-diolate) bridging ligand, as indicated by the general formula $[(dbbpy)_{3-n}Ru((\mu\text{-dpcat})Pt(dbbpy))_n](PF_6)_2$ ($n = 1-3$) where dbbpy = di-*tert*-butylbipyridine. A different dinuclear complex has a tetrapyridophenazine (tppz) bridge connecting a Ru(diimine)$_3^{2+}$ chromophore with a Pt diimine dithiolate center and has the formula $[(dbbpy)_2Ru(\mu\text{-tppz})Pt(tdt)]^{2+}$ where tdt = toluene-3,4-dithiolate. The dpcat-bridged complexes exhibit numerous redox processes that are assigned on the basis of comparison of those shown by mononuclear precursors and analogues, i.e., Ru(diimine)$_3^{2+}$ and Pt(dbbpy)(dpcat). The dpcat-bridged complexes display distinct absorption bands due to Ru(diimine)$_3^{2+}$ and Pt(diimine)(diolate) chromophores at ca. 450 and 540 nm, respectively. Emission from the Pt center is observed at 77 K (but not at room temperature in fluid solution) upon direct irradiation of this center as well as excitation of the Ru center. The latter suggests the occurrence of energy transfer between Ru- and Pt-based components. The energy transfer appears to be efficient, but not complete for the dinuclear species $[(dbbpy)_2Ru(\mu\text{-dpcat})Pt(dbbpy)](PF_6)_2$, as indicated by residual Ru emission from this complex. In contrast with the observation of a Pt-based emission from the bridged dinuclear complexes, the mononuclear complex Pt(dbbpy)(dpcat) does not luminesce, even in rigid media at low temperature. The spectroscopic properties of the tppz-bridged complex $[(dbbpy)_2Ru(\mu\text{-tppz})Pt(tdt)]^{2+}$ are very similar to those of $[(dbbpy)_2Ru(\mu\text{-dpcat})Pt(dbbpy)]^{2+}$.

Introduction

A number of recent studies on luminescent transition metal complexes have focused on the design, synthesis, and spectroscopy of multicomponent and supramolecular systems.[1−3] One of the goals of this research is the development of photochemical molecular devices capable of light-to-chemical energy conversion. The majority of the systems reported thus far contain chromophores based on d^6 transition metal ions such as Ru(II), Os(II), and Rh(III) that are interconnected via polypyridyl bridging ligands.[4−19] Photoinduced energy- and electron-transfer processes in these polynuclear complexes have been studied as a function of the distance between chromophoric components, the structure and rigidity of the bridging ligands, the relative energies of the excited states of the chromophores, and the extent of conjugation of the ligand bridges, as well as the temperature and medium of the reaction.

Our interest in luminescent Pt(II) diimine dithiolate complexes[20−22] in which the emissive state is a highly directional charge transfer from an orbital of mixed Pt/S/dithiolate character to a π^*(diimine) orbital has led us to consider the incorporation of this chromophore into multicomponent systems for light-driven chemical reactions. Closely related complexes are the Pt(II) diimine catecholate systems that exhibit solvatochromism

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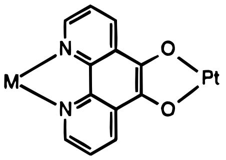
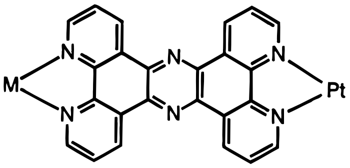
S0020-1669(97)01447-X CCC: $15.00

characteristic of the dithiolate analogues but, unlike the dithiolates, do not luminesce in ambient-temperature fluid solution. Recently we reported the synthesis and characterization of dipyridocatecholate complexes containing Pt(II) and a coordinated di-*tert*-butylbipyridine (dbbpy) ligand and the incorporation of this moiety into bi- and polynuclear complexes.[23] The dpcat ligand serves in these systems as a "polar" bridge with the diolate side of the ligand bound to Pt(II) and the diimine side bound to the other metal as shown in **A**.



A

One of the complexes described in the earlier report had the formula $[(dbbpy)_2Ru(\mu\text{-dpcat})Pt(dbbpy)](PF_6)_2$ and was found to display emission characteristic of a tris diimine-chelated Ru(II) chromophore. Since emission from a $Ru(diimine)_3{}^{2+}$ center was expected to occur at *higher* energy than Pt(diimine)(dithiolate) emissions and since the Pt(diimine)(catecholate) moiety was anticipated to have a charge transfer state at *lower* energies than the corresponding dithiolate complexes, we undertook the preparation and spectroscopic characterization of several closely related complexes. The compounds that serve as the focus of the present report have the formula $[(dbbpy)_{3-n}Ru((\mu\text{-dpcat})Pt(dbbpy))_n](PF_6)_2$ ($n = 1-3$) in which one, two, or three Pt(II) diimine diolate moieties are linked via dpcat bridges to a single tris diimine-chelated Ru(II) center. Comparison of the properties of these complexes with those of the model complexes $[Ru(dbbpy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$, and $Cl_2Pt(\mu\text{-dpcat})Pt(dbbpy)$ makes possible an interesting analysis. Additionally, a Ru−L−Pt binuclear complex containing $Ru(diimine)_3{}^{2+}$ and Pt(II) diimine dithiolate chromophores is described in which L is the symmetrical tetrapyridophenazine (tppz) ligand as shown in **B**. The properties of this complex, $[(dbbpy)_2Ru(\mu\text{-tppz})Pt(tdt)]^{2+}$ (tdt = toluene-3,4-dithiolate), are compared with those of the dpcat-bridged system $[(dbbpy)_2Ru(\mu\text{-dpcat})Pt(dbbpy)]^{2+}$. The important difference between these two complexes lies in the orientation of the Pt(diimine)(dithiolate) and Pt(diimine)(diolate) charge transfers relative to that of the $Ru(diimine)_3{}^{2+}$ moiety. In the μ-tppz case, the charge transfer is directed *toward* the Ru center, whereas, for the dpcat-bridged complexes, the charge transfer is *away* from the Ru center.



B

Experimental Section

Materials and Procedures. Methylene chloride was dried over Na/benzophenone and distilled prior to use. Other high-grade solvents and toluene-3,4-dithiol were purchased from Aldrich and used as received. The complexes $Pt(PhCN)_2Cl_2$,[24] Pt(dpcat)(dbbpy), (tdt)Pt(μ-dpcat)Pt(dbbpy), (dbcat)Pt(μ-dpcat)Pt(dbbpy),[23] and $Ru(DMSO)_4Cl_2$[25] were synthesized according to published protocols. $Ru(DMSO)_2(dbbpy)Cl_2$ was prepared using the procedure reported for the corresponding phenanthroline analogue although with longer reaction time. The complexes $Ru(dbbpy)_2Cl_2$[26] and $[Ru(dbbpy)_2(tppz)](PF_6)_2$[18] were synthesized using the procedures reported for the corresponding bpy complexes.

$[(dbbpy)Ru((\mu\text{-dpcat})Pt(dbbpy))_2](PF_6)_2$. A mixture of 0.070 g (0.103 mmol) of $Ru(DMSO)_2(dbbpy)Cl_2$ and 0.155 g (0.203 mmol) of Pt(dpcat)(dbbpy) in 40 mL of degassed methanol was heated at reflux for 16 h. No significant color change was observed. After the mixture had cooled to room temperature, a 10-fold excess of NH_4PF_6 in 20 mL of methanol was added, followed by just enough water to cause precipitation. The resulting mixture was stirred for 30 min and then filtered through fine filter paper. The solid was washed with a methanolic solution of NH_4PF_6 and then with water. Prolonged drying in air yielded 0.188 g (91%) of the product. The material was recrystallized by dissolution in CH_3CN and precipitation with NH_4PF_6 solution in CH_3OH/H_2O. Anal. Calcd for $C_{78}H_{84}F_{12}N_{10}O_4P_2Pt_2Ru$: C, 46.69; H, 4.22; N, 6.98. Found: C, 45.42; H, 4.00; N, 6.75. MS (ESI): *m/e* 1864 $(M{\cdot}PF_6)^+$, 858 (M^{2+}). ^{1}H NMR (ppm; DMSO-d_6): 9.20 (d, 2H, $J = 6.0$ Hz), 9.17 (d, 2H, $J = 6.0$ Hz), 8.85 (d, 2H, $J = 1.6$ Hz), 8.79 (dd, 2H, $J = 8.4, 0.8$ Hz), 8.69 (dd, 2H, $J = 8.4, 0.8$ Hz), 8.67 (m, 4H), 7.8 (m, 6H), 7.71 (dd, 2H, $J = 8.4, 5.0$ Hz), 7.51 (m, 6H), 7.41 (dd, 2H, $J = 6.0, 1.6$ Hz), 1.46 (s, 18H), 1.45 (s, 18H), 1.36 (s, 18H). UV/vis (nm; CH_2Cl_2): 438 ($\epsilon = 26\,000$ M^{-1} cm^{-1}), 540 ($\epsilon = 20\,000$ M^{-1} cm^{-1}).

$[Ru((\mu\text{-dpcat})Pt(dbbpy))_3](PF_6)_2$. A mixture of 0.120 g (0.247 mmol) of $Ru(DMSO)_4Cl_2$ and 0.500 g (0.742 mmol) of Pt(dpcat)(dbbpy) in 50 mL of degassed methanol was heated at reflux for 16 h. No significant color change was observed. After the mixture had cooled to room temperature, a 10-fold excess of NH_4PF_6 in 20 mL of methanol was added. The resulting mixture was stirred for 30 min and then filtered through fine filter paper. The precipitate was washed with a methanolic solution of NH_4PF_6 and then with water. Prolonged drying in air yielded 0.489 g (82%) of somewhat impure product. The complex was recrystallized three times by dissolution in CH_3CN and precipitation with NH_4PF_6 solution in CH_3OH/H_2O. Anal. Calcd for $C_{90}H_{90}F_{12}N_{12}O_6P_2Pt_3Ru$: C, 44.82; H, 3.76; N, 6.97. Found: C, 44.00; H, 4.04; N, 6.17. MS (ESI): *m/e* 1061 (M^{2+}). ^{1}H NMR (ppm; CD_2Cl_2): 9.19 (d, 6H, $J = 6.0$ Hz), 8.72 (d, 6H, $J = 8.0$ Hz), 8.67 (s, 6H), 7.80 (d, 6H, $J = 5$ Hz), 7.66 (d, 6H, $J = 5$ Hz), 7.54 (dd, 6H, $J = 8.0, 5$ Hz), 1.45 (s, 54H). UV/vis (nm; CH_2Cl_2): 438 ($\epsilon = 27\,000$ M^{-1} cm^{-1}), 540 ($\epsilon = 26\,000$ M^{-1} cm^{-1}).

$[(dbbpy)_2Ru(\mu\text{-tppz})PtCl_2](PF_6)_2$. A mixture of 0.275 g (0.210 mmol) of $[(dbbpy)_2Ru(tppz)](PF_6)_2$ and 0.200 g (0.423 mmol) of $Pt(PhCN)_2Cl_2$ in 30 mL of degassed $CHCl_3$ was heated at reflux for 16 h, during which a precipitate formed. Upon cooling, the mixture was filtered, and the precipitate was washed with 10 mL of $CHCl_3$ and air-dried. Yield: 0.311 g (94%). The solid was sufficiently pure for the next synthetic step, but for spectroscopic measurements, it was recrystallized by dissolution in CH_3CN and reprecipitation with NH_4PF_6 solution in CH_3OH/H_2O. Anal. Calcd for $C_{60}H_{60}F_{12}N_{10}P_2PtRu$: C, 45.66; H, 3.83; N, 8.88. Found: C, 44.94; H, 3.61; N, 8.69. MS (ESI): *m/e* 1434 $(M{\cdot}PF_6)^+$, 644 (M^{2+}). ^{1}H NMR (ppm; DMSO-d_6): 10.01 (d, 2H, $J = 8.0$ Hz), 9.95 (d, 2H, $J = 8.0$ Hz), 9.56 (d, 2H, $J = 4.0$ Hz), 8.92 (s, br, 2H), 8.88 (s, br, 2H), 8.38 (dd, 2H, $J = 8.0, 6.0$ Hz), 8.29 (d, 2H, $J = 8.0$ Hz), 8.19 (dd, 2H, $J = 8.0, 6.0$ Hz), 7.78 (d, 2H, $J = 8.0$ Hz), 7.69 (d, 2H, $J = 8.0$ Hz), 7.65 (dd, 2H, $J = 8.0, 2.0$ Hz), 7.32 (dd, 2H, $J = 8.0, 2.0$ Hz), 1.45 (s, 18H), 1.38 (s, 18H). UV/vis (CH_2Cl_2): 443 nm ($\epsilon = 23\,000$ M^{-1} cm^{-1}).

$[(dbbpy)_2Ru(\mu\text{-tppz})Pt(tdt)](PF_6)_2$. A sample of 0.201 g of $[(dbbpy)_2Ru(\mu\text{-tppz})PtCl_2](PF_6)_2$ was dissolved in 15 mL of degassed

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DMSO, to which a solution of 30 mg of tdtH$_2$ in CH$_3$OH containing one pellet of KOH was added. The initial yellow-orange color quickly darkened. The solution was stirred for 1 h. Then a solution of NH$_4$PF$_6$ in CH$_3$OH was added, resulting in precipitation. The mixture was stirred for an additional 1 h, filtered, and the solid was washed with dilute methanolic NH$_4$PF$_6$, followed by 5 mL of cold CH$_3$OH. Drying in air yielded 0.194 mg (92%) of the product. Anal. Calcd for C$_{67}$H$_{66}$F$_{12}$N$_{10}$P$_2$PtRuS$_2$: C, 48.43; H, 4.00; N, 8.43. Found: C, 48.08; H, 3.92; N, 8.26. MS (ESI): *m*/*e* 1517 (M·PF$_6$)$^+$, 686 (M^{2+}). ^{1}H NMR (ppm; DMSO-*d*$_6$): 10.1 (s, br, 2H), 9.9 (s, br, 2H), 9.8 (s, br, 2H), 9.0 (s, br, 2H), 8.9 (s, br, 1H), 8.7 (s, br, 1H), 8.5 (s, br, 2H), 8.2 (m, 6H), 7.8 (m, 2H), 7.7 (s, br, 2H), 7.5 (s, br, 2H), 6.3 (s, br, 1H), 6.0 (s, br, 1H), 5.0 (s, br, 1H), 1.47 (s, 18H), 1.34 (s, 18H). UV/vis (nm; CH$_2$Cl$_2$): 447 (ϵ = 25 000 M^{-1} cm^{-1}), 610 (ϵ = 8 800 M^{-1} cm^{-1}).

Physical Measurements. ^{1}H NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer, and electronic absorption spectra were obtained using a Hitachi U2000 UV/visible spectrophotometer. FAB and electrospray mass spectra were obtained from the Mass Spectrometry Facility, University of California at Riverside. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ or Quantitative Technologies Inc., Whitehouse, NJ.

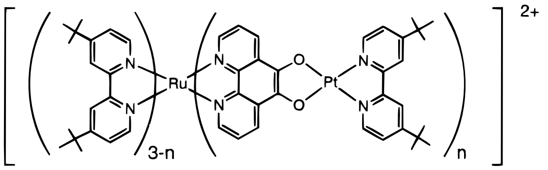
Emission Measurements. Steady-state emission measurements were performed on a Spex Fluorolog-2 fluorescence spectrophotometer. Room-temperature spectra were collected using 1 × 1 cm quartz fluorescence cells with degassed, dry methylene chloride as a solvent. Low-temperature measurements were made on degassed butyronitrile and DMM (DMF, methylene chloride, methanol; 1:1:1) solutions in 3 mm (internal diameter) quartz tubes. The concentrations of solutions were in the 10^{-5} M range. Emission spectra and excitation measurements were collected using an internal rhodamine B quantum counter and corrected for detector sensitivity.

Lifetime measurements were carried out using a previously described configuration.[27] A bubble-degassed butyronitrile solution containing the sample was immersed in a finger dewar of liquid nitrogen and positioned in the beam of a pulsed laser. Excitation pulses were generated using an excimer (Lambda Physik Lextra 50, XeCl, 308 nm) pumped dye laser (Lambda Physik LPD 3002, DPS LC4090, 400 nm). The pulse energy was severely attenuated (0.3 mJ) to avoid cracking of the frozen glass. The emission was collected at right angles to excitation using appropriate long-wavelength pass filters

Electrochemical Measurements. Electrochemical experiments were performed using an EG&G PAR 263A pontentiostat/galvanostat and a cell having a Pt disk working electrode, a Pt auxiliary electrode, and a Ag wire pseudoreference electrode. All measurements were done on nitrogen-saturated acetonitrile solutions containing ca. 0.1 M [(*n*-Bu)$_4$N](PF$_6$) electrolyte. The results are reported for a scan rate of 0.1 V/s. An internal Fc/Fc$^+$ couple (0.400 V relative to NHE) was used to calibrate the cell potential.

Results

Syntheses of dpcat-Bridged Systems. Complexes of the general formula [(dbbpy)$_{3-n}$Ru((μ-dpcat)Pt(dbbpy))$_n$](PF$_6$)$_2$ (n = 1−3) were prepared according to eq 1. The procedure to synthesize these RuPt$_n$ complexes is simple and uniform, requiring a suitable Ru starting complex with two, four, or six labile ligands (DMSO or Cl$^-$) and the requisite equivalents of Pt(dpcat)(dbbpy) (1, 2, or 3). All syntheses were carried out in refluxing methanol, and upon precipitation with NH$_4$PF$_6$, the products were obtained in excellent yields. The RuPt$_n$ complexes were identified and characterized by elemental analyses, mass spectrometry, and ^{1}H NMR spectroscopy. The mass spectra of the complexes display parent ion peaks as M^{2+} and the anion-associated cation (M·PF$_6$)$^+$ with good agreement between observed and calculated isotope patterns. The ^{1}H NMR spectra of the complexes display sharp resonances and allow adequate identification of the complexes. Interestingly, for all of the complexes, the chemical shifts of five of the six resonances of the (dpcat)Pt(dbbpy) moiety remain essentially unchanged from those of the precursor complex, Pt(dpcat)(dbbpy). Only one resonance exhibits a significant chemical shift change from δ 8.7 ppm for the mononuclear Pt complex to 7.6−7.8 ppm for the polynuclear RuPt$_n$ systems. This resonance corresponds to the proton on the carbon atom next to the imine donor of the dpcat ligand. Thus, the ^{1}H NMR spectra of Pt(dpcat)(dbbpy) and [Ru((μ-dpcat)Pt(dbbpy))$_3$](PF$_6$)$_2$ appear strikingly similar and differ only in the position of the proton resonance of the diimine ring α-carbons. All of the complexes are stable in the solid state but undergo slow decomposition in solution when exposed to air, possibly due to the oxidation of the dpcat moiety. This decomposition, which can be observed by monitoring changes in UV/vis spectra, is much slower in the case of the RuPt$_n$ complexes than for Pt(dpcat)(dbbpy).



Syntheses of tppz-Bridged Systems. The complex [(dbbpy)$_2$Ru(μ-tppz)Pt(tdt)](PF$_6$)$_2$ was synthesized according to eq 2 via the intermediacy of [(dbbpy)$_2$Ru(μ-tppz)PtCl$_2$](PF$_6$)$_2$ from [(dbbpy)$_2$Ru(tppz)](PF$_6$)$_2$, the bpy analogue of which was reported recently.[18] Coordination of the Pt(II) metal center to the free end of the tppz ligand was achieved by reaction with PtCl$_2$(PhCN)$_2$ to give orange [(dbbpy)$_2$Ru(μ-tppz)PtCl$_2$](PF$_6$)$_2$, followed by reaction with tdt^{2-} to afford the greenish-brown

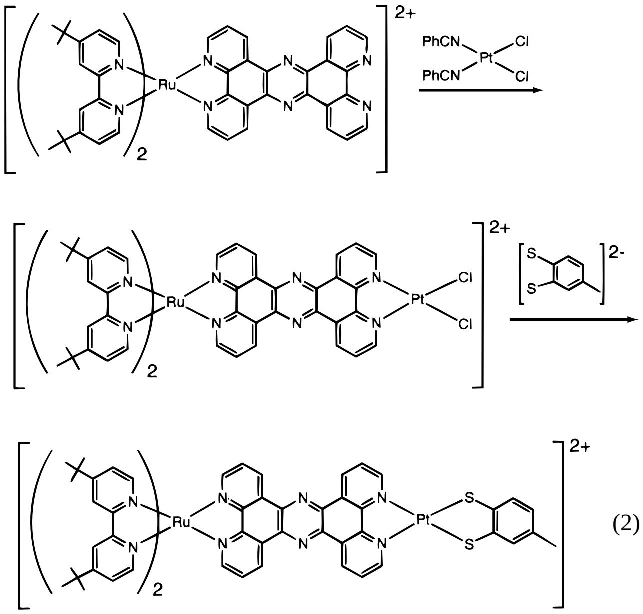


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Table 1. Electrochemical Data for $[(dbbpy)_{3-n}Ru((\mu\text{-}dpcat)Pt(dbbpy))_n](PF_6)_2$ (RuPt$_n$, $n = 1-3$), $[Ru(dbbpy)_3](PF_6)_2$ (Ru), and Pt(dpcat)(dbbpy) (Pt) in CH_3CN/0.1 M $[(n\text{-}Bu)_4N](PF_6)$[a]

	Ru^{3+}/Ru^{2+}	μ-dpcat$^{-/2-}$	Pt(dbbpy)/Pt(dbbpy)$^-$	Ru(dbbpy)/Ru(dbbpy)$^-$	Ru(dbbpy)/Ru(dbbpy)$^-$	μ-dpcat$^{2-/3-}$
Ru	+0.74			−1.88[b]	−2.04[b]	
Pt		−0.19	−1.77			
RuPt$_1$ (**1**)	+1.0[b]	+0.17[c]	−1.73	−1.89	−2.10	−2.40
RuPt$_2$ (**2**)	+1.1[b]	+0.18[c]	−1.73	−1.95		−2.26
RuPt$_3$ (**3**)	+1.3[b]	+0.22[c]	−1.77			−2.14

[a] All potentials are in volts calculated using the Fc/Fc$^+$ couple (0.400 V relative to NHE) as an internal reference. [b] Irreversible; anodic or cathodic peak potential reported. [c] Quasi-reversible.

$[(dbbpy)_2Ru(\mu\text{-}tppz)Pt(tdt)](PF_6)_2$ product. As was the case with the dpcat-bridged complexes, the μ-tppz systems were characterized by elemental analyses, mass spectrometry, and ^{1}H NMR spectroscopy. The mass spectra display parent ion peaks corresponding to M^{2+} and anion-associated peaks $(M{\cdot}PF_6)^+$ that have good agreement between observed and calculated isotope patterns. From ^{1}H NMR spectroscopy, coordination of the $PtCl_2$ fragment to the free side of the tppz ligand in $[(dbbpy)_2Ru(tppz)](PF_6)_2$ is indicated by a significant shift of the resonance of the diimine α-C proton from 9.08 to 9.60 ppm and an accompanying change in the chemical shift and splitting pattern of the resonance for the β-C proton from δ 8.02 ppm (8.0, 4.0 Hz) in $[(dbbpy)_2Ru(tppz)](PF_6)_2$ to δ 8.40 ppm (8.0, 5.5 Hz) in $[(dbbpy)_2Ru(\mu\text{-}tppz)PtCl_2](PF_6)_2$. The ^{1}H NMR spectrum of $[(dbbpy)_2Ru(\mu\text{-}tppz)Pt(tdt)](PF_6)_2$ displays much broader resonances that are more difficult to assign; nevertheless, the resonances due to the coordinated tdt ligand at 6.3, 6.0, and 5.0 ppm are well-resolved at significantly higher field compared to those of the free ligand.

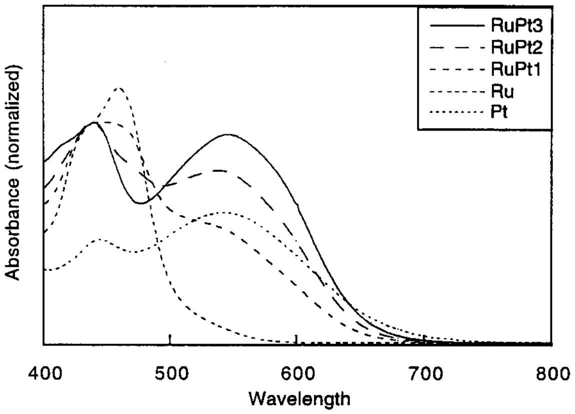

Figure 1. UV/visible absorption spectra of $[(dbbpy)_{3-n}Ru((\mu\text{-}dpcat)Pt(dbbpy))_n](PF_6)_2$ (RuPt$_n$, $n = 1-3$), $[Ru(dbbpy)_3](PF_6)_2$ (Ru), and $Cl_2Pt(\mu\text{-}dpcat)Pt(dbbpy)$ (Pt) in CH_2Cl_2.

Electrochemistry. The cyclic voltammetry data for the dpcat bridged complexes are collected in Table 1. Comparison of the observed redox processes in the series $[(dbbpy)_{3-n}Ru((\mu\text{-}dpcat)Pt(dbbpy))_n](PF_6)_2$ with those of Pt(dpcat)(dbbpy), $[Ru(dbbpy)_3]^{2+}$, and $[Ru(phen)_3]^{2+}$ allows for rational analysis and assignment. A quasi-reversible oxidation wave at low potential is seen for all of the RuPt$_n$ complexes at ca. 0.20 V vs Fc/Fc$^+$. This wave is absent in the mononuclear $Ru(diimine)_3{}^{2+}$ complexes and is significantly shifted to more negative potential by ca. 0.40 V in the starting Pt(dpcat)(dbbpy) complex. This oxidation, which is less reversible in the RuPt$_n$ complexes than in the mononuclear Pt(II) dpcat complex, is assigned to an oxidation of the dpcat ligand. The second oxidation wave which is seen at ca. 1.0−1.3 V is typical of the tris diimine-chelated Ru^{2+}/Ru^{3+} couple. The process is irreversible for the RuPt$_n$ complexes and occurs at higher potentials than that of $[Ru(dbbpy)_3]^{2+}$. As n progresses from 1 to 3, a shift of the oxidation wave is noted, reflecting the change of diimines bound to the Ru center from dbbpy to dpcat-*N,N*. The $Ru(diimine)_3{}^{2+}$ ion in RuPt$_3$ more closely resembles $[Ru(phen)_3]^{2+}$ than $[Ru(dbbpy)_3]^{2+}$, and it is known that the former is oxidized at a potential ca. 0.2 V more positive than the latter.[28] A common reduction appears in the $[(dbbpy)_{3-n}Ru((\mu\text{-}dpcat)Pt(dbbpy))_n](PF_6)_2$ series and in Pt(dpcat)(dbbpy) at ca. −1.75 V and is unaffected by coordination to Ru. This reduction is assigned to the Pt-coordinated dbbpy ligand. This assignment receives support from past studies of related Pt(II) diimine dithiolate or diolate complexes in which it is established that the LUMO is essentially a π^* orbital of the diimine.[21] The remaining reduction processes at slightly more negative potentials are attributed to other diimines bound to the two metal centers. As expected, the number of these processes decreases with increasing n in the general formula of these systems.

The cyclic voltammograms of $[(dbbpy)_2Ru(\mu\text{-}tppz)PtCl_2](PF_6)_2$ and $[(dbbpy)_2Ru(\mu\text{-}tppz)Pt(tdt)](PF_6)_2$ are very similar. Both complexes display Ru-centered oxidations at +0.82 V and +0.85 V, respectively. An additional, irreversible oxidation for the latter complex is observed at +0.28 V and is typical of Pt(diimine)(dithiolate) complexes. The cathodic processes for both complexes appear between −1.8 and −2.5 V and are more difficult to assign but, on the basis of analogy with the μ-dpcat RuPt$_n$ complexes, arise from dbbpy- and tppz-centered reductions. A broad, irreversible wave around −1.3 V is most likely associated with the tppz ligand as well.

Absorption Spectra. Absorption spectra of the RuPt$_n$ complexes along with $[Ru(dbbpy)_3](PF_6)_2$ and $Cl_2Pt(\mu\text{-}dpcat)Pt(dbbpy)$ in CH_2Cl_2 are presented in Figure 1. The spectra of all Ru-containing complexes display a characteristic Ru(II)-to-diimine MLCT band near 450 nm. The position of the maximum of this band shifts from 460 to 440 nm with increasing n, consistent with the gradual change of the diimine environment around the Ru center from $Ru(dbbpy)_3{}^{2+}$ to $Ru(dpcat\text{-}N,N)_3{}^{2+}$. A second band appears at 550 nm in complexes containing Pt centers, and this band increases in intensity as n progresses from 1 to 3. A similar band is observed in the spectrum of $Cl_2Pt(\mu\text{-}dpcat)Pt(dbbpy)$, strongly suggesting that this transition is associated with the (dpcat)Pt(dbbpy) chromophore.

A similar Ru-centered absorption is observed at 460 nm in the spectra of $[(dbbpy)_2Ru(\mu\text{-}tppz)PtCl_2](PF_6)_2$ and $[(dbbpy)_2Ru(\mu\text{-}tppz)Pt(tdt)](PF_6)_2$ in CH_2Cl_2 (Figure 2). While for the former complex this is the lowest energy absorption feature, a second band occurs near 600 nm in the spectrum of the latter. This low-energy band is assigned to the Pt(tppz)(tdt) chromophore. By subtraction of the spectrum of the dichloride complex from that of the tdt system, the low-energy absorption band maximum is estimated to occur at 610 nm, which is similar

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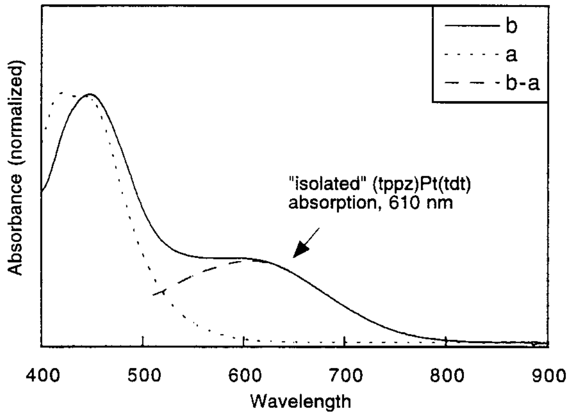

Figure 2. UV/visible absorption spectra of (a) $[(dbbpy)_2Ru(\mu\text{-}tppz)PtCl_2](PF_6)_2$ and (b) $[(dbbpy)_2Ru(\mu\text{-}tppz)Pt(tdt)](PF_6)_2$ in CH_2Cl_2.

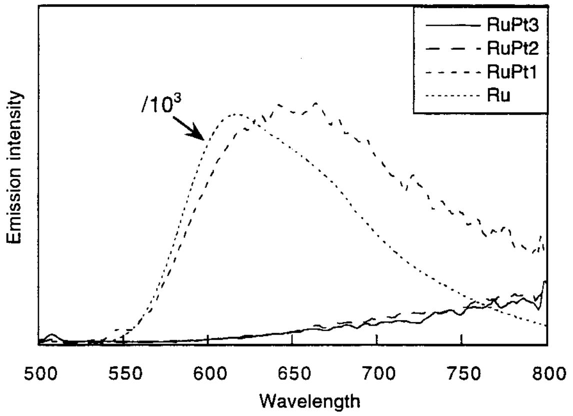

Figure 3. Room-temperature emission spectra (irradiation at 440 nm) of $[(dbbpy)_{3-n}Ru((\mu\text{-}dpcat)Pt(dbbpy))_n](PF_6)_2$ (RuPt$_n$, $n = 1-3$) and $[Ru(dbbpy)_3](PF_6)_2$ (Ru) in CH_2Cl_2.

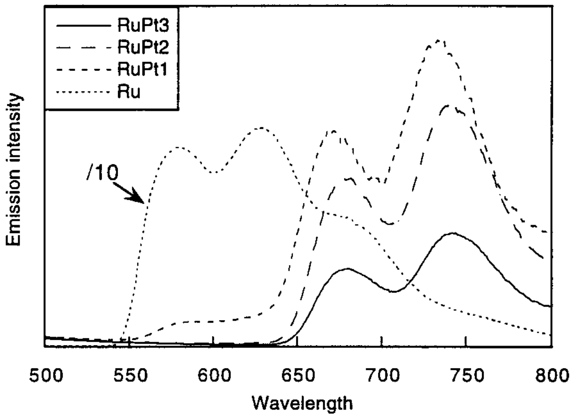

Figure 4. Emission spectra (irradiation at 440 nm) of $[(dbbpy)_{3-n}Ru((\mu\text{-}dpcat)Pt(dbbpy))_n](PF_6)_2$ (RuPt$_n$, $n = 1-3$) and $[Ru(dbbpy)_3](PF_6)_2$ (Ru) in butyronitrile glass at 77 K.

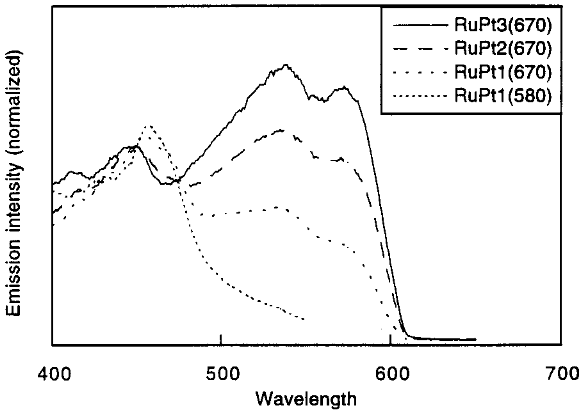

Figure 5. Excitation spectra of $[(dbbpy)_{3-n}Ru((\mu\text{-}dpcat)Pt(dbbpy))_n](PF_6)_2$ (RuPt$_n$, $n = 1-3$) in butyronitrile glass at 77 K with emission monitored at wavelengths indicated in parentheses.

in value to those displayed by the mononuclear complexes Pt(phen)(tdt) (583 nm) and Pt(5-Cl-phen)(tdt) (605 nm) in the same solvent. In addition, this feature is highly solvatochromic as has been found in the spectra of other Pt(diimine)(dithiolate) complexes. Thus, in analogy to the mononuclear systems, this band is attributed to a Pt/dithiolate-to-diimine ligand charge transfer.

Emission Properties. Irradiation of a CH_2Cl_2 solution of $[(dbbpy)_2Ru(\mu\text{-}dpcat)Pt(dbbpy)]^{2+}$ at 440 nm, where the Ru center absorbs predominantly, results in a typical $Ru(diimine)_3{}^{2+}$ emission at 620 nm (Figure 3), although the intensity is 3 orders of magnitude less than that of $[Ru(dbbpy)_3]^{2+}$. This emission overlaps with features in the absorption spectrum arising from the Pt chromophore (550 nm). The related $n = 2$, 3 complexes—i.e., $[(dbbpy)Ru((\mu\text{-}dpcat)Pt(dbbpy))_2]^{2+}$ and $[Ru((\mu\text{-}dpcat)Pt(dbbpy))_3]^{2+}$—do not display any emission under these conditions. Similarly, irradiation at 570 nm, where exclusive excitation of the Pt chromophore is expected, does not result in any emission for the RuPt$_n$ complexes with $n = 1-3$ in fluid solution.

In contrast, when $[(dbbpy)_2Ru(\mu\text{-}dpcat)Pt(dbbpy)]^{2+}$ is irradiated at 440 nm in butyronitrile glass at 77 K, a weak emission from the Ru chromophore is observed at 570 nm accompanied by a second, stronger emission band at 670 nm with a vibronic feature at 730 nm (Figure 4); the vibronic spacing of 1200 cm^{-1} is characteristic of ligand participation in the excited state. The low-temperature emission spectra of both $[(dbbpy)Ru((\mu\text{-}dpcat)Pt(dbbpy))_2]^{2+}$ and $[Ru((\mu\text{-}dpcat)Pt(dbbpy))_3]^{2+}$ do not exhibit emission at 570 nm, but emission features at 670 and 730 nm are observed. These bands are also observed in the emission spectra of all three RuPt$_n$ ($n = 1-3$) complexes with comparable intensity upon irradiation at 570 nm, where the Pt chromophore absorbs exclusively. Lifetime measurements performed on butyronitrile glasses of these complexes at 77 K reveal that the excited states giving the 670 and 730 nm emissions are short-lived ($\tau < 15$ ns). Under the same conditions, $Ru(dbbpy)_3{}^{2+}$ displays a lifetime of 5.1 μs, which is in excellent agreement with the literature value of 5.3 μs in MeOH/EtOH glass at 77 K.[28] Thus, it seems likely that the 670 nm emission originates from the Pt diimine diolate chromohore, and by analogy with the corresponding diimine dithiolate complexes, the emitting state may be assigned to a low lying metal/ligand(diolate)-to-ligand(diimine) charge transfer.

The corresponding excitation spectra of the $[(dbbpy)_{3-n}Ru((\mu\text{-}dpcat)Pt(dbbpy))_n]^{2+}$ ($n = 1-3$) complexes are displayed in Figure 5. The excitation spectra obtained for emission monitored at 670 and 730 nm are nearly identical and very similar to the room-temperature absorption spectra of the complexes. The most notable difference lies in the relative intensity of the bands at ca. 540 and 440 nm with the intensity of the former relative to the latter consistently greater in the excitation spectrum than in the corresponding absorption spectrum. The data thus indicate that the lower energy emission (670 and 730 nm) originating from the Pt chromophore is obtained upon excitation of the Ru chromophore. Interestingly, the mononuclear complex Pt(dpcat)(dbbpy) does not luminesce

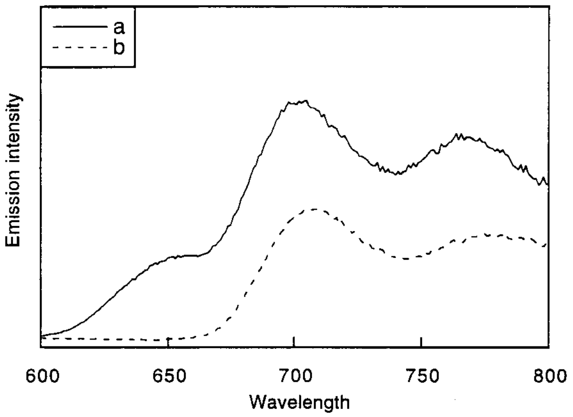

Figure 6. Emission spectra of (a) (tdt)Pt(μ-dpcat)Pt(dbbpy) and (b) (dbcat)Pt(μ-dpcat)Pt(dbbpy) in butyronitrile glass at 77 K.

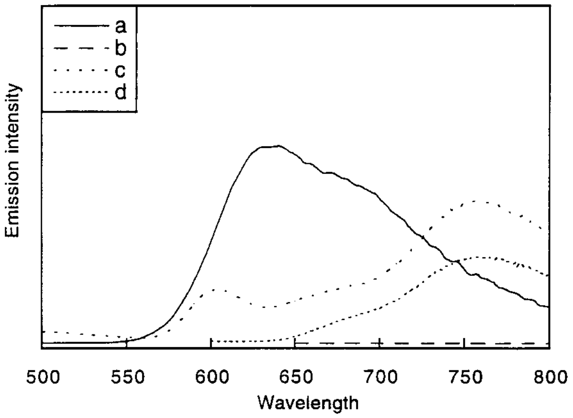

Figure 7. Emission spectra of [(dbbpy)$_2$Ru(μ-tppz)Pt(tdt)](PF$_6$)$_2$: (a) room temperature in CH$_2$Cl$_2$ with irradiation at 480 nm; (b) room temperature in CH$_2$Cl$_2$ with irradiation at 615 nm; (c) 77 K in butyronitrile glass with irradiation at 440 nm; (d) 77 K in butyronitrile glass with irradiation at 575 nm.

in room-temperature CH$_2$Cl$_2$ solution or in butyronitrile glass at 77 K.

We also have reexamined the emission spectra of the related complexes (dbcat)Pt(μ-dpcat)Pt(dbbpy) and (tdt)Pt(μ-dpcat)Pt(dbbpy) at low temperature, since these complexes contain the chromophore (dpcat)Pt(dbbpy) in which the dpcat ligand is bridging to another metal. These Pt$_2$ complexes might therefore be expected to exhibit low-energy emission similar to that of the RuPt$_n$ complexes. Indeed, irradiation at 550 nm of butyronitrile glasses of both of these complexes results in relatively weak, yet clearly observable emissions with maxima at 700 and 770 nm (Figure 6). The energies and profiles of the emission bands for both complexes are almost identical, and thus we conclude that this emission originates from the (dpcat)Pt(dbbpy) chromophore. Unlike the case of RuPt$_n$ complexes, selective irradiation of the different chromophores in these dinuclear Pt$_2$ species is not possible, because the absorption bands of the two Pt centers closely overlap.

Irradiation of a room-temperature CH$_2$Cl$_2$ solution of [(dbbpy)$_2$Ru(μ-tppz)Pt(tdt)](PF$_6$)$_2$ at 480 nm results in a Ru(diimine)$_3^{2+}$-centered emission (maximum at 630 nm) similar to that of [(dbbpy)$_2$Ru(μ-dpcat)Pt(dbbpy)]$^{2+}$. The results of low-temperature experiments are also very similar (Figure 7). Irradiation of a 77 K butyronitrile glass of [(dbbpy)$_2$Ru(μ-tppz)Pt(tdt)](PF$_6$)$_2$ at 440 nm results in a weak emission near 600 nm and a more intense, broad band maximizing at 750 nm. The latter band is also observed upon irradiation at 575 nm, where the (tppz)Pt(tdt) chromophore is selectively excited. For comparison, the mononuclear complex Pt(5-Cl-phen)(tdt) displays a relatively narrow emission band with emission onset at 635 nm and a maximum at 683 nm. The broad 750 nm emission from [(dbbpy)$_2$Ru(μ-tppz)Pt(tdt)](PF$_6$)$_2$ originates near 650 nm.

Discussion

The dpcat Systems. The dpcat-bridged RuPt$_n$ complexes represent an interesting series of bimetallic systems with electronic communication between component chromophores known to have charge-transfer excited states. All complexes contain a Ru(diimine)$_3^{2+}$ center connected through a polar dpcat bridge to one, two, or three Pt diimine diolate moieties. The spectroscopic data for the complexes [(dbbpy)$_{3-n}$Ru((μ-dpcat)Pt(dbbpy))$_n$]$^{2+}$ together with those of mononuclear model systems lead to an analysis that is supported by electrochemical experiments. For each complex, two well-separated, relatively low energy bands around 440 and 550 nm are observed in the visible region and can be assigned to the two different chromophores, Ru(diimine)$_3^{2+}$ and Pt(dpcat)(dbbpy), respectively. In fluid solution, only the RuPt$_1$ complex exhibits emission that is observable at 620 nm and is attributable to the Ru(diimine)$_3^{2+}$ chromophore. In rigid-glass media at 77 K, the three dpcat-bridged complexes ($n = 1-3$) show emission at 670 nm characteristic of the Pt(dpcat)(dbbpy) chromophore. The RuPt$_1$ system also shows a very weak Ru-centered emission at 570 nm.

The excitation spectra of the RuPt$_n$ complexes collected with emission monitored at the Pt emission wavelengths are very similar to the absorption spectra. The presence of the Ru(diimine)$_3^{2+}$-based excitation bands at ca. 460 nm in these spectra strongly suggests that energy transfer between the Ru and Pt chromophores is occurring in these complexes. For all of the RuPt$_n$ complexes, the 460 nm excitation bands are more intense than what would be expected for any Pt-based excitation at that wavelength as estimated from absorption spectra of the Pt$_2$ complex Cl$_2$Pt(μ-dpcat)Pt(dbbpy) and the mononuclear analogue Pt(dpcat)(dbbpy).

On the basis of the absorption, emission, and excitation spectra, it can be concluded that (1) selective irradiation of the Pt center is possible with $\lambda_{ex} > 550$ nm and (2) irradiation of the Ru center in the RuPt$_n$ systems leads to energy transfer to the Pt chromophore. The energy transfer is not complete in the RuPt$_1$ system, however, since this complex shows weak Ru-based emission in both fluid-solution and rigid-glass media. Specifically, irradiation of [(dbbpy)$_2$Ru(μ-dpcat)Pt(dbbpy)]$^{2+}$ at $\lambda < 480$ nm yields emission that is very weak compared to that of the mononuclear complex Ru(dbbpy)$_3^{2+}$. The lower intensity of this emission may be viewed as the result of partial quenching by the attached (dpcat)Pt(dbbpy) chromophore, which possesses a lower energy excited state and emits at 77 K. In the cases of [(dbbpy)Ru((μ-dpcat)Pt(dbbpy))$_2$]$^{2+}$ and [Ru((μ-dpcat)Pt(dbbpy))$_3$]$^{2+}$ ($n = 2$, 3), the emission from the Ru emission center is completely absent, and at 77 K, only emission from the Pt chromophore is observed. Presumably the same energy transfer occurs in room-temperature fluid solution, but under those conditions, efficient nonradiative deactivation of the excited state of the (dpcat)Pt(dbbpy) chromophore precludes emission.

Recently, Yam reported studies of related binuclear complexes in which tris(diimine)-coordinated Ru(II) centers are connected to PtX$_2$ moieties (X = Cl, Me) by the bridging ligands 2,3-dipyridylpyrazine (dpp) and 2,2′-bipyrimidine.[29] A relevant observation in these studies is that, whereas the emission from the mononuclear complexes [Ru(bpy)$_2$(BL)]$^{2+}$ (BL = bridging ligand) is strong in both fluid solution and the solid state, the emission is greatly attenuated upon coordination of PtX_2 to BL and in the solid state is very weak or absent completely. A similar absence of Ru-based emission has also been noted by Brewer for related dipyridylquinoxaline (dpq) and dipyridylbenzoquinoxoline (dpb) bridged analogues containing $PtCl_2$.[30] The basis of the quenching of the Ru-based emission in these systems is not discussed, and no mention is made of any emission from the Pt(diimine)X_2 part of the complexes. Further comment on the relative orientation of the Ru−BL and Pt−BL charge-transfer transitions in these complexes is made below in the discussion on the tppz-bridged systems.

The presence of Ru(diimine)$_3^{2+}$-centered emission from the $RuPt_1$ complex may be considered in light of other studies of linked emissive chromophores having excited states of differing energies. Systems of this type have been reported over the past 5 years, in which Ru(II) and Os(II) tris(diimine) centers are connected via spacers such as short alkyl chains $(CH_2)_n$ (n = 2, 3, 5, 7)[13] and the more rigid 1,4-bis(ethylene)bicyclo[2.2.2]-octane moiety,[12] as well as another Ru(II)/Os(II) system having terpy ligands and a bis-cyclometalated bridging ligand containing dipyridylbenzene fragments linked by a variable number of phenylene spacers.[10] In all of these systems, a residual Ru emission was observed which tended to be weaker for shorter spacers. These and related systems indicate that the energy transfer within a dinuclear complex or diad is more efficient for shorter, conjugated, and more rigid linkers. The complexes discussed in the present report are such systems, and consequently, the energy transfer between Ru and Pt chromophores was expected to be 100% efficient, but the appearance of a weak Ru-based emission in $RuPt_1$ suggests otherwise. The comparison of $RuPt_1$ with the linked Ru/Os systems should also be viewed in light of the relative strength of the lower energy emitter. In the present case, this is the weakly emissive (dpcat)-Pt(dbbpy) chromophore whereas, in the Ru/Os systems, it is the strongly emissive Os(diimine)$_3^{2+}$ moiety. The latter may mask very weak Ru-based emission that the former does not.

All of the emission measurements in this study including the ones on low-temperature glasses were carried out on degassed media. While the presence of oxygen did not affect emission spectra in freshly prepared solutions, it did have a significant effect over time. In aerated solutions, slow changes occurred as monitored by a progressive decrease in the intensities of both absorption bands in the visible region. Under the same conditions, the 570 nm band in the spectrum of the mononuclear complex Pt(dpcat)(dbbpy) disappeared completely, indicating instability of the Pt chromophore to possible oxidation. The emission spectra of the $RuPt_n$ complexes were dramatically affected in the presence of air after long times, resulting in a strongly enhanced Ru(diimine)$_3^{2+}$ emission for the $RuPt_1$ system, and observation of Ru-based emissions for the $n = 2$ and 3 derivatives (the latter only weakly) in rigid glasses at 77 K. However, by ^1H NMR spectroscopy, no change was seen in the spectrum of the $RuPt_2$ complex in aerated acetonitrile after several weeks. The absorption and emission results are consistent with slow oxidative degradation of the Pt(dpcat)-(dbbpy) chromophore in aerated samples of the $RuPt_n$ complexes, but the identity of decomposition products has yet to be established.

In terms of the direction of energy transfer, the $RuPt_n$ series of complexes shares an inverse relationship with one reported recently by Barigeletti et al. in which a central Ru(diimine)$_3^{2+}$ chromophore is surrounded by one, two, or three units of the Re(diimine)(CO)Cl chromophore.[31] In those systems, energy transfer occurred from the peripheral Re centers to the central Ru center, thus in a direction opposite to that of the $RuPt_n$ series discussed here.

The emission from the (dpcat)Pt(dbbpy) chromophore is also observed at low temperature in the dinuclear Pt_2 complexes (dbcat)Pt(μ-dpcat)Pt(dbbpy) and (tdt)Pt(μ-dpcat)Pt(dbbpy) although it appears to be much weaker than in the $RuPt_n$ series of complexes. In the Pt_2 complexes, the absorption bands due to the two different Pt(diimine) chromophores overlap significantly. Both Pt_2 complexes exhibit absorptions at lower energy than the corresponding Cl_2Pt(μ-dpcat)Pt(dbbpy) system, suggesting that the lower energy bands may be localized on the (dbcat)Pt(dpcat) and (tdt)Pt(dpcat) chromophores, respectively. However, the similarity of emission spectra of these complexes supports the notion that (dpcat)Pt(dbbpy) is the source of this luminescence. The comparison of low-temperature emission spectra of $[(dbbpy)_2Ru(\mu\text{-dpcat})Pt(dbbpy)]^{2+}$ and (dbcat)Pt(μ-dpcat)Pt(dbbpy) recorded for glasses of comparable absorbances reveals that the emission from the (dpcat)Pt(dbbpy) in the former complex is more intense by 2 orders of magnitude, indicating a lower rate of nonradiative decay in the former relative to the latter.

The tppz-Bridged System. The tppz-bridged complex $[(dbbpy)_2Ru(\mu\text{-tppz})Pt(tdt)]^{2+}$ shows spectroscopic behavior similar to the dpcat-bridged RuPt system. That is, irradiation of the complex in room-temperature fluid solution at 480 nm, where the Ru(diimine)$_3^{2+}$ chromophore absorbs, leads to weak emission at 600 nm assignable to the Ru chromophore, whereas in rigid media at 77 K, the same irradiation yields greatly attenuated Ru-based emission and luminescence from the Pt-(diimine)(dithiolate) part of the complex. The Ru-based emission at room temperature is similar to that observed for the $[(dbbpy)_2Ru(\mu\text{-tppz})PtCl_2]^{2+}$ precursor and is considerably weaker than that of Ru(dbbpy)$_3^{2+}$. It is surprising that no Pt-based emission is observed in fluid solution for this complex in light of the fact that mononuclear Pt(diimine)(dithiolate) complexes are known to luminesce under these conditions. These results indicate that, while the energy transfer occurs from the Ru center to the Pt(diimine)(dithiolate) moiety, the nonradiative deactivation of the latter is also enhanced in $[(dbbpy)_2Ru(\mu\text{-tppz})Pt(tdt)]^{2+}$.

The Pt(diimine)(dithiolate) chromophore of $[(dbbpy)_2Ru(\mu\text{-tppz})Pt(tdt)]^{2+}$ emits at 77 K upon selective irradiation of the Pt center at 575 nm, as well as when the complex is irradiated at 480 nm corresponding mainly to a Ru-based absorption. In this regard, the spectroscopic properties of the complex are very similar to those of $[(dbbpy)_2Ru(\mu\text{-dpcat})Pt(dbbpy)]^{2+}$. However, two important differences exist between these two complexes. First, the bridging ligands are different in the donor atom sets provided to the two metal ions and, second, the orientation of the Pt-based charge transfer is different relative to the bridging ligand and the Ru center. With respect to the latter, the direction of the Pt-based charge transfer is from the metal dithiolate (or diolate) part of the chromophore to the coordinated diimine. For the tppz-bridged complex $[(dbbpy)_2Ru(\mu\text{-tppz})Pt(tdt)]^{2+}$, the charge transfer is from the Pt(tdt) fragment to the tppz ligand

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which connects to the Ru center, while for the dpcat-bridged complex [(dbbpy)$_2$Ru(μ-dpcat)Pt(dbbpy)]$^{2+}$, the charge-transfer proceeds from the Pt(dpcat) fragment away from the Ru center and toward the Pt-coordinated dbbpy ligand.

The symmetrical nature of the tppz bridge with both metal centers coordinated by equivalent diimine moieties makes [(dpbpy)$_2$Ru(μ-tppz)Pt(tdt)]$^{2+}$ more similar to the bpm- and 2,3-dpp-bridged systems described by Yam[29] and the dpq- and dpb-bridged complexes reported by Rillema and Brewer.[30,32] In the absorption spectra of the complexes having one Ru and a single BL-bound PtCl$_2$, the Ru → π*(bpy) bands are observed at ∼420−430 nm with the Ru → π*(BL) bands at longer wavelengths ranging from 509 nm for the dpp system to 630 nm for the dpb complex. In [(dbbpy)$_2$Ru(μ-tppz)PtCl$_2$]$^{2+}$, this lower energy feature is not seen whereas, for the tdt analogue, [(dbbpy)$_2$Ru(μ-tppz)Pt(tdt)]$^{2+}$, a solvatochromic band appears in this region (610 nm) that is ascribed to the Pt/dithiolate-to-diimine charge transfer reported for mononuclear diimine dithiolate complexes.

Conclusions

The systems described in this study represent the first series in which the Pt(diimine)(diolate) or Pt(diimine)(dithiolate) chromophore has been linked to other emissive chromophores. They thus contribute to our understanding of two-component systems or diads containing charge transfer-type chromophores. The polar bridging ligand dpcat (1,10-phenanthroline-5,6-diolate) has been used for the first time in this capacity. Despite the rigidity and conjugation of the bridges in the di- and polynuclear dpcat and tppz complexes, the absorption spectra of the complexes exhibit low-energy bands that are characteristic of the individual chromophores. The emission energies also suggest that they correspond to excited states of the isolated chromophores. Only in terms of a greatly reduced or absent Ru-based emission and the presence of a Pt-based emission at 77 K when irradiated into the low-energy Ru-based absorption does one see the effect of one chromophore on the other. Our results thus show that linking the nonemissive Pt(diimine)-(diolate) center to another component having a higher energy charge transfer state can result in emission from the Pt center. However, the energy transfer in these systems which proceeds via a short, rigid, conjugated bridge is not completely efficient.

Acknowledgment. We wish to thank the Department of Energy, Division of Chemical Sciences, for support of this research and Johnson Matthey Alpha/Aesar Co. for a generous loan of platinum salts.

IC971447K

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