Acknowledgment. This work was supported by grants from the National Institutes of Health, GM22172 and GM30301. We also thank Dr. Thomas Hohn of the USDA, Agricultural Research Laboratory, in Peoria, IL, for sharing with us his results on the isolation of aristolochene synthase from *P. roquefortii* in advance of publication.

Square-Planar Complexes of Platinum(II) That Luminesce in Fluid Solution

Juan A. Zuleta, Carlos A. Chesta, and Richard Eisenberg*

Department of Chemistry, University of Rochester
Rochester, New York 14627

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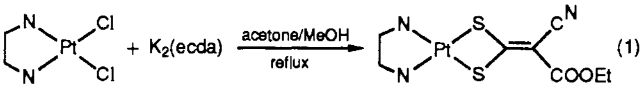
Very few mononuclear complexes of square-planar geometry luminesce in fluid solution,[1,2] principally because efficient radiationless decay occurs via collisions with solvent in the open coordination sites. Of the few d^8 complexes that do emit in fluid solution, only the cyclometalated species Pt(thpy)$_2$ (thpy = 2-(2-pyridyl)thiophenide) possesses an emitting state showing metal involvement.[3] Other luminescent Pt(II) complexes either are not mononuclear[4a] or emit only as solids at low temperature.[4b-e] In this paper we describe two new Pt(II) complexes that exhibit strong solution luminescence, show solvatochromic behavior, and undergo electron-transfer quenching with both donors and acceptors. These complexes are members of a larger class of solution luminescent dithiolate diimine d^8 systems.[5]

The complexes Pt(N$\frown$N)(ecda), where ecda = ethyl 2-cyano-3,3-dimercaptoacrylate and N$\frown$N = 4,4′-dimethyl-2,2′-bipyridine (**1**), and 4,7-diphenyl-1,10-phenanthroline (**2**) were prepared via eq 1 from Pt(N$\frown$N)Cl$_2$ and K$_2$(ecda). The complexes were



(1)

recrystallized from either CH$_2$Cl$_2$ or acetone, yielding analytically pure samples. Through characterization by electronic absorption, infrared, and ^{1}H NMR spectroscopies and field desorption mass spectrometry, the complexes were determined to be mononuclear square-planar systems.[6] Complex **1** exists in two forms depending on its solvent of crystallization—**1a** from CH$_2$Cl$_2$ is yellow and **1b** from acetone is red—but in all solution measurements, **1a** and **1b** are identical and show the same parent ion peak at m/e 566. Both **1** and **2** possess significantly greater solubility than the other Pt(II) diimine dithiolate complexes, which permitted their complete characterization including photochemical behavior.

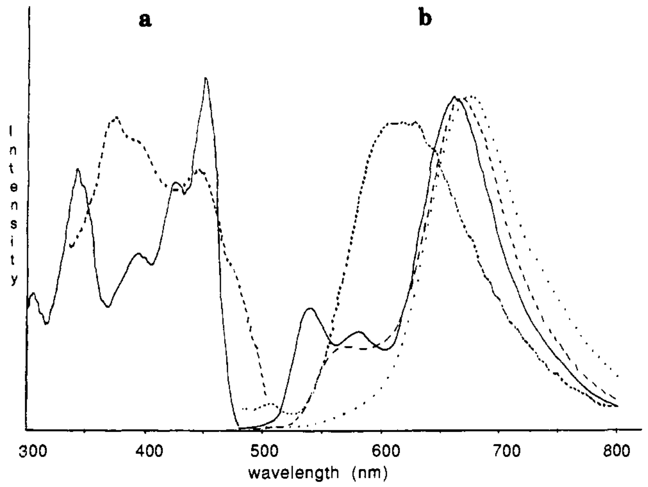


Figure 1. (a) Excitation spectra of Pt(dpphen)(ecad), **2** at 77 K in DMF/CH$_2$Cl$_2$/MeOH collected at 540 nm (—) and 640 nm (– – –). (b) Emission spectra at 80 K (—), 140 K (– – –), 165 K (–·–), and 210 K (- - -).

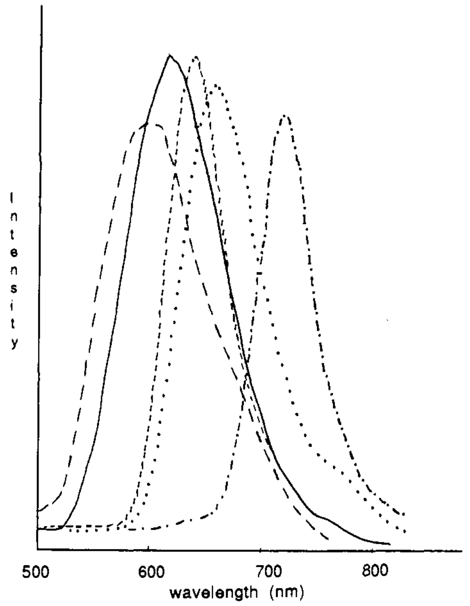


Figure 2. Emission spectra of **1** in CH$_2$Cl$_2$ (– – –) and in the solid state: yellow form at 298 K (—) and 77 K (- - -); red form at 298 K (···) and 77 K (–·–).

Solutions of **1** and **2** exhibit an intense absorption in the 400–500-nm region ($\epsilon \sim$ 14000–15000) which shifts to higher energy with increasing solvent polarity. For **1** the absorption maximum changes from 450 nm in CHCl$_3$ to 418 nm in DMSO, while for **2** the change is from 468 to 438 nm. Titration of CH$_2$Cl$_2$ solutions of the complexes with DMF also leads to a gradual shift of the absorption maxima to higher energy. Both complexes exhibit similar electrochemical behavior, undergoing two reversible reductions and an irreversible oxidation in DMF. The values of $E_{1/2}^{\mathrm{red}(1)}$, $E_{1/2}^{\mathrm{red}(2)}$ and $E_{\mathrm{p}}^{\mathrm{ox}}$ are −1.28, −1.77, and 0.83 V for **1** and −1.12, −1.68, and 0.75 V for **2** relative to Fc$^+$/Fc at 0.40 V (determined by using a glassy carbon electrode and a Ag wire quasi-reference).

Both complexes show the extraordinary property of luminescing in fluid solution at room temperature. The emissions are broad and asymmetric as shown in Figures 1 and 2. For complex **2** the emission in CH$_2$Cl$_2$/DMF/MeOH (1:1:1 v/v/v) shifts to lower energy upon cooling to a glass with emergence of two higher energy bands below 90 K (Figure 1). The excitation spectra of **1** and

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[5] In these Pt(N$\frown$N)(S$\frown$S) complexes, the diimine ligands include 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 4,4′-dimethyl-2,2′-bipyridine (dmpby), 4,4′-diphenyl-2,2′-bipyridine (dpbpy), and 4,7-diphenyl-1,10-phenanthroline (dpphen) while the dithiolates are maleonitriledithiolate (mnt), 2,2-dicyano-1,1-ethylenedithiolate (i-mnt), and ethyl 2-cyano-3,3-dimercaptoacrylate (ecda). See: (a) Zuleta, J. A.; Burberry, M.; Eisenberg, R. 8th International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Santa Barbara, Aug 13–17, 1989. (b) Zuleta, J. A.; Burberry, M.; Eisenberg, R. *Coord. Chem. Rev.* In press.

[6] ^{1}H NMR (CH$_2$Cl$_2$) for **1**: δ 8.31 (d, 1 H), 8.21 (d, 1 H), 7.92 (s, 2 H), 7.34 (d, 2 H), 4.22 (q, 5.5 Hz, 2 H), 2.59 (s, 6 H), 1.33 (t, 5.5 Hz, 3 H). IR spectra (KBr) show peaks due to coordinated diimine by comparison to Pt(N$\frown$N)Cl$_2$ and to ecda at 2203, 1449, and 1153 cm^{-1} for **1** and 2201, 1451, and 1158 cm^{-1} for **2**. Field desorption mass spectrometry gives parent peaks at m/e of 566 for **1** and 714 for **2**.

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2 exhibit large Stokes shifts, and for **2** collection at the higher energy bands results in a different excitation spectrum from that of the lower energy band. In the solid state, both forms of **1** and **2** show intense, unstructured emissions at room temperature which increase modestly in intensity at 77 K, but with no development of appreciable structure. The solid state emission maxima are shifted to lower energy by ~800–1500 cm^{-1} relative to the solution values. For **1** the red and yellow forms exhibit different λ_{em}'s which shift to lower energies at 77 K as illustrated in Figure 2. In contrast, solid samples of **2** show no energy shift upon cooling to 77 K but do exhibit slightly increased emission intensity.

Relative quantum yields for solution emission of **1** and **2** were measured by using $[Ru(bpy)_3]^{2+}$ in DMF as a standard ($\Phi_{em} = 0.068$).[7] For these measurements, solvents were rigorously dried, distilled, and degassed. In all solvents, the relative quantum yield for **2** was about an order of magnitude greater than for **1**. The values of Φ_{em} varied with solvent, ranging from 1.63×10^{-4} and 1.39×10^{-4} in acetone and DMF to 2.67×10^{-4} in CH_2Cl_2 for **1** and 1.33×10^{-3} and 1.95×10^{-3} in acetone and DMF to 2.69×10^{-3} in CH_2Cl_2 for **2**. In mixtures of CH_2Cl_2 and DMF, the quantum yield increased as a function of the solvent ratio.

Emission lifetimes of **1** and **2** were measured by single photon counting in fluid solution, frozen glass, and pure solid. Complex **2** was found to exhibit single exponential decay in CH_2Cl_2/DMF/MeOH fluid solution at 298 K (τ = 22 ns) and in frozen glass at 77 K (1.8 μs), but double exponential decay in the pure solid at 77 K (324 ns, 1.26 μs). In contrast, complex **1** shows multiple exponential decay in all samples run with values of τ, obtained from deconvolution, of 3.4 and 13.5 ns in fluid solution at 298 K, 16.4 and 109 ns for the solid yellow form, and 15.7 and 47.9 ns for the red form. In all three cases, a possible third component with a much shorter lifetime also exists (0.5–2 ns).[8]

Quenching studies of **2** in CH_2Cl_2 were performed by using the electron donor *N,N*-dimethylaniline (DMA) and the electron acceptor *o*-nitrobenzaldehyde (ONB). The concentration of **2** employed was 2×10^{-5} M while the concentrations of quencher ranged from 7.9×10^{-4} to 1.6×10^{-2} M for DMA and 1.1×10^{-2} to 6.7×10^{-2} M for ONB. Good Stern–Volmer plots were obtained in both cases with K_{SV} of 24.8 and 188 for ONB and DMA, respectively. The corresponding k_q values calculated from K_{SV} and the solution excited state lifetime of **2** are 6.8×10^8 and 9×10^9 M^{-1} s^{-1}, respectively. The nature of the quenching as electron transfer is supported by the electrochemistry and the fact that the triplet energies of both ONB (61 kcal/mol)[9] and DMA (74 kcal/mol)[10] are significantly larger than that estimated for **2** from its emission (52 kcal/mol). Consistent also with the electrochemistry is the fact that irradiation of **2** in the presence of DMA (1.6×10^{-2} M) yields no change in the absorption spectrum after 24 h whereas a sample containing ONB (1.1×10^{-2} M) shows bleaching of the 454-nm band over 5 h indicating degradation of the complex by irreversible oxidation.

The nature of the emissive state in these Pt(II) complexes is uncertain. However, the structureless emissions and the fact that no emission is observed for the Pd and Ni analogues provide evidence against an intra- or interligand excited state.[11] Moreover, related Pt(II) diimine complexes with chloride ligands (which are similar in ligand field strength to dithiolates[12]) have a ligand field (LF) state as the lowest energy transition, but they do not show the strong absorption band in the visible and only emit as solids at low temperature.[13] Based on this spectroscopic evidence and the electron-transfer quenching outlined above, we favor a charge-transfer excited state involving the metal center and the dithiolate ligand. However, the multiple lifetimes and emergence of new bands in the low-temperature emission spectrum of **2** (Figure 1) suggest more than one emitting state. With regard to the latter, these new bands are assigned to a dpphen-based IL (intraligand) emitting state similar to that found for $Pt(N^\frown N)Cl_2$.[14]

The discovery of new compounds possessing long-lived excited states leads not only to a better understanding of photochemical and photophysical principles but also to development of new applications of light-induced reactions. In contrast to the well-studied $Ru(bpy)_3{}^{2+}$, the compounds described here are coordinatively unsaturated, making them good candidates as photocatalysts. On the basis of the experiments described above, reductive quenching of these complexes may permit direct reduction of H^+ and CO_2 at the metal center, and this possibility is under active investigation.

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Synthesis of Rhenium–Alkene Complexes from the Reaction of the Heterobimetallic Dihydride $C_5H_5(CO)_2HRe–PtH(PPh_3)_2$ with Alkynes

Charles P. Casey* and Edward W. Rutter, Jr.

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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Heterobimetallic compounds hold great promise as catalysts since the two different metals have the potential of acting cooperatively. However, since the problem of optimizing a system for each of two metals is an added complication, there are few examples of homogeneous heterobimetallic catalysts.[1] Here we report that the new heterobimetallic dihydride $C_5H_5(CO)_2HRe–PtH(PPh_3)_2$ (**1**)[2] acts as a catalyst for ethylene hydrogenation and reacts stoichiometrically with alkynes to produce rhenium–alkene complexes.

When the synthesis of **1** from *trans*-$Cp(CO)_2ReH_2$ (**2**) and $(CH_2{=}CH_2)Pt(PPh_3)_2$ (**3**) was carried out in a sealed NMR tube, we noticed the slow formation of small amounts of ethane. Consequently, we began a study of the hydrogenation of ethylene catalyzed by **1**. We found that **1** slowly catalyzed the hydrogenation of ethylene to ethane in benzene-d_6 at room temperature and 0.6 atm of H_2. After 2 days, the hydrogenation ceased after producing 4.2 equiv of ethane. When the reaction was monitored by ^1H NMR, we noted an initial reaction of **1** with ethylene that

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