Inorg. Chem. **1998,** *37,* 4139−4141 **4139**

Synthesis and Characterization of (Di-*tert*-butylbipyridine)bis(pyridine-4-thiolato)platinum(II), Pt(dbbpy)(S-4-py)$_2$: A Synthon for Supramolecular Systems Containing the Platinum Diimine Bis(Thiolate) Chromophore

Witold Paw, Rene J. Lachicotte, and Richard Eisenberg*

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

Received December 11, 1997

Introduction

There is increasing interest in the design and synthesis of supramolecular systems capable of harvesting and using light energy.[1−9] The bulk of research involving transition metal complexes in this field has been devoted to systems incorporating $M(diimine)_3^{2+}$ (M = Ru, Os) and other d^6 diimine-containing chromophores.[5,6,9−27] Studies over the past decade have shown that Pt diimine dithiolate complexes may also prove of value in this venue. Specifically, these complexes possess a directional charge-transfer emitting state formed upon electron excitation from an orbital of mixed metal/dithiolate character to a vacant π^* level of the diimine moiety.[28−33] The complexes are emissive in fluid solution and undergo electron transfer quenching both oxidatively and reductively. However, only under reductive quenching conditions are the complexes stable upon prolonged irradiation.

The notion of using the Pt diimine dithiolate chromophore in a multicomponent system for light-driven reactions has stimulated the design and synthesis of related complexes having ligands capable of functioning as bridges. Complexes of one such ligand, dipyridocatecholate or phenanthroline-5,6-diolate, have recently been reported.[34,35] In the present study, the dithiolate ligand is replaced by two thiolates having pyridyl groups for connection to another metal. We describe herein the synthesis, characterization, and X-ray structure determination of the resultant complex, Pt(dbbpy)(S-4-py)$_2$ (dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, S-4-py = pyridine-4-thiolate). Diimine bis(thiolate) complexes of platinum(II) have not been studied as extensively as the corresponding dithiolate systems, but they appear to have a similar electronic structure with an intense solvatochromic absorption band in the visible region of the spectrum and an associated charge-transfer emission that is observable at 77 K.[28,29,36−38]

Experimental Section

Physical Measurements. ^{1}H NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer, and electronic absorption spectra were obtained on a Hitachi U2000 UV−visible spectrophotometer. Emission spectra were collected at room temperature on a Spex Fluorolog-2 fluorescence spectrophotometer using 1 cm × 1 cm quartz fluorescence cells with degassed and dry methylene chloride as a solvent. The concentrations of solutions were in the 10^{-5} M range. The emission spectra were measured using an internal rhodamine B quantum counter and corrected for detector sensitivity. Electrochemical measurements were performed using an EG&G PAR 263A poten-

---

(1) *Supramolecular Photochemistry*; Balzani, V., Ed.; D. Reidel Publishing Co.: Dordrecht, Holland, 1987.

(2) Balzani, V.; Moggi, L.; Scandola, F. In *Supramolecular Photochemistry*; Balzani, V., Ed.; D. Reidel Publishing Co.: Dordrecht, Holland, 1987; pp 1−28.

(3) *Supramolecular Chemistry*; Balzani, V., DeCola, L., Eds.; Kluwer Academic Publishers: Dordrecht, Holland, 1992.

(4) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163−170.

(5) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26−34.

(6) Issberner, J.; Vogtle, F.; DeCola, L.; Balzani, V. *Chem. Eur. J.* **1997**, *3*, 706−712.

(7) Flamigni, L.; Armaroli, N.; Barigelletti, F.; Balzani, V.; Collin, J. P.; Dalbavie, J. O.; Heitz, V.; Sauvage, J. P. *J. Phys. Chem.* **1997**, *101*, 5936−5943.

(8) Ashton, P. R.; Ballardini, R.; Balzani, V.; Boyd, S. E.; Credi, A.; Gandolfi, M. T.; GomezLopez, M.; Iqbal, S.; Philp, D.; Preece, J. A.; Prodi, L.; Ricketts, H. G.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1997**, *3*, 152−170.

(9) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759−833.

(10) Grosshenny, V.; Harriman, A.; Hissler, M.; Ziessel, R. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2223−2238.

(11) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707−1716.

(12) Indelli, M. T.; Scandola, F.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *Inorg. Chem.* **1996**, *35*, 303−312.

(13) Indelli, M. T.; Bignozzi, C. A.; Harriman, A.; Schoonover, J. R.; Scandola, F. *J. Am. Chem. Soc.* **1994**, *116*, 3768−3779.

(14) Vögtle, F.; Frank, M.; Nieger, M.; Belser, P.; von Zelewsky, A.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1643−1646.

(15) Barigelletti, F.; Flamigni, L.; Balzani, V.; Collins, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E. C.; Thompson, A. M. W. C. *J. Am. Chem. Soc.* **1994**, *116*, 7692−7699.

(16) Barigelletti, F.; Flamigni, L.; Guardigli, M.; Juris, A.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1996**, *35*, 136−142.

(17) Barigelletti, F.; Flamigni, L.; Collin, J.-P.; Sauvage, J.-P. *Chem. Commun.* **1997**, 333−338.

(18) De Cola, L.; Balzani, V.; Barigelletti, F.; Flamigni, L.; Belser, P.; von Zelewsky, A.; Frank, M.; Vögtle, F. *Inorg. Chem.* **1993**, *32*, 5228−5238.

(19) Furue, M.; Yoshidzumi, T.; Kinoshita, S.; Kushida, T.; Nozakura, S.; Kamachi, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1632−1640.

(20) Balzani, V.; Bardwell, D. A.; Barigelletti, F.; Cleary, R. L.; Guardigli, M.; Jeffery, J. C.; Sorvrani, T.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 3601−3608.

(21) Denti, G.; Campagna, S.; Serroni, S.; Ciano, M.; Balzani, V. *J. Am. Chem. Soc.* **1992**, *114*, 2944−2950.

(22) Vogler, L. M.; Brewer, K. J. *Inorg. Chem.* **1996**, *35*, 818−824.

(23) Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 1799−1800.

(24) Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J.-P. *Inorg. Chem.* **1996**, *35*, 2937−2944.

(25) Haga, M.; Meser Ali, M.; Arakawa, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 76−78.

(26) Balzani, V.; Barigelletti, F.; Belser, P.; Bernhard, S.; DeCola, L.; Flamigni, L. *J. Phys. Chem.* **1996**, *100*, 16786−16788.

(27) Hasenknopf, B.; Hall, J.; Lehn, J. M.; Balzani, V.; Credi, A.; Campagna, S. *New J. Chem.* **1996**, *20*, 725−730.

(28) Zuleta, J. A.; Bevilacqua, J. M.; Proserpio, D. M.; Harvey, P. D.; Eisenberg, R. *Inorg. Chem.* **1992**, *31*, 2396.

(29) Zuleta, J. A.; Bevilacqua, J. M.; Eisenberg, R. *Coord. Chem. Rev.* **1992**, *111*, 237.

(30) Bevilacqua, J. M.; Eisenberg, R. *Inorg. Chem.* **1994**, *33*, 2913−2923.

(31) Bevilacqua, J. M.; Eisenberg, R. *Inorg. Chem.* **1994**, *33*, 1886−1890.

(32) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.* **1995**, *34*, 2007−2014.

(33) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949−1960.

(34) Paw, W.; Eisenberg, R. *Inorg. Chem.* **1997**, *36*, 2287−2293.

(35) Paw, W.; Connick, W. B.; Eisenberg, R. *Inorg. Chem.* **1998**, in press.

(36) Cummings, S. D.; Cheng, L.-T.; Eisenberg, R. *Chem. Mater.* **1997**, *9*, 440−450.

(37) Base, K.; Grinstaff, M. W. *Inorg. Chem.* **1998**, *37*, 1432−1433.

(38) Hartl, F.; Stufkens, D. J.; Weinstein, J.; Mel'nikov, M.; Zheligovskaya, N. *12th International Symposium on Photochemistry & Photophysics of Coordination Compounds,* Saint Michael's College, Burlington, Vermont, June 1997, p 92.

S0020-1669(97)01557-7 CCC: $15.00

Table 1. Crystallographic Data for Pt(dbbpy)(S-4-py)$_2$

formula	$C_{28}H_{32}N_4PtS_2$
fw	683.89
temp	193(2) K
wavelength	0.717 03 Å
space group	$P\bar{1}$
a (Å)	9.8484(3)[a]
b (Å)	11.4826(5)[a]
c (Å)	13.3472(5)[a]
α (deg)	113.5590(10)[a]
β (deg)	97.0060(10)[a]
γ (deg)	95.6940(10)[a]
V (Å^3)	1354.95(9)[a]
Z	2
D_{calc} (g/cm^3)	1.676
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0679$, w$R_2 = 0.1222$[b]
R indices (all data)	$R_1 = 0.0920$, w$R_2 = 0.1356$[b]

[a] It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10× the listed values. [b] $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; w$R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [f(\mathrm{Max};0,F_o^2) + 2F_c^2]/3$; GOF $= [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n and p denote the number of data and parameters. $R_{int} = \sum|F_o^2 - F_o^2(\mathrm{mean})|/\sum[F_o^2]$; $R_{sigma} = \sum[\sigma(F_o^2)]/\sum[F_o^2]$.

tiostat/galvanostat and a cell having a Pt disk working electrode, a Pt auxiliary electrode, and a Ag wire pseudoreference. Measurements were done at room temperature on nitrogen-saturated acetonitrile solutions containing ca. 0.1 M [(n-Bu)$_4$N](PF$_6$) electrolyte. The Fc/Fc$^+$ couple (0.400 V relative to NHE) was used as an internal reference to calibrate the cell potential, and values are quoted relative to that couple. Elemental analyses were obtained from Quantitative Technologies Inc.,Whitehouse, NJ.

Synthesis of Pt(dbbpy)(S-4-py)$_2$. Pt(dbbpy)Cl$_2$ was synthesized according to the literature report.[39] A sample of 0.290 g of Pt(dbbpy)Cl$_2$ was suspended in 30 mL of degassed 1:1 mixture of CH$_2$Cl$_2$/acetone, to which was added a degassed solution of 0.160 g of 4-mercaptopyridine in CH$_3$OH containing one pellet of KOH. The mixture was stirred for 3 h at room temperature. As the starting dichloride complex dissolved slowly, the color of the solution changed from yellow to orange. After evaporation to dryness, the residue was dissolved in 2 mL of CH$_2$Cl$_2$ (orange solution) and precipitated with hexanes (yellow solid). This recrystallization was repeated once. The solid was isolated by filtration and dried in air. Yield: 0.330 g (89%). Anal. Calcd for $C_{28}H_{32}N_4S_2Pt$: C, 49.18; H, 4.72; N, 8.19. Found: C, 48.77; H, 4.40; N, 7.92. ^{1}H NMR (ppm, CDCl$_3$): 9.57 (d, 2H, $J = 6.0$ Hz), 8.00 (d, 2H, $J = 2.0$ Hz), 7.98 (m, 4H), 7.54 (dd, 2H, $J = 6.0$, 2.0 Hz), 7.51 (m, 4H), 1.43 (s, 18H). UV/vis (nm): DMF, 435; CH$_2$Cl$_2$, 452; THF, 464; toluene, 490.

X-ray Structural Determination of Pt(dbbpy)(S-4-py)$_2$. A summary of selected crystallographic data for Pt(dbbpy)(S-4-py)$_2$ is given in Table 1. Crystals were grown by cooling a concentrated CH$_3$OH solution of the complex. An orange fragment of aproximate dimensions 0.12 × 0.10 × 0.08 mm was cut from a cluster of plates under Paratone-8277, mounted under the oil on a glass fiber, and immediately placed in a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD area detector system equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 10 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.52°). The total data collection time was approximately 6 h. Frames were integrated to 0.75 Å with the Siemens SAINT program to yield a total of 7998 reflections, of which 5683 were independent ($R_{int} = 3.70\%$, $R_{sig} = 10.10\%$; see Table 1 for definitions) and 4585 were above $2\sigma(I)$. Laue symmetry revealed a triclinic crystal system, and the final unit cell parameters (at −80 °C) were determined from a least-squares refinement of three-dimensional centroids of 3807 reflections. The space group was assigned as $P\bar{1}$, and the structure was solved by using direct methods and refined by employing full-matrix least-squares on F^2 (Siemens, SHELXTL, version 5.04).[40] For a Z value of 2, there is one independent molecule in the asymmetric unit. The methyl groups of one of the *t*-Bu substituents of the dbbpy ligand were found to be rotationally disordered. The SOFs (site occupations factors) of the disordered atom pairs refined to a 60:40 ratio, leading to acceptable isotropic thermal parameters for the disordered atoms. All other non-hydrogen atoms were refined anisotropically with hydrogen atoms included in idealized positions giving a data:parameter ratio of approximately 12:1. The structure refined to a goodness of fit (GOF) of 1.017 and final residuals of $R_1 = 6.79\%$ ($I > 2\sigma(I)$) and w$R_2 = 12.22\%$ ($I > 2\sigma(I)$) as defined in Table 1.

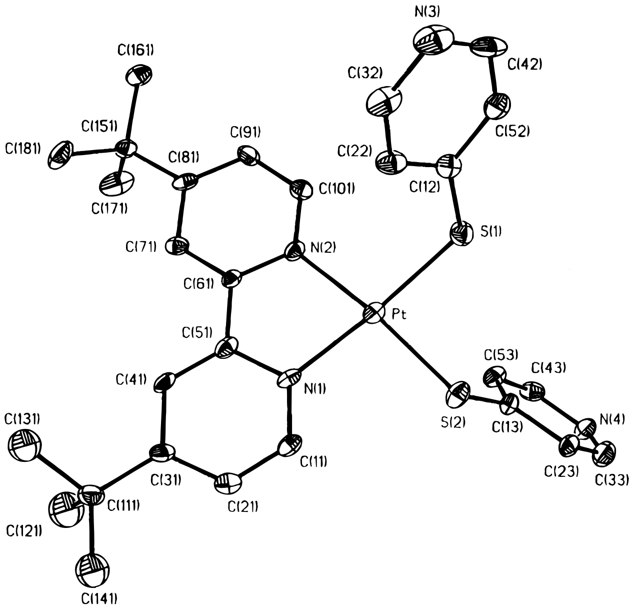
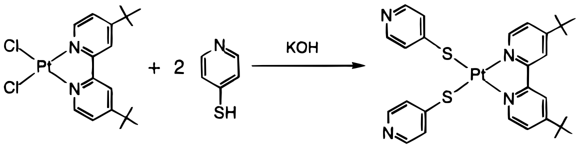


Figure 1. ORTEP diagram of Pt(dbbpy)(S-4-py)$_2$.

Results and Discussion

The orange complex Pt(dbbpy)(S-4-py)$_2$ has been prepared in high yield from Pt(dbbpy)Cl$_2$ and 4-mercaptopyridine in the presence of base, eq 1. This complex was characterized by



(1)

elemental analysis, ^{1}H NMR and electronic spectroscopies, and single-crystal X-ray diffraction. The ORTEP diagram of Pt(dbbpy)(4-Spy)$_2$ obtained from the crystal strucuture analysis is shown in Figure 1, while selected bond lengths and angles for the structure are presented in Table 2. The Pt(II) complex possesses a square planar coordination geometry with the two thiolate donors trans to the diimine N atoms. The Pt−N distances of 2.058(7) and 2.060(8) Å and the N−Pt−N bond angle of 79.1(3)° agree well with values found for other Pt(II) diimine complexes including Pt(bpy)(bdt), Pt(Me$_2$bpy)(met), and Pt(Ph$_2$phen)(SB$_{10}$C$_2$H$_{11}$)$_2$.[30,37,41] The structure is only the second of a Pt(II) diimine bis(thiolate) complex to be reported, and the observed Pt−S distances are in close agreement between the two structures (2.290(3) and 2.294(3) Å in the present study

---

(39) Hodges, K. D.; Rund, J. V. *Inorg. Chem.* **1975**, *14*, 525.

(40) *SHELXTL: Structure Analysis Program*, version 5.04; Siemens Industrial Automation Inc.: Madison, WI, 1995.

(41) Connick, W. B.; Gray, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 11620.

Table 2. Selected Structural Parameters for Pt(dbbpy)(S-4-py)$_2$

Bond Distances (Å)			
Pt−N(2)	2.057(8)	Pt−S(1)	2.291(3)
Pt−N(1)	2.059(8)	Pt−S(2)	2.293(3)
S(1)−C(12)	1.742(11)	S(2)−C(13)	1.751(10)
Bond Angles (deg)			
N(2)−Pt−N(1)	79.5(3)	N(1)−Pt−S(1)	175.0(2)
N(2)−Pt−S(1)	96.7(2)	N(1)−Pt−S(2)	94.9(2)
N(2)−Pt−S(2)	174.4(2)	S(1)−Pt−S(2)	88.88(10)
C(12)−S(1)−Pt	106.3(4)	C(13)−S(2)−Pt	107.4(3)

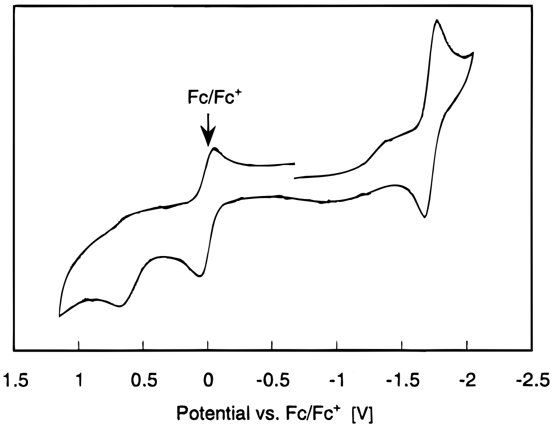


Figure 2. Cyclic voltammogram of Pt(dbbpy)(S-4-py)$_2$.

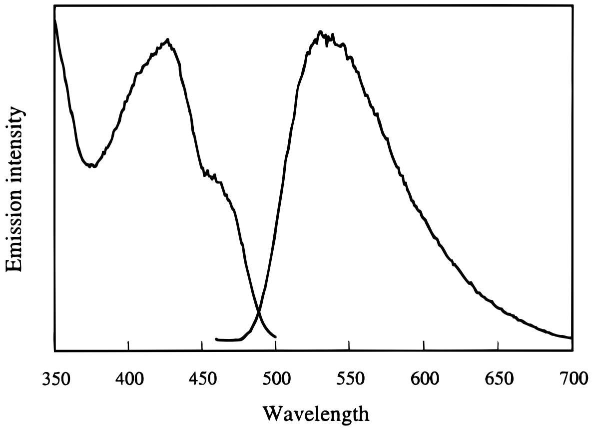


Figure 3. Emission and excitation spectra of Pt(dbbpy)(S-4-py)$_2$ collected at 77 K in a DMM glass (DMF, methylene chloride, methanol, 1:1:1).

and 2.313 and 2.286 Å for Pt(Ph$_2$phen)(SB$_{10}$C$_2$H$_{11}$)$_2$[37]). However, the Pt−S distances are longer than the average value of 2.246 Å reported in the analogous dithiolate systems.[30,41] Deviation of the bond angles in the square planar coordination sphere from perfect right angles arises from constraints due to the small bite of the diimine chelate. While the core of the bipyridine ligand lies in the same plane as the PtN$_2$S$_2$ coordination sphere, the pyridyl substituents of the thiolate donors deviate out of the plane. As can be seen in Figure 1, one pyridyl is oriented above the coordination plane while the other is directed below it. The arrangement is similar to that seen in the other reported bis(thiolate) structure, namely Pt(Ph$_2$phen)(SB$_{10}$C$_2$H$_{11}$)$_2$.[37]

The cyclic voltammogram of the Pt(dbbpy)(4-Spy)$_2$ complex (Figure 2) shows one irreversible oxidation at $+0.66$ V (E_p) and one reversible reduction at -1.73 V ($E_{1/2}$) vs Fc/Fc$^+$. These results can be compared to the data available for closely related Pt(II) diimine dithiolate and bis(thiolate) complexes, which typically display one reversible reduction and one irreversible oxidation.[33,37,38] In these complexes, reduction is associated with the diimine ligand and is consistent with the lowest unoccupied molecular orbital being of nearly pure π^*(diimine) character. The value of -1.73 V vs Fc$^+$/Fc found for the reduction is in reasonable agreement with $E_{1/2}$ values reported for a series of Pt(dbbpy)(dithiolate) complexes[33] when adjusted to a common reference. The irreversible oxidation wave is more problematic to compare—it is slightly more positive than the irreversible oxidation waves of the Pt(dbbpy)(dithiolate) series, but it agrees with the corresponding process reported for Pt(bpy)(*p*-SC$_6$H$_4$-NO$_2$)$_2$.[38] On the other hand, Pt(Ph$_2$phen)(SB$_{10}$C$_2$H$_{11}$)$_2$ does not exhibit an oxidation process out to 1.8 V vs Ag/AgCl.[37] In the diimine dithiolate complexes, oxidation is associated with a highest occupied orbital of mixed-metal−dithiolate character and a similar assignment for a metal−thiolate HOMO appears operative for the bis(thiolate) systems as well. This conclusion receives additional support from the spectroscopic data described below.

The absorption spectrum of Pt(dbbpy)(S-4-py)$_2$ displays a low-energy band in the visible region. This band is solvatochromic with absorption energies ranging from 435 nm in DMF to 490 nm in toluene. The shift to lower energy with decreasing solvent polarity has been classified as negative. It is reminiscent of the Pt(II) diimine dithiolate complexes and indicates a similar polar ground state in Pt(dbbpy)(S-4-py)$_2$ with a metal/thiolate-to-diimine charge transfer. The related Pt bis(thiolate) complexes Pt(diimine)(SR)$_2$ (diimine = 4,4′-dimethylbipyridine (dmbpy), 4,7-diphenylphenanthroline (dpphen); R = Et Ph),[28] Pt(diimine)(SC$_6$H$_4$X)$_2$ (diimine = phen or bpy, X = H, NO$_2$, OCH$_3$, N(CH$_3$)$_2$),[38] and Pt(Ph$_2$phen)(SB$_{10}$C$_2$H$_{11}$)$_2$[37] all show a similar, strongly allowed charge-transfer band having negative solvatochromism. Unlike the Pt(II) diimine dithiolate complexes, Pt(dbbpy)(S-4-py)$_2$ does not display emission at room temperature when this solvatochromic band is irradiated. An emission is observed, however, at 77 K with the maximum at 530 nm (Figure 2). Possible explanations for the increased nonradiative decay that precludes room temperature emission include greater flexibility of the coordination sphere resulting from the nonchelated thiolate donors and uncoordinated pyridyl N atoms that may interact rapidly and reversibly with available protons in the solvent. It should be noted, however, that the emissions from other Pt(II) diimine bis(thiolate) complexes have only been reported for rigid media samples at 77 K.[28,37,38]

Syntheses of multicomponent complexes incorporating Pt(dbbpy)(S-4-py)$_2$ are currently underway. It is expected that coordination of the pyridyl groups will reduce nonradiative deactivation of the excited charge transfer state in this chromophore. Such a reduction in the rate of nonradiative decay was previously observed in the case of dipyridocatecholate complexes of Pt(II), where coordination of the phenanthroline moiety to a second metal center resulted in emission from the normally nonemissive Pt(II) diimine catecholate center.[35] For the title complex, the presence of uncoordinated pyridyl groups creates the possibility of synthesizing novel multicomponent complexes/supramolecular systems containing the Pt(diimine)(thiolate)$_2$ chromophore with its directional metal/thiolate-to-diimine charge transfer.

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.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for complex Pt(dbbpy)(S-4-py)$_2$ is available on the Internet only. Access information is given on any current masthead page.

IC971557R