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Syntheses and Structural Characterization of Luminescent Platinum(II) Complexes Containing Di-*tert*-butylbipyridine and New 1,1-Dithiolate Ligands

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Three new di-*tert*-butylbipyridine (dbbpy) complexes of platinum(II) (**1**−**3**) containing 1,1-dithiolate ligands have been synthesized and characterized. The 1,1-dithiolates are 2,2-diacetylethylene-1,1-dithiolate ($S_2C{=}C(C(O)Me)_2$) (**1**), 2-cyano-2-*p*-bromophenylethylene-1,1-dithiolate ($S_2C{=}C(CN)(p\text{-}C_6H_4Br)$) (**2**), and *p*-bromophenyl-2-cyano-3,3-dithiolatoacrylate ($S_2C{=}C(CN)(COO\text{-}p\text{-}C_6H_4Br)$) (**3**). Complex **1** exhibits a solvatochromic charge-transfer absorption in the 430−488 nm region of the spectrum and a luminescence around 635 nm in ambient temperature CH_2Cl_2 solution. These observations are consistent with what has been seen previously in related Pt diimine 1,1-dithiolate complexes. The nature of the emissive state is assigned as a ^{3}(mixed metal/dithiolate-to-diimine) charge transfer, while the solvatochromic absorption band corresponds to the singlet transition of similar orbital character. The other complexes also exhibit a low-energy solvatochromic absorption. The crystal structures of two of the complexes have been determined, representing the first time that Pt(diimine)(1,1-dithiolate) complexes have been crystallographically studied. The structures confirm the expected square planar coordination geometry with distortions in bond angles dictated by the constraints of the chelating ligands. The Pt−S and Pt−N bond lengths and S−Pt−S and N−Pt−N bond angles for the two structures are identical within experimental error (2.283(2) and 2.278(2) Å; 2.053(6) and 2.050(8) Å; 75.01(8)° and 75.40(8)°; 79.2(2)° and 79.0(2)°, respectively). Crystal data for **1**: monoclinic, space group $P2_1/n$ (No. 14), with $a = 7.20480(10)$ Å, $b = 20.53880(10)$ Å, $c = 19.1072(2)$ Å, $\beta = 93.83°$, $V =$ Å^3, $Z = 4$, R1 = 3.34% ($I > 2\sigma(I)$), wR2 = 9.88% ($I > 2\sigma(I)$) for 3922 unique reflections. Crystal data for **2**: monoclinic, space group $P2_1/n$ (No. 14), with $a = 15.0940(5)$ Å, $b = 9.5182(3)$ Å, $c = 20.4772(7)$ Å, $\beta = 111.151(1)°$, $V =$ Å^3, $Z = 4$, R1 = 4.07% ($I > 2\sigma(I)$), wR2 = 8.64% ($I > 2\sigma(I)$) for 3859 unique reflections.

Introduction

Platinum diimine dithiolate complexes have been found to have a number of interesting electronic structural properties that have served to stimulate interest in these systems.[1−14] Foremost among them is the luminescence that these complexes exhibit in ambient temperature fluid solutions. The nature of this luminescence has been the subject of several investigations that have led to its assignment as a charge transfer to diimine phosphoresence from an orbital of mixed metal/sulfur/dithiolate character.[3,4,7,9] The complexes also show a solvatochromic absorption that is similar to the emissive state in terms of orbital character. Variation of substituents on both diimine and dithiolate ligands reveals that the excited-state properties of these complexes, including energy, lifetime, and redox potentials, can be systematically tuned.[9] In general, complexes containing 1,1-dithiolate ligands have both emission and solvatochromic bands at higher energies than analogous 1,2-dithiolate systems. The excited platinum diimine dithiolate complexes have also been found to undergo self-quenching as solution concentration is increased,[11,15] most probably via Pt···Pt interactions.

The directionality of the charge-transfer excited state in the Pt diimine dithiolate complexes has made these systems of particular interest in the development of multicomponent assemblies for photoinduced charge separation and molecular photochemical devices for light-driven, energy-storing reactions.[16,17] One approach to the linking of components in these systems is through Pd-catalyzed coupling reactions involving

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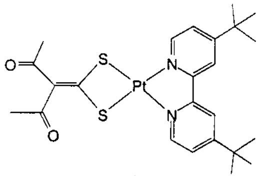
alkynes and aryl bromides,[18−23] while a second has utilized Schiff-base condensation reactions.

In the present paper, we describe three new Pt diimine dithiolate complexes **1**−**3** and their structural and spectroscopic characterization. The sulfur ligands in these complexes are of the 1,1-dithiolate type and are formed by the reaction of active methylene compounds with CS_2 in the presence of base. Two of the complexes have been characterized crystallographically, making them the first Pt diimine 1,1-dithiolate systems to be so analyzed. The dithiolate ligand in **1** was first reported in 1997, and its coordination to Au and Tl(I) has been examined.[24,25a] Mono-, di-, and tetranuclear Pt(II), Pd(II), and Ag(I) complexes with the same ligand, including the Pt(II) and Pd(II) complexes homologous to **1** with unsubstituted bpy, were previously synthesized by one of us (S.H.) using the same method here reported.[25b] The other two dithiolates have not been reported previously, although the one in **3** represents simply a different ester of the well-studied Rcda (alkyl 2-cyano-3,3-dithiolatoacrylate) system.[1−3,26,27] The dithiolate substituents in **1**−**3** provide interesting opportunities for connection to donor components in the construction of photoinduced charge separation devices.



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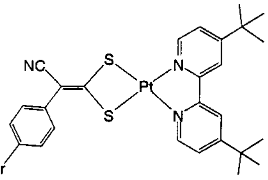

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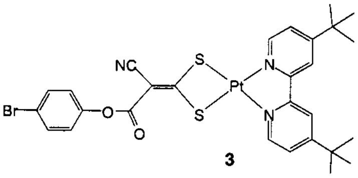

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Experimental Section

Chemicals. Cyanoacetic acid, oxalyl chloride, 4-bromophenol, 4-bromophenylacetonitrile, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were used as received from Aldrich, and K_2PtCl_4 was used as received from Alfa/AESAR Johnson-Matthey. Reagent grade CS_2, acetone, acetonitrile, diethyl ether (Et_2O), and 2-propanol (ipa) were deoxygenated with an N_2 purge but otherwise used as received (Aldrich or Fisher Chemical). Spectroscopic grade *N*,*N*-dimethylformamide (DMF), methanol (MeOH), chloroform ($CHCl_3$), and dichloromethane (CH_2Cl_2) were used as received from Burdick and Jackson. The compounds 4,4′-di-*tert*-butyl-2,2′-bipyridine (dbbpy),[28] $[Tl_2\{\eta^2\text{-}(S,S')\text{-}S_2C{=}C\{C(O)Me\}_2\}]$,[25] and cyanoacetyl chloride were prepared as described in the literature.

The complex $Pt(dbbpy)Cl_2$ was prepared following the method of Rund by heating a suspension of dbbpy in an aqueous solution of 1 equiv of K_2PtCl_4 acidified with one drop of HCl until a yellow precipitate formed (ca. 2 h).[29] ^1H NMR (DMSO-d_6): δ 9.34 (2 H, d, J = 5.6 Hz), 8.58 (2H, s), 7.83 (2H, d, J = 5.2 Hz), 1.41 (18 H, s).

Physical Measurements. ^1H NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400 MHz. Chemical shifts are referenced relative to TMS and were determined on the basis of residual proton solvent resonances. Infrared spectra were recorded on Mattson Galaxy 6020 FTIR and Nicolet Impact 400 spectrophotometers as KBr pellets. Absorption spectra were recorded on a Hitachi U2000 UV−visible spectrophotometer. Steady-state emission measurements were performed on a Spex Fluorolog-2 fluorescence spectrophotometer equipped with a 450 W xenon lamp and Hamamatsu R929 photomultiplier tube detector. Room-temperature measurements were made using 1 cm × 1 cm quartz fluorescence cells; solutions were freeze−pump−thaw degassed four times and then placed under high-purity nitrogen. Low-temperature emission spectra were recorded in 3:1 EtOH/MeOH solvent glass formed in 4 mm diameter quartz EPR tubes placed in a liquid nitrogen Dewar equipped with quartz windows. Emission was collected at 90° from the excitation for both experiments. Cyclic voltammetry experiments were carried out using an EG&G PAR 263A potentiostat/galvanostat employing a three-electrode single-cell compartment. All samples were degassed with nitrogen or argon. A Pt working electrode, a Pt auxiliary electrode, and a Ag/$AgNO_3$/acetonitrile reference electrode were used. For all of the measurements, the ferrocene/ferrocenium couple at 0.40 V vs NHE was used to calibrate the cell potential. Elemental analysis of complexes **1**−**3** was performed by the Analytical Technology Division, Kodak Research Laboratories.

Syntheses of Pt(dbbpy)(dithiolate) Complexes. The Pt(dbbpy)(dithiolate) complexes were prepared by displacement of the two chlorides in the $Pt(dbbpy)Cl_2$ precursor with the appropriate 1,1-dithiolate chelating ligand. The precursor to the dithiolate ligand used to synthesize **3**, i.e., 4-bromophenylcyanoacetate, was prepared by the reaction of cyanoacetyl chloride and 4-bromophenol in dichloromethane for 9 days. The reaction solution was concentrated using a rotary evaporator, diethyl ether (60 mL) was added, and a cream-colored precipitate formed. The precipitate was separated by filtration under a nitrogen atmosphere and vacuum-dried. Yield: 13.10 g, (99%). $p\text{-Br}{-}C_6H_4OOCCH_2CN$. ^1H NMR (MeOH-d_4): δ 7.56 (d, 2 H, J_{HH} = 7.7 Hz), 7.12 (d, 2 H, J_{HH} = 7.7 Hz), 4.87 (s, 2 H, CH_2).

[Pt(dbbpy){$S_2C{=}C(C(O)Me)_2$}] (1). $Pt(dbbpy)Cl_2$ (710.7 mg, 1.33 mmol) was added to a suspension of $[Tl_2\{\eta^2\text{-}(S, S'){-}S_2C{=}C(C(O)Me)_2\}]$ (775.4 mg, 1.33 mmol) in chloroform (70 mL). The mixture was stirred at reflux temperature for 5 h and filtered, and the residue was extracted with chloroform (3 × 30 mL). The combined filtrates were concentrated using a rotary evaporator, diethyl ether (70 mL) was added, and an orange precipitate formed. The precipitate was separated by filtration and purified by recrystallization from dichloromethane/diethyl ether. Yield: 653 mg, (76.7%). ^1H NMR ($CDCl_3$): δ 8.31 (d, 2 H, J_{HH} = 7 Hz Hdbbpy), 7.99 (s, 2 H, Hdbbpy), 7.43 (d, 2 H, J_{HH} = 7 Hz, Hdbbpy), 2.36 (s, 6 H, CH_3), 1.39 (s, 18 H, ^tBu). FT-IR (KBr) ν (cm^{-1}): 1701 (s, ν_{CO}), 1619 (s, $\nu_{C=N}$), 1503 (s, $\nu_{C=C}$). MS *m*/*z* 638 $[M + H]^+$. Anal. Calcd for $C_{24}H_{30}N_2O_2PtS_2$ (M_r = 637.73 g mol^{-1}): C, 45.20; H, 4.74; N, 4.39. Found: C, 44.95; H, 4.61; N, 4.28.

[Pt(dbbpy){$S_2C{=}C(CN)(4\text{-}C_6H_4Br)$}] (2). To a solution of 4-bromophenylacetonitrile (103.9 mg, 0.53 mmol) in THF (15 mL), DBU (0.16 mL, 1.06 mmol) was added under N_2. The solution was stirred at room temperature for 5 min, during which time its color changed from colorless to pale-yellow. Carbon disulfide (0.032 mL, 0.53 mmol) was then added, and the solution turned bright-yellow. The solution was stirred for an additional 2 h and was then transferred dropwise via cannula to a solution of $Pt(dbbpy)Cl_2$ (282.8 mg, 0.53 mmol) in dichloromethane (60 mL). The resulting solution turned red. The solution was stirred at room temperature for 1 day, after which the solvent was removed using a rotary evaporator. The crude precipitate was chromatographed on silica gel using dichloromethane/methanol

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as the eluent. The red compound was further purified by recrystallization from chloroform. Yield: 233.3 mg (60%). ^{1}H NMR (CDCl$_3$): δ 8.47 (pseudotriplet, 2 H, Hdbbpy), 7.97 (s, 2 H, Hdbbpy), 7.73 (d, 2 H, J_{HH} = 8.4 Hz, Ph), 7.51 (dd, 1 H, dbbpy, J_{HH} = 1.6 Hz, J_{HH} = 5.6 Hz), 7.47 (d, 2 H, J_{HH} = 1.6 Hz, J = 6 Hz), 7.44 (dd, 1 H, dbbpy, J = 8.4 Hz, Ph), 1.55 (s, 9 H, ^{t}Bu), 1.42 (s, 9 H, ^{t}Bu). FT-IR (KBr) ν (cm^{-1}): 2195 (s, $\nu_{C\equiv N}$), 1630, 1508 (s, $\nu_{C=N}$, $\nu_{C=C}$). MS m/z 734 [M + H]$^+$. Anal. Calcd for $C_{27}H_{28}N_3BrPtS_2$ (M_r = 733.65 g mol^{-1}): C, 44.26; H, 3.85; N, 5.74. Found: C, 44.41; H, 3.48; N, 5.84.

[Pt(dbbpy){S_2C=C(CN)(C(O)-4-OC_6H_4Br)}] (3). To a solution of 4-bromophenylcyanoacetate (199.2 mg, 0.83 mmol) in THF (15 mL), DBU (0.25 mL, 1.66 mmol) was added under N_2. The solution was stirred at room temperature for 5 min followed by the addition of CS_2 (0.05 mL, 0.83 mmol). The solution, which turned yellow, was stirred for an additional 2 h, after which it was transferred dropwise via cannula to a solution of [PtCl$_2$(dbbpy)] (443.5 mg, 0.83 mmol) in dichloromethane (60 mL). The resulting solution turned red. The solution was stirred at room temperature for 1 day, after which solvent was removed using a rotary evaporator. The crude precipitate was chromatographed on silica gel using dichloromethane/methanol as the eluent. The red compound was further purified by recrystallization from chloroform. Yield: 374 mg (58%). ^{1}H NMR (CDCl$_3$): δ 8.29 (d, 1 H, Hdbbpy), 8.24 (d, 1 H, Hdbbpy), 7.99 (s, 2 H, Hdbbpy), 7.48 (dd, 1 H, J_{HH} = 2 Hz, J_{HH} = 6.8 Hz, dbbpy), 7.44 (dd, 1 H, J_{HH} = 2 Hz, J_{HH} = 6 Hz, dbbpy), 7.40 (d, 2 H, J_{HH} = 8.8 Hz, Ph), 7.04 (d, 2 H, J_{HH} = 8.8 Hz, Ph), 1.50 (s, 9 H, ^{t}Bu), 1.41 (s, 9 H, ^{t}Bu). FT-IR (KBr) ν (cm^{-1}): 2200 (s, $\nu_{C\equiv N}$), 1699, 1625, 1562, 1537 (s, $\nu_{C=N}$, $\nu_{C=C}$). MS m/z 779 [M + H]$^+$. Anal. Calcd for $C_{28}H_{28}N_3O_2PtBrS_2$ (M_r = 777.66 g mol^{-1}): C, 43.25; H, 3.63; N, 5.40. Found: C, 43.37; H, 4.10; N, 5.14.

X-ray Structural Determination of 1. Crystals were grown by slow evaporation of a CH_2Cl_2/ether solution of the complex in air. A yellow needle of approximate dimensions 0.16 × 0.16 × 0.24 mm^3 was mounted under Paratone-8277 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 30 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.6°). The total data collection time was approximately 12 h. Frames were integrated to a maximum 2θ angle of 46.3° with the Siemens SAINT program to yield a total of 11 530 reflections, of which 3922 were independent and 3364 were above 2$\sigma(I)$. Laue symmetry revealed a monoclinic crystal system, and the final unit cell parameters (at −80 °C) were determined from the least-squares refinement of three-dimensional centroids of 7702 reflections.

The space group was assigned as $P2_1/n$, and the structure was solved using direct methods and refined employing full-matrix least-squares on F^2 (Siemens, SHELXTL, version 5.04). For a Z value of 4, there is one molecule and two waters in the asymmetric unit. All of the non-H atoms were refined anisotropically except the oxygen atoms of the water molecules, and hydrogen atoms were included in idealized positions. H atoms were neither found nor included for the water molecules. The structure was refined to a goodness of fit (GOF) of 1.112 and final residuals of R1 = 3.34% ($I > 2\sigma(I)$), wR2 = 9.88% ($I > 2\sigma(I)$). Crystallographic and selected data collection parameters for **1** are given in Table 1; a complete tabulation is provided in the Supporting Information.

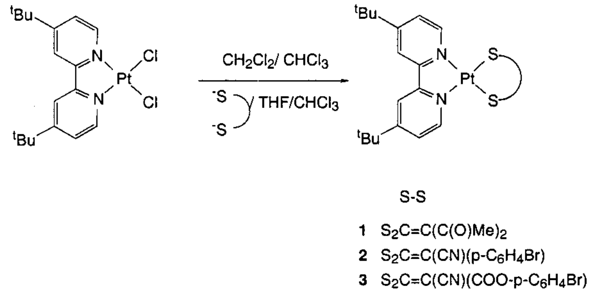
X-ray Structural Determination of 2. A red plate of approximate dimensions 0.04 × 0.18 × 0.38 mm^3 was mounted under Paratone-8277 on a glass fiber and immediately placed in a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected as for **1** with exposure times of 5 s/frame and total data collection time of 12 h. Frames were integrated to a maximum 2θ angle of 46.6° to yield a total of 11 994 reflections, of which 3859 were independent and 2956 were above 2$\sigma(I)$. Laue symmetry revealed a monoclinic crystal system, and the final unit cell parameters (at −80 °C) were determined from the least-squares refinement of three-dimensional centroids of 4242 reflections.

Table 1. Crystallographic Data for **1** and **2**

	1	**2**
chemical formula	$C_{24}H_{34}N_2O_4PtS_2$	$C_{27}H_{28}BrN_3PtS_2$
fw	673.74	733.64
cryst syst	monoclinic	monoclinic
space group (No.)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z	4	4
a,[a] Å	7.2048(1)[a]	15.0940(5)[a]
b,[a] Å	20.5388(1)[a]	9.5182(3)[a]
c,[a] Å	19.1072(2)[a]	20.4772(7)[a]
β,[a] deg	93.830(1)[a]	111.151(1)[a]
vol, Å^3	2821.12(5)	2743.7(2)
ρ_{calcd}, g cm^{-3}	1.586	1.776
cryst dimens, mm^3	0.16 × 0.16 × 0.24	0.04 × 0.18 × 0.38
temp, K	193(2)	193(2)
Mo radiation, Å	0.710 73	0.710 73
no. obsd data ($I > 2\sigma(I)$)	3922	2956
no. params varied	288	313
μ, cm^{-1}	5.15	6.743
R1(F_o), wR2(F_o^2) ($I > 2\sigma$)[b]	0.0334, 0.0988	0.0407, 0.0864
R1(F_o), wR2(F_o^2) (all data)[b]	0.0428, 0.1030	0.0668, 0.0939

[a] It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small because systematic error is not included. More reasonable errors might be estimated at 10 times the listed value. Structures were refined using *SHELXTL: Structure Analysis Program*, version 5.04; Siemens Industrial Automation Inc.: Madison, WI, 1995. [b] R1 = $(\sum||F_o| - |F_c||)/\sum|F_o|$; wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(0,F_o^2) + 2F_c^2]/3$.

Scheme 1



The space group was assigned as $P2_1/n$, and the structure was solved using direct methods and refined employing full-matrix least-squares on F^2 (Siemens, SHELXTL, version 5.04). For a Z value of 4, there is one molecule in the asymmetric unit. All of the non-H atoms were refined anisotropically, and hydrogen atoms were included in idealized positions. The structure refined to a goodness of fit (GOF) of 1.043 and final residuals of R1 = 4.07% ($I > 2\sigma(I)$), wR2 = 8.64% ($I > 2\sigma(I)$). Crystallographic and selected data collection parameters for **2** are given in Table 1; a complete tabulation is provided in the Supporting Information.

Results and Discussion

Syntheses and Characterization of Pt Di-*tert*-butylbipyridine Dithiolates 1−3. As shown in Scheme 1, the three Pt complexes described here are conveniently prepared by reaction of Pt(dbbpy)Cl$_2$ with the alkali metal salt of the respective 1,1-ethylenedithiolate ligand. All complexes are isolated in moderate yields (58−77%) as orange or bright-red powders. The complexes are soluble in most organic solvents but insoluble in ether, alcohol, pentane, and hexane. The complexes were characterized by electronic, infrared, and ^{1}H NMR spectroscopies and, in two cases, by X-ray crystallography. All three complexes are air-stable in the solid state and in degassed solutions at room temperature.

The ^{1}H NMR spectrum for complex **1** shows three resonances at δ 8.31, 7.99, and 7.43 ppm, corresponding to the aromatic protons of the dbbpy ligand, a resonance at δ 1.39 ppm

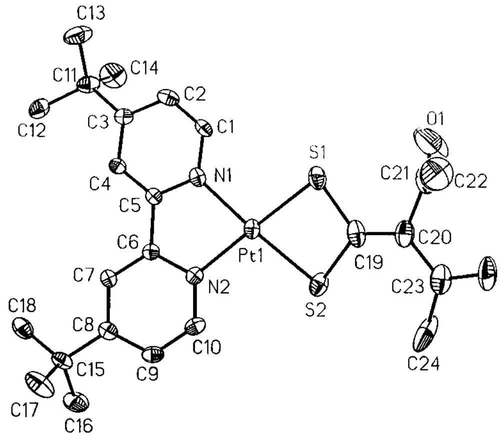


Figure 1. Perspective view of the molecular structure of Pt(dbbpy){$S_2C{=}C(C(O)Me)_2$}, **1**.

assignable to the dbbpy methyl protons, and a resonance at δ 2.36 ppm corresponding to the methyl protons of the dithiolate ligand. Complexes **2** and **3** have ^{1}H NMR spectra that are more complicated because of the asymmetry of the dithiolate ligand, leading to inequivalence of dbbpy protons that were equivalent in **1**. The dbbpy methyl resonances for **2** are observed at δ 1.42 (9 H) and 1.55 (9 H) ppm, while the corresponding resonances for **3** are seen at δ 1.50 (9 H) and 1.41 (9 H) ppm. The aromatic resonances for these complexes are listed in the Experimental Section.

Crystallographic Studies of 1 and 2. The square planar geometry about platinum was confirmed by single-crystal X-ray diffraction studies for complexes **1** and **2**. Despite the increasing interest in Pt diimine dithiolate complexes, these studies represent the first ones done on 1,1-dithiolate systems. The crystallographic and data collection parameters for both structure determinations are shown in Table 1. ORTEP views of the complexes are presented in Figures 1 and 2, while abbreviated tables of bond distances and angles are given in Tables 2 and 3, respectively. Complete tabulations of refined positional and thermal parameters and all bond distances and angles for both structures are given in the Supporting Information.

Both structures exhibit the expected coordination geometry. The constraints of the four-membered chelate rings lead to S−Pt−S bond angles of 75.01(8)° and 75.40(8)° for **1** and **2**, respectively, with average Pt−S bond lengths of 2.283(3) Å and 2.278(3) Å. The Pt−S distances are in the range of values reported for other structurally characterized Pt(II) 1,1-dithiolate complexes.[5,27,30] The average Pt−N bond distances and N−Pt−N bond angles in the two structures are statistically equivalent (2.052(6) and 2.050(6) Å, and 79.2(2) and 79.0(3)°, respectively) and agree closely with Pt−N distances and N−Pt−N bond angles reported for other square planar Pt diimine complexes. All other metrical parameters are similar to corresponding values reported previously.[5,11]

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **1**

Pt(1)−N(1)	2.050(6)	O(2)−C(23)	1.272(11)
Pt(1)−N(2)	2.055(6)	N(1)−C(1)	1.347(9)
Pt(1)−S(2)	2.281(2)	N(1)−C(5)	1.359(9)
Pt(1)−S(1)	2.285(2)	N(2)−C(10)	1.341(9)
S(1)−C(19)	1.757(9)	N(2)−C(6)	1.374(9)
S(2)−C(19)	1.753(9)	C(5)−C(6)	1.484(10)
O(1)−C(21)	1.239(14)	C(19)−C(20)	1.361(11)

N(1)−Pt(1)−N(2)	79.2(2)	N(1)−C(1)−C(2)	122.6(7)
N(1)−Pt(1)−S(2)	175.7(2)	N(1)−C(5)−C(4)	121.6(7)
N(2)−Pt(1)−S(2)	103.7(2)	N(1)−C(5)−C(6)	114.4(6)
N(1)−Pt(1)−S(1)	102.3(2)	C(4)−C(5)−C(6)	123.9(6)
N(2)−Pt(1)−S(1)	175.9(2)	N(2)−C(6)−C(7)	121.2(7)
S(2)−Pt(1)−S(1)	75.01(8)	N(2)−C(6)−C(5)	114.3(6)
C(19)−S(1)−Pt(1)	89.8(3)	N(2)−C(10)−C(9)	122.7(7)
C(19)−S(2)−Pt(1)	90.1(3)	C(20)−C(19)−S(2)	130.8(8)
C(1)−N(1)−C(5)	118.2(6)	C(20)−C(19)−S(1)	124.3(7)
C(1)−N(1)−Pt(1)	125.3(5)	S(2)−C(19)−S(1)	104.8(4)
C(5)−N(1)−Pt(1)	116.3(5)	C(19)−C(20)−C(23)	127.3(9)
C(10)−N(2)−C(6)	117.7(6)	C(19)−C(20)−C(21)	117.5(8)
C(10)−N(2)−Pt(1)	126.6(5)	C(23)−C(20)−C(21)	115.2(8)
C(6)−N(2)−Pt(1)	115.5(5)		

Visible−UV Spectroscopy of Complexes 1−3. Complex **1** exhibits four ultraviolet−visible absorption bands in fluid solution at room temperature. In degassed acetonitrile, the two highest energy bands at 233 and 290 nm (in acetonitrile) have molar extinction coefficients ϵ of 17 000 and 13 000 M^{-1} cm^{-1} and are assignable to ligand-based transitions. The third band is seen at 347 nm (12 700 M^{-1} cm^{-1}), while the fourth occurs in the visible region of the spectrum at 430 nm. The former is relatively insensitive to solvent, shifting from 347 nm in acetonitrile to 357 nm (12 340 cm^{-1} M^{-1}) in toluene, and is assigned to a ligand $p\pi{-}p\pi^*$ transition. In contrast, the latter absorption band at 430 nm (11 300 cm^{-1} M^{-1}) is strongly solvatochromic, similar to what has been reported for closely related Pt diimine dithiolate complexes.[1,3,7,9] The great solubility of **1** in a variety of organic solvents allowed for a detailed investigation of the solvatochromic shift of the 430 nm transition, and the results are presented in Table 4 and Figure

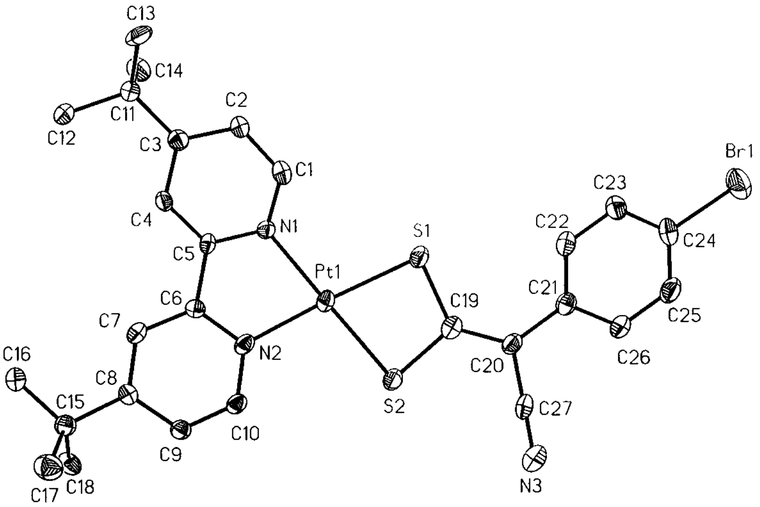


Figure 2. Perspective view of the molecular structure of Pt(dbbpy){$S_2C{=}C(CN)(p{-}C_6H_4Br)$}, **2**.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **2**

Pt(1)−N(2)	2.040(7)	C(1)−C(2)	1.377(12)
Pt(1)−N(1)	2.060(6)	C(2)−C(3)	1.394(12)
Pt(1)−S(2)	2.278(2)	C(3)−C(4)	1.397(11)
Pt(1)−S(1)	2.279(2)	C(4)−C(5)	1.362(11)
Br(1)−C(24)	1.895(9)	C(5)−C(6)	1.471(11)
S(1)−C(19)	1.724(9)	C(6)−C(7)	1.394(11)
S(2)−C(19)	1.747(9)	C(7)−C(8)	1.371(11)
N(1)−C(5)	1.330(10)	C(8)−C(9)	1.397(11)
N(1)−C(1)	1.336(11)	C(9)−C(10)	1.361(11)
N(2)−C(10)	1.342(10)	C(19)−C(20)	1.376(11)
N(2)−C(6)	1.347(10)	C(20)−C(27)	1.408(13)
N(3)−C(27)	1.157(12)	C(20)−C(21)	1.478(12)

N(2)−Pt(1)−N(1)	79.0(3)	N(1)−C(1)−C(2)	122.4(8)
N(2)−Pt(1)−S(2)	101.8(2)	N(1)−C(5)−C(4)	121.0(8)
N(1)−Pt(1)−S(2)	179.2(2)	N(1)−C(5)−C(6)	114.8(7)
N(2)−Pt(1)−S(1)	176.6(2)	C(4)−C(5)−C(6)	124.1(8)
N(1)−Pt(1)−S(1)	103.9(2)	N(2)−C(6)−C(7)	120.8(7)
S(2)−Pt(1)−S(1)	75.40(8)	N(2)−C(6)−C(5)	115.4(7)
C(19)−S(1)−Pt(1)	89.1(3)	N(2)−C(10)−C(9)	122.3(8)
C(19)−S(2)−Pt(1)	88.6(3)	C(20)−C(19)−S(1)	129.6(7)
C(5)−N(1)−C(1)	119.1(7)	C(20)−C(19)−S(2)	123.5(7)
C(5)−N(1)−Pt(1)	115.5(5)	S(1)−C(19)−S(2)	106.8(5)
C(1)−N(1)−Pt(1)	125.4(6)	C(19)−C(20)−C(27)	115.8(8)
C(10)−N(2)−C(6)	118.6(7)	C(19)−C(20)−C(21)	127.8(8)
C(10)−N(2)−Pt(1)	126.2(6)	C(27)−C(20)−C(21)	116.4(8)
C(6)−N(2)−Pt(1)	115.2(5)	N(3)−C(27)−C(20)	179.3(13)

Table 4. Absorption Bands for Complex **1** as a Function of Solvent[a]

solvent	UV−vis λ_{max}, nm	ϵ, M^{-1} cm^{-1}
toluene	488	6 860
	357	12 340
	306 (sh)	
chloroform	460	10 580
	350	14 560
dichloromethane	452	10 460
	353	13 900
acetone	444	8 120
	347	11 000
N,*N*-dimethylformamide	430	16 620
	350	19 200
acetonitrile	430	11 260
	347	12 680
dimethyl sulfoxide	433	17 680
	352	18 580

[a] 5×10^{-5} M.

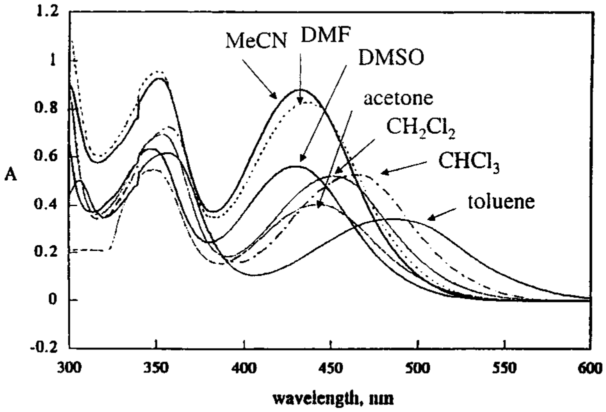


Figure 3. Lowest energy absorption bands for Pt(dbbpy){S_2C=C(C(O)Me)$_2$}, **1**, as a function of solvent.

3. As solvent polarity decreases, the strongly allowed band at 430 nm in MeCN shifts to lower energy, consistent with the notion of a highly polar ground state and a transition in which the polarity of the complex is greatly reduced.[10] Recent results by Hupp and co-workers using transient dc photoconductivity for a related Pt diimine 1,1-dithiolate complex support this view.[31] The degree of solvatochromism for **1** compares well with that reported previously for Pt diimine toluenedithiolate (tdt) complexes using an empirical scale devised in our laboratory;[9] a linear correlation exists between the lowest absorption energies of Table 4 and the Cummings solvent parameter with a linear regression agreement R^2 of 0.957. The direction of the observed shift in absorption energy with solvent polarity is termed "negative" solvatochromism, in accord with the assignment of this transition as a charge transfer from an orbital of mixed metal/dithiolate character to a diimine π^* orbital.[7,9] This assignment differs in degree from the LLCT assignment proposed by Dance and Vogler for related complexes in that the HOMO is thought to possess significant metal as well as dithiolate character.[32−34] Finally, it is noted that in toluene, complex **1** does not rigorously follow Beer's law at concentrations greater than 0.10 mM; specifically, the 488 nm band ceases to increase linearly with concentration, suggestive of possible aggregation at higher concentrations. Such aggregation has been proposed for Pt diimine dithiolate complexes in nonpolar solvents.[31,35]

Complexes **2** and **3** show absorption bands similar to **1** above 300 nm. In each case, the lower energy band exhibits substantial solvatochromism whereas the higher energy band does not. For complex **2**, the two bands in chloroform are 492 and 357 nm, while in acetonitrile, they are at 448 and 352 nm. For **3**, the bands appear at 428 and 349 nm in chloroform and at 404 and 342 nm in acetonitrile. The lower energy band for each complex is given the same assignment as that for complex **1**, namely, a charge transfer from an orbital of mixed metal/dithiolate character to a π^*(diimine) acceptor function.

Electrochemical Results. The electrochemical behavior of **1**−**3** was determined by cyclic voltammetry in dichloromethane with NBu_4PF_6 (0.20 M) as the electrolyte. Ferrocene (0.400 V vs NHE) was used to calibrate the observed redox processes, which are given vs NHE. For **1**, a reversible reduction is seen at −1.36 V (NHE) and a quasi-reversible oxidation is noted at +1.05 V corresponding to the peak anodic current. A reversible reduction is seen at −1.27 V for **2** and at −1.28 V for **3**. As seen for **1**, the oxidations of **2** and **3** are quasi-reversible but **2** and **3** are more difficult to oxidize than **1** with peak anodic currents observed at +1.43 and +1.47 V (NHE), respectively. Both processes are typical for Pt(diimine)(dithiolate) complexes in which reduction leads to placement of an electron in the π^* orbital of the diimine ligand and oxidation involves removal of an electron from an orbital of mixed metal/sulfur/dithiolate character.[9] Specifically, the reduction potentials for **1**−**3** are in the range of −1.27 to −1.40 V (NHE) observed for the dbbpy 1,1- and 1,2-dithiolate complexes reported earlier.[9] While the peak anodic potentials for **2** and **3** are more positive than for **1** and the previously reported analogues, these values should be viewed with greater caution because of the irreversibility of the oxidation in these systems.

Emission Spectroscopic Results. Complex **1** is emissive in fluid solution at ambient temperature. Irradiation into the solvatochromic charge-transfer band gives rise to a broad

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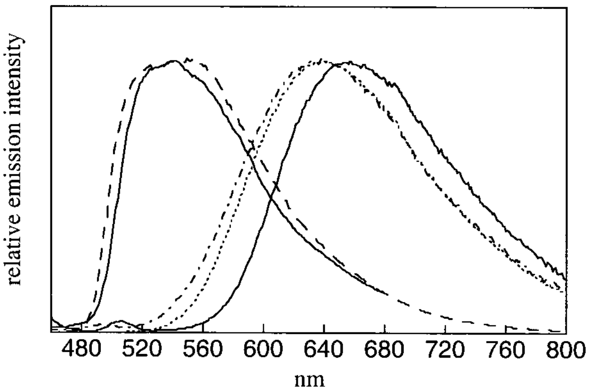

Figure 4. Emission spectra of **1** (2×10^{-5} M) at 77 K in 3:1 ethanol/methanol with excitation at 355 nm (dashed) and at 430 nm (solid) and at room temperature in acetonitrile (dot−dashed line), dichloromethane (dotted line), and toluene (solid) with excitation in the lowest energy absorption band.

emission that shows less sensitivity to solvent polarity in terms of relative energy than the corresponding absorption. In CH_2Cl_2 the emission maximum occurs at 635 nm as seen in Figure 4. Relative quantum yields of emission for **1** were determined using $Ru(bpy)_3(PF_6)_2$ in MeCN ($\Phi = 0.062$) as the standard[36] and were found to be 1.3×10^{-4} in MeCN and 0.011 in toluene. The excitation spectrum measured with λ_{em} of 600 nm shows bands that match closely with the absorption bands at 451 and 354 nm. Lifetime measurements reveal a significant dependence of excited-state lifetime with solvent polarity. In MeCN and CH_2Cl_2, excited-state lifetimes were measured to be 3.4 ± 0.1 ns and 11.0 ± 0.1 ns, respectively, by time-correlated single-photon counting (TCSPC), while in toluene the lifetime was determined to be 250 ± 30 ns using a previously described nanosecond excimer system.[37] This variation in excited-state lifetime with solvent polarity has been seen for other Pt-(diimine)(dithiolate) complexes and may relate to the coordinating ability of the solvent as well.[7]

The 77 K emission spectrum of **1** in 3:1 EtOH/MeOH glass reveals a shift to higher energy for the emission band relative to that seen in fluid solution at ambient temperature. The rigidochromic shift leads to an observed emission maximum at 77 K of 535 nm. The profile of this emission is slightly broader when generated with excitation at 355 nm vs that seen with 430 nm excitation.

Emission studies of **2** were more limited in scope. Complex **2** is weakly emissive in acetonitrile at ambient temperature with a broad band centered around 580 nm. This is similar to that seen for $Pt(dbbpy)(S_2C{=}C(C(O)Me)_2)$, **1**. In addition, there is a second weak emission feature at 490 nm, the basis of which is uncertain at the present time. At 77 K in 3:1 EtOH/MeOH glass, the emission is substantially greater in intensity with evidence of a 1320 cm^{-1} vibronic progression and a significant blue shift for the highest energy transition to ca. 495 nm. Similar vibronic progressions have been observed for other Pt diimine 1,1-dithiolate and Pt diimine bis(acetylide) complexes.[9,38] No studies of the emission properties of **3** were conducted, but it should be mentioned that very closely related analogues, differing only in the nature of the ester substituent of the dithiolate ligand, have been well studied in this regard.[1−3,9]

Conclusions

The three complexes in the present study are members of the class of Pt diimine dithiolates that have been extensively studied over the past decade. They exhibit electronic properties similar to what has been described previously in terms of a solvatochromic charge-transfer absorption in the visible region of the spectrum and a fluid solution emission (for **1** and **2**) from an excited state of similar orbital character. The excited-state lifetime of **1** is consistent with the emissive state having spin-forbidden character corresponding to $^3(Pt(d)/S(p)\text{-}\pi^*_{diimine})$. The Pt diimine 1,1-dithiolates described here, as well as previously, have higher energy CT absorptions and emissions than their 1,2-dithiolate analogues. The structures of two of the complexes have been determined crystallographically, confirming the anticipated square planar coordination distorted only by the constraints of the chelate rings. The functionality of the different dithiolates used for complexes **1**−**3** should make possible their facile connection to potential donors and reductive quenchers in the construction of dyads and multicomponent systems for photoinduced charge transfer using well-established coupling reactions.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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