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Synthesis, Characterization, and Spectroscopy of Dipyridocatecholate Complexes of Platinum

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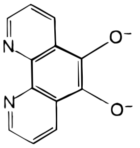
Several new complexes containing 1,10-phenanthroline-5,6-diolate (dipyridocatecholate, $dpcat^{2-}$) ligand are reported. The complex (dpcat)Pt(dbbpy) (**4**; dbbpy = di-*tert*-butylbipyridine) was synthesized from $Cl_2Pt(dbbpy)$ and $dpcat^{2-}$. The reaction of (dpcat)Pt(dbbpy) with $Cl_2Pt(PhCN)_2$ yielded $Cl_2Pt(dpcat)Pt(dbbpy)$ (**5**). The latter complex was reacted with 3,4-dimercaptotoluene (toluenedithiolate, tdt^{2-}), 3,5-di-*tert*-butylcatecholate ($dbcat^{2-}$), and $dpcat^{2-}$ to give (tdt)Pt(dpcat)Pt(dbbpy) (**6**), (dbcat)Pt(dpcat)Pt(dbbpy) (**7**), and (dpcat)Pt(dpcat)Pt(dbbpy) (**8**), respectively. All of these complexes containing Pt(diimine)(diolate) centers display intense absorption bands in the 500−600 nm range. However, excitation at these wavelengths does not result in photoemission similar to that seen for closely related Pt(diimine)(dithiolate) complexes. The absorption bands of the dinuclear species are unsymmetrical, possibly indicating isolated but overlapping transitions for the two chromophores in each complex. The complex (dpcat)Pt(dbbpy) was found to react with $(dbbpy)_2RuCl_2$ and NH_4PF_6 to yield $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)](PF_6)_2$ (**10**). A connectivity structure of this compound confirms the structural arrangement and the role of dpcat as a bridging ligand between a square planar Pt(II) center and an octahedral Ru(II) moiety. In an analogous synthesis, the trinuclear complex $[(dbbpy)_2Ru(dpcat)Pt(dpcat)Pt((dbbpy)](PF_6)_2$ (**11**) was obtained by reacting (dpcat)Pt(dpcat)Pt(dbbpy) with $(dbbpy)_2RuCl_2$ and NH_4PF_6. The complex $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)](PF_6)_2$ displays absorption bands associated with individual Ru and Pt centers and photoemission that arises from $Ru(diimine)_3{}^{2+}$. A trinuclear complex $(dbcat)Co\{(dpcat)Pt(dbbpy)\}_2$ (**9**) was also obtained from the reaction of (dpcat)Pt(dbbpy) and $Co_4(dbsq)_8$ (dbsq = di-*tert*-butylsemiquinone).

Introduction

The construction of multicomponent molecular systems represents an important evolution in the development of molecular and supramolecular systems for catalysis, light-to-chemical energy conversion, and molecularly-based devices.[1−3] For systems in which components are complexed metal moieties, bridging ligands are a critical element in successful design. One of the simplest and most interesting of such ligands is the dipyridocatecholate (dpcat) unit (**1**), which is obtainable in principle by two-electron reduction of the corresponding quinone, phenanthroline-5,6-dione (**2**).



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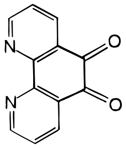

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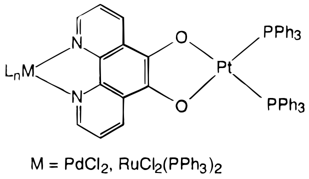
Quinone **2** has been known for many years,[4,5] and its dual chelating ability as either a diimine or a catecholate was reported in 1975 by Balch.[6] In 1991, Pierpont reported the bimetallic complexes shown schematically as **3** in which the bridging ligand is dpcat.[7] The electrochemical behavior of complexes **3**



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showed that the first and second oxidations of these systems were dpcat-based. More recently, Doherty has described the formation of bi- and trimetallic complexes having dpcat as the bridging ligand with the objective of constructing chain structures.[8] In both series of studies, the formation of dpcat-bridged complexes has been accomplished using the diimine properties of **2** to displace labile ligands and oxidative addition of the quinone part of **2** to generate catecholate, the latter requiring reaction with a low-valent metal center.

In this paper we describe the synthesis of new dpcat-bridged systems in which the bridging moiety is introduced as the catecholate **1** by prior reduction of **2** to the diol and deprotonation. The specific systems studied all contain platinum(II) centers coordinated with diimine and dithiolate or catecholate ligands. Square planar diimine dithiolate complexes of Pt(II) have been investigated in our laboratory over the past decade because of their unusual photoluminescence in fluid solution

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at ambient temperatures.[9−11] These systems exhibit an intense solvatochromic absorption in addition to their solution luminescence. Both have been assigned to charge transfer states possessing metal/dithiolate-to-diimine character. The Pt(diimine)(dithiolate) complexes have been found to undergo electron transfer quenching with excited state reduction potentials in the range +0.448 to +1.226 V vs NHE. As part of a strategy to develop multicomponent systems for light to chemical energy conversion, we report here the use of dpcat to generate bi- and trinuclear complexes containing the platinum diimine catecholate chromophore, which is closely related to the corresponding dithiolate systems.

Experimental Section

Physical Measurements. ^{1}H NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer, IR spectra were recorded on a Mattson 6020 Galaxy FTIR spectrometer, and electronic absorption spectra were obtained on a Hitachi U2000 UV−visible spectrophotometer. Emission measurements were made on methylene chloride solution samples at room temperature and butyronitrile glasses at liquid nitrogen temperature using a Spex Fluorolog-2 fluorescence spectrophotometer. Electrochemical experiments were performed using a BAS-100B/W electrochemical workstation and a cell having a Pt disk working electrode, a Pt auxiliary electrode, and a Ag wire pseudoreference. All measurements were carried out on dichloromethane solutions containing *ca.* 0.1 M $[(n\text{-Bu})_4N](PF_6)$ electrolyte and are referenced to the Fc/Fc$^+$ couple, which occurs at 0.400 V relative to NHE). Mass spectrometric results were obtained from the Mass Spectrometry Facility at the University of California at Riverside. Ionization was obtained by either FAB or electrospray techniques. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ.

Materials and Procedures. THF and toluene were dried over Na/benzophenone and distilled prior to use. Anhydrous and air-free DMSO and DMF were purchased from Aldrich. Other high-grade solvents were not purified but were degassed by saturation with N_2 before use. Di-*tert*-butylbipyridine (dbbpy),[12,13] $Pt(dbbpy)Cl_2$,[14] $Pt(PhCN)_2Cl_2$,[15] and $Co_4(dbsq)_8$[16] (dbsq = di-*tert*-butylsemiquinone) were synthesized according to literature reports. $Ru(dbbpy)_2Cl_2$ was synthesized using the procedure reported for the corresponding bpy analog.[17] Toluene-3,4-dithiol ($tdtH_2$), 3,5-di-*tert*-butylcatechol ($dbcatH_2$), and all other materials were purchased from Aldrich and used as received.

1,10-Phenanthroline-5,6-dione (Dipyridobenzoquinone, dpq). The following procedure is based on the report by Yamada,[18] and it yields the product almost quantitatively. An ice cold mixture of concentrated H_2SO_4 (40 mL) and HNO_3 (20 mL) was added to 4.0 g of 1,10-phenanthroline and 4.0 g of KBr. The mixture was heated at reflux for 3 h. The hot yellow solution was poured over 500 mL of ice and neutralized carefully with NaOH until neutral to slightly acidic pH. Extraction with $CHCl_3$ followed by drying with Na_2SO_4 and removal of solvent gave 4.5 g (96%) of dpq. This product is quite pure spectroscopically, but it may be purified further by crystallization from ethanol.

5,6-Dihydroxy-1,10-phenanthroline (Dipyridocatechol, $dpcatH_2$). This compound has been reported previously.[19,20] A different procedure is reported herein. A mixture of 0.700 g (3.33 mmol) of dpq and 0.480 g (3.99 mmol) of dithiooxamide was refluxed in 25 mL of ethanol for 16 h. Upon cooling of the reaction mixture to room temperature, the product in the form of a yellow-brown precipitate was separated by filtration and washed with ethanol (20 mL). Subsequent washing of the product with $CHCl_3$ served to remove unreacted and coprecipitated dpq. The product was dried briefly in air and then *in vacuo*. Yield: 0.585 g (83%). The catechol $dpcatH_2$ is relatively insoluble in common organic solvents and only sparingly soluble in DMSO. The latter solution exhibits air sensitivity, with $dpcatH_2$ being reoxidized to dpq. Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.88; H, 3.48; N, 13.17. ^{1}H NMR (ppm, DMSO-d_6, dissolved upon heating): 9.48 (s, br, 2H), 8.92 (dd, 2H, J = 4.4, 1.6 Hz), 8.58 (dd, 2H, J = 8.4, 1.6 Hz), 7.72 (dd, 2H, J = 8.4, 4.4 Hz). The resonance at 9.48 ppm disappears upon addition of D_2O. IR (cm^{-1}, KBr): 3200−2500 (O−H (hydrogen bond)), 1618 (C−C).

Sodium Dipyridocatecholate (Na_2dpcat). To a suspension of 0.51 g (2.5 mmol) of $dpcatH_2$ in 40 mL of THF under nitrogen was added 0.14 g (6.9 mmol) of Na(Hg). The mixture was stirred for 16 h, during which time the suspension changed color from yellow-brown to orange. (If dpq is present in the sample, the suspension turns green.) The suspension was decanted from the amalgam, and the orange product was collected by filtration. Upon drying, 0.55 g (89%) of solid was obtained. The product turns dark green within minutes when exposed to air. We were not able to obtain a sample of analytical purity. ^{1}H NMR (ppm, DMSO-d_6): 8.56 (dd, 2H, J = 4.4, 1.6 Hz), 8.40 (dd, 2H, J = 8.4, 1.6 Hz), 7.44 (dd, 2H, J = 8.4, 4.4 Hz).

(dpcat)Pt(dbbpy) (4). A. Procedure 1. A mixture of 0.30 g (0.56 mmol) of $Pt(dbbpy)Cl_2$, 0.30 g (1.4 mmol) of $dpcatH_2$, and a pellet of NaOH in 80 mL of degassed methanol was heated at reflux for 24 h. The color gradually changed from brown to brown-red. After the reaction solution cooled, the solvent was removed by evaporation. The product was extracted from the residue with methylene chloride and precipitated after partial removal of solvent and the addition of hexane. Yield: 0.31 g (81%). Anal. Calcd for $C_{30}H_{30}N_4O_2Pt{\cdot}CH_2Cl_2$: C, 49.08; H, 4.25. Found: C, 48.59; H, 4.18. MS (FAB): *m/e* 674. ^{1}H NMR (ppm, CD_2Cl_2): 9.34 (d, 2H, J = 6.4 Hz), 8.79 (dd, 2H, J = 4.0, 1.8 Hz), 8.66 (dd, 2H, J = 8.0, 1.8 Hz), 7.81 (d, 2H, J = 2.0 Hz), 7.56 (dd, 2H, J = 6.0, 2.0 Hz), 7.50 (dd, 2H, J = 8.0, 4.0 Hz), 1.44 (s, 18H). UV/vis (nm, CH_2Cl_2): 372 (ϵ = 7500 M^{-1} cm^{-1}), 598 (ϵ = 3800 M^{-1} cm^{-1}). The complex possesses a highly solvatochromic absorption band displaying the following maxima in the solvents listed: methanol, 510 nm; acetonitrile, 549 nm; DMSO, 549 nm; acetone, 584 nm; dichloromethane, 598 nm; THF, 631 nm; toluene/dichloromethane, 2:1, 657 nm.

B. Procedure 2. A mixture of 0.25 g (0.47 mmol) of $Pt(dbbpy)Cl_2$ and 0.24 g (0.94 mmol) of Na_2dpcat in 10 mL of DMSO was prepared under N_2 and heated with stirring at 50 °C for 5 h. During this time the color changed from red-brown to purple. After the solution cooled to room temperature, the precipitate was collected by filtration. The product was then extracted with CH_2Cl_2 and precipitated by the addition of hexanes and partial solvent removal. Filtration of the purple-brown precipitate yielded 0.15 g (48%) of the complex.

$Cl_2Pt(dpcat)Pt(dbbpy)$ (5). A mixture of 82 mg (0.12 mmol) of (dpcat)Pt(dbbpy) and 77 mg (0.16 mmol) of $Pt(PhCN)_2Cl_2$ was refluxed in 20 mL of $CHCl_3$ for 4 h. Upon cooling to room temperature, the blue, practically insoluble solid was isolated by filtration, washed with $CHCl_3$, and dried in air and then *in vacuo*. Yield: 101 mg (88%). Anal. Calcd for $C_{30}H_{30}Cl_2N_4O_2Pt_2$: C, 38.35; H, 3.22; N, 5.96. Found: C, 37.88; H, 3.23; N, 5.85. MS (FAB): *m/e* 939. UV/vis (nm, CH_2Cl_2): 543.

(tdt)Pt(dpcat)Pt(dbbpy) (6). A mixture of 92 mg (0.098 mmol) of $Cl_2Pt(dpcat)Pt(dbbpy)$ and 42 mg (0.27 mmol) of $tdtH_2$ along with a small pellet of NaOH was heated at 40 °C with stirring in 20 mL of CH_3OH for 5 h. Upon cooling to room temperature, the purple solid was isolated by filtration, washed with methanol, and dried briefly in air and then *in vacuo*. Yield: 76 mg (76%). Anal. Calcd for

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$C_{37}H_{36}N_4O_2S_2Pt_2$: C, 43.44; H, 3.55. Found: C, 43.33; H, 3.51. MS (FAB): *m/e* 1022. ^{1}H NMR (ppm, CD_2Cl_2): 8.8 (m, 4H), 8.53 (d, 2H, $J = 8.0$ Hz), 7.6 (m, 4H), 7.55 (two dd, 2H), 7.05 (d, 1H, $J = 8.0$ Hz), 6.99 (s, 1H), 6.56 (d, 1H, $J = 8.0$ Hz), 2.26 (s, 3H), 1.50 (s, 9H), 1.50 (s, 9H). UV/vis (nm, CH_2Cl_2): 554 (ϵ = 9,800 M^{-1} cm^{-1}, unsymmetrical).

(dbcat)Pt(dpcat)Pt(dbbpy) (7). A mixture of 80 mg (0.085 mmol) of Cl_2Pt(dpcat)Pt(dbbpy) and 60 mg (0.27 mmol) of dbcatH_2 along with a small pellet of NaOH was heated at 50 °C with stirring in 5 mL of DMSO for 16 h. Upon cooling to room temperature, the purple-violet solid was isolated by filtration, washed with 2 mL of toluene, and dried briefly in air and then *in vacuo*. Yield: 64 mg (69%). A sample, which was pure by ^{1}H NMR, gave unsatisfactory elemental analysis. MS (FAB): *m/e* 1089. ^{1}H NMR (ppm, CD_2Cl_2): 9.06 (d, 1H, $J = 6.0$ Hz), 8.99 (d, 1H, $J = 6.0$ Hz), 8.91 (m, 2H), 8.72 (d, 1H, $J = 8.0$ Hz), 8.69 (d, 1H, $J = 8.0$ Hz), 7.91 (s, 2H), 7.58 (m, 2H), 7.55 (m, 1H), 7.42 (m, 1H), 6.60 (d, 1H, $J = 2.0$ Hz), 6.39 (d, 1H, $J = 2.0$ Hz), 1.56 (s, 9H), 1.49 (s, 9H), 1.41 (s, 9H), 1.31 (s, 9H). UV/vis (nm, CH_2Cl_2): 570 (ϵ = 12 000 M^{-1} cm^{-1}, unsymmetrical).

(dpcat)Pt(dpcat)Pt(dbbpy) (8). A mixture of 118 mg (0.126 mmol) of Cl_2Pt(dpcat)Pt(dbbpy) and 53 mg (0.25 mmol) of dpcatH_2 along with a small pellet of NaOH was heated at 50 °C with stirring in 5 mL of DMSO for 16 h. Upon cooling to room temperature, 70 mL of toluene was added and the blue solid was isolated by filtration. The solid, which is very sparingly soluble in CH_2Cl_2 and DMSO, was then washed with two 5 mL portions of methanol and dried briefly in air and then *in vacuo*. Yield: 107 mg (78%). Poor solubility precluded obtaining a sample of analytical purity. MS (FAB): *m/e* 1079. ^{1}H NMR (ppm, DMSO-d_6): 9.07 (m, br, 2H), 8.97 (m, br, 2H), 8.72 (s, br, 2H), 8.58 (d, br, 2H), 8.38 (s, br, 2H), 8.24 (s, br, 2H), 7.81 (m, br 2H), 7.74 (m, br, 2H), 7.55 (m, 2H), 1.38 (s, 18H). UV/vis (nm, CH_2Cl_2): 557 (broad).

(dbsq)Co((dpcat)Pt(dbbpy))$_2$ (9). A mixture of 75 mg (0.11 mmol) of (dpcat)Pt(dbbpy) and 28 mg (0.014 mmol) of $Co_4(dbsq)_8$ was stirred in 30 mL of toluene under N_2 for 16 h, during which time the solution turned purple. The reaction mixture was cooled in the freezer. The bluish precipitate was isolated by filtration, washed with 5 mL of cold toluene, and dried. Yield: 82 mg (91%). The complex is paramagnetic. MS (FAB): *m/e* 1626. UV/vis (nm, CH_2Cl_2): 555.

[(dbbpy)$_2$Ru(dpcat)Pt(dbbpy)](PF$_6$)$_2$ (10). A mixture of 102 mg (0.152 mmol) of (dpcat)Pt(dbbpy) and 103 mg (0.145 mmol) of Ru(dbbpy)$_2$Cl$_2$ was refluxed in 40 mL of methanol for 20 h. Upon cooling to room temperature, a solution of 10-fold excess of NH_4PF_6 in 15 mL of water was added. The mixture was stirred for 15 min. The solid was isolated by filtration, washed with H_2O, and dried briefly in air and then *in vacuo* for 2 days. Yield: 202 mg (83%). Anal. Calcd for $C_{66}H_{78}N_8O_2PtRuP_2F_{12}$: C, 49.50; H, 4.91; N, 7.00. Found: C, 48.80; H, 4.96; N, 7.02. MS (FAB): *m/e* 1457 $(M{\cdot}PF_6)^+$. ^{1}H NMR (ppm, CD_2Cl_2): 9.28 (d, 2H, $J = 6.4$ Hz), 8.84 (dd, 2H, $J = 8.4$, 1.2 Hz), 8.29 (d, 2H, $J = 2.0$ Hz), 8.24 (d, 2H, $J = 2.0$ Hz), 7.98 (d, 2H, $J = 2.0$ Hz), 7.73 (d, 2H, $J = 6.0$ Hz), 7.68 (dd, 2H, $J = 6.0$, 2.0 Hz), 7.62 (dd, 2H, $J = 5.0$, 1.4 Hz), 7.55 (dd, 2H, $J = 8.0$, 5.0 Hz), 7.48 (dd, 2H, $J = 6.0$, 2.0 Hz), 7.41 (d, 2H, $J = 6.0$ Hz), 7.19 (dd, 2H, $J = 6.0$, 2.0 Hz), 1.49 (s, 18H), 1.45 (s, 18H), 1.36 (s, 18H). UV/vis (nm, CH_2Cl_2): 450 (ϵ = 19 000 M^{-1} cm^{-1}), 540 (shoulder, ϵ = 10 000 M^{-1} cm^{-1}).

[(dbbpy)$_2$Ru(dpcat)Pt(dpcat)Pt(dbbpy)](PF$_6$)$_2$ (11). A mixture of 64 mg (0.059 mmol) of (dpcat)Pt(dpcat)Pt(dbbpy) and 42 mg (0.062 mmol) of Ru(dbbpy)$_2$Cl$_2$ was refluxed in 20 mL of methanol for 20 h. Upon cooling, the solution was filtered and a 10-fold excess of NH_4PF_6 in 10 mL of water was added to the filtrate. The mixture was stirred for 15 min, and the solid formed was isolated by filtration, washed with H_2O, and dried briefly in air and then *in vacuo* for 2 days. Yield: 32 mg. The product is impure, but the trinuclear complex was identified by the mass peak for the monocationic adduct formed with PF_6^- and the associated isotope distribution (MS (FAB): *m/e* 1866 $(M{\cdot}PF_6)^+$). The UV/vis spectrum is similar to that of [(dbbpy)$_2$Ru(dpcat)Pt(dbbpy)](PF$_6$)$_2$.

Connectivity Structure Determination of [(dbbpy)$_2$Ru(dpcat)Pt(dbbpy)](PF$_6$)$_2$. Microcrystals of the complex were grown by slow evaporation from a toluene/dichloromethane solution. Experimental details for the structure determination are provided below, but the resultant structure is unsuitable for detailed metrical analysis. The results of the structure determination are included solely to show the connectivity within the structure, confirming the role of dpcat as a bridging ligand. All attempts to grow more suitable crystals for an X-ray structure determination, including variations of counter anions, have been unsuccessful.

A dark brown crystal of approximate dimensions 0.20 × 0.07 × 0.04 mm was selected for X-ray analysis. The crystal was mounted on a glass fiber with epoxy and immediately placed in a cold nitrogen stream at −50 °C on the X-ray diffractometer. Although the breadth of the peak profiles from the initial cell determination indicated a very high degree of mosaicity, data were collected with the anticipation of determining the connectivity of the complex. 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 1.5 kW (50 kV, 30 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 60 s/frame. The total data collection time was approximately 26 h. Frames were integrated with the Siemens SAINT program to yield a total of 24 524 reflections, of which 10 077 were independent ($R_{\text{int}} = 12\%$, $R_{\text{sig}} = 20\%$) and only 5095 were above $4\sigma(F)$. The unit cell parameters (at −50 °C) of a = 39.366(1) Å, b = 21.279(3) Å, and c = 18.513(3) Å, α = 89.95(1)°, β = 101.41(2)°, and γ = 90.03(1)° were based upon the least-squares refinement of three-dimensional centroids of 4214 reflections. The space group was assigned as $C2/c$ on the basis of systematic absences by using the XPREP program (Siemens, SHELXTL 5.04). The intensity statistics suggested the space group Cc; however, the structure could not be solved successfully in this space group. The structure was solved using direct methods included in the SHELXTL program (version 5.04) and refined by full-matrix least squares on F^2. There is one independent molecule in the asymmetric unit. All nonhydrogen atoms of the cation except for two of the *t*-Bu groups of the dbbpy ligand were refined anisotropically with hydrogen atoms included in idealized positions. The two PF_6^- counterions were highly disordered. With a data:parameter ratio of approximately 7:1, the structure refined to a goodness of fit of 1.28 and a final residual of $R_1 = 15.3\%$ ($I > 4\sigma$).

Results

Synthesis of Phenanthroline-5,6-dione (dpq) and its Corresponding Catechol (dpcatH$_2$). Phenanthroline-5,6-dione has been known since 1947,[4] but earlier reports of its synthesis gave very poor yields. Following the procedure of Yamada *et al.*,[18] we have optimized the preparation of dpq, obtaining an overall yield of 96%. In this procedure, 1,10-phenanthroline is oxidized using H_2SO_4/HNO_3/KBr, in which bromide is first oxidized to Br_2, facilitating the transformation shown in eq 1. Phenanthroline-5,6-dione (dpq, **2**) can be reduced electrochemically[21] or chemically with the use of hydrazine[19] or $NaBH_4$[20] to produce 5,6-dihydroxy-1,10-phenanthroline (dpcatH_2). We find that when dithiooxamide is used as the reductant, the reaction shown as eq 2 proceeds in very good yield. The possible condensation product that may be surmised by the reaction of dithiooxamide with dpq was not observed to form.

The catechol dpcatH_2 has been discussed in the literature,[19,20] but there was no report of its direct use as a ligand. The catechol dpcatH_2 reacts easily with sodium to give orange sodium dipyridocatecholate (Na$_2$dpcat). This species is highly air-sensitive, turning dark green within minutes when exposed to air. It is soluble in DMSO and displays sharp ^{1}H NMR resonances in air-free solvent.

Syntheses of Metal Complexes. The catecholate salt Na$_2$dpcat reacts readily with the di-*tert*-butylbipyridine complex

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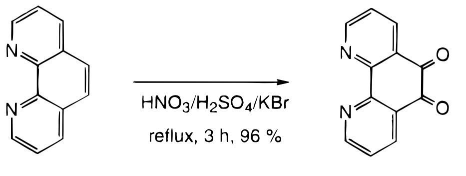

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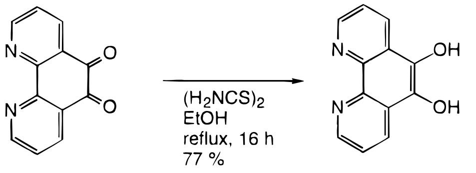
(1)



1H$_2$

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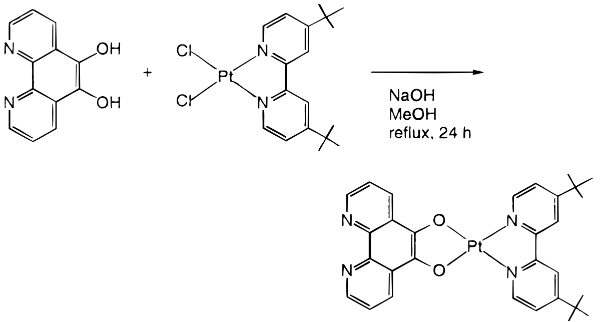
Pt(dbbpy)Cl$_2$ to give (dpcat)Pt(dbbpy) (**4**) in 45% yield (eq 3).



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(3)

In the product complex, dpcat is coordinated to the metal center through its catecholate functionality. When DMF is employed as the solvent, the reaction takes longer to achieve and conversion of Pt(dbbpy)Cl$_2$ to (dpcat)Pt(dbbpy) is only partial. The synthesis of (dpcat)Pt(dbbpy) may also be carried out in MeOH beginning with the catechol and added base to generate the Na$^+$ salt *in situ*. The latter procedure is more convenient and also more efficient.

The ^{1}H NMR spectrum of (dpcat)Pt(dbbpy) displays six sharp resonances of equal intensity in the aromatic region and a single methyl proton resonance for the *t*-Bu groups that integrates as 9:1 relative to each of the aromatic resonances. The mass spectrum reveals a parent ion peak with *m*/*e* 674 and an isotope distribution that matches the theoretical distribution perfectly. The absence of a C═O stretching band in the IR spectrum of (dpcat)Pt(dbbpy) suggests that the dpcat ligand is coordinated through O donor atoms to the Pt(II) center, while high solubility of the complex in organic solvents supports its formulation as a neutral complex.

The complex (dpcat)Pt(dbbpy) displays a moderately intense solvatochromic absorption band that ranges from 510 nm in methanol to 657 nm in toluene/CH$_2$Cl$_2$ (2:1). This property is similar to that observed previously for related Pt(dithiolate)(diimine) complexes in which the solvatochromic absorption has been ascribed to a charge transfer-to-diimine excitation from an orbital of mixed metal and dithiolate character.[10] The solvatochromic shift of 0.50 for (dpcat)Pt(dbbpy) can be compared to the values displayed by Pt(dithiolate)(diimine) complexes, which ranged from 0.33 to 0.43. The shifts were determined from plots of the solvent-dependent CT energies (in 10^3 cm^{-1}) *vs* empirically derived solvent polarity parameters based on Pt(dbbpy)(toluene-3,4-dithiolate).[10] In contrast with Pt(dithiolate)(diimine) complexes, (dpcat)Pt(dbbpy) does not display a low-energy (>500 nm) emission band that has been assigned as a triplet state of the charge transfer-to-diimine type. However, a high-energy emission at 420 nm is observed, and this is presumed to be an intraligand process since, as discussed later, this transition is present for all complexes studied. A similar emission is observed for Cl$_2$Pt(dbbpy) at 450 nm.

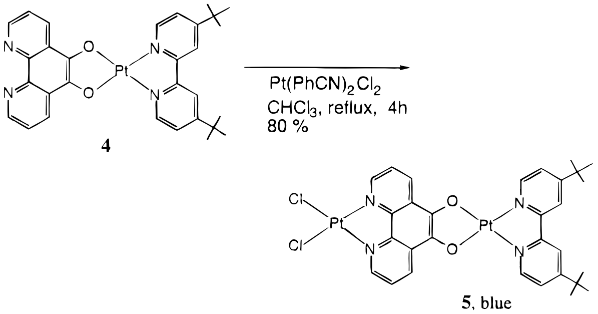
Table 1. Cyclic Voltammetry Data for the dpcat-Bridged Complexes (dbcat)Pt−M, (tdt)Pt−M, and [(dbbpy)$_2$Ru−M](PF$_6$)$_2$ (M = (dpcat)Pt(dbbpy))[a]

M	(dbcat)Pt−M	(tdt)Pt−M	[(dbbpy)$_2$Ru−M]$^{2+}$
+1.18, irr[b]	+1.17, q-r, 128	+0.49, q-r, 104	+1.08, q-r, 170
+0.16, q-r, 63[c]	+0.70, q-r, 88	+0.24, q-r, 85	+0.37, q-r, 102
−1.41, q−r, 99	+0.51, q-r, 64	−0.18, q-r (adsorption)	−1.63, q-r, 190
	+0.05, q-r, 67	−1.61, q-r, 61	−1.8, q-r, 200
	−1.45, q-r, 69	−1.91, q-r, 72	
	−1.78, q-r, 144		

[a] Conditions: Pt (working), Pt (auxiliary), Ag (reference) electrodes; 0.1 M [(*n*-Bu)$_4$N](PF$_6$) in CH$_2$Cl$_2$; 25 °C; 100 mV/s (except (tdt)Pt−M at 1 V/s); all potentials (in volts) are given relative to the Fc$^+$/Fc reduction potential (0 V), which occurs at +0.400 V versus NHE. [b] irr = irreversible; q-r = quasi-reversible. [c] Peak separation (in millivolts) for quasi-reversible couples.

Cyclic voltammetry of (dpcat)Pt(dbbpy) as given in Table 1 reveals a reversible oxidation at +0.16 V (ΔE = 63 mV) (referenced to Fc$^+$/Fc reduction potential, which occurs at +0.400 V relative to NHE), an irreversible oxidation at +1.18 V ($E_p{}^a$), and a quasi-reversible reduction at −1.41 V (ΔE = 99 mV). The two oxidation processes are assigned to catecholate to semiquinone (+0.16 V) and semiquinone to quinone (+1.18 V) transitions of the dpcat ligand. This assignment is based on the general observation that metal complexes containing catecholate complexes typically display reversible catecholate-to-semiquinone (cat → sq) and irreversible or quasi-reversible semiquinone-to-quinone (sq → q) ligand localized redox couples.[22] The closely related complex (dpcat)Pt(PPh$_3$)$_2$ displays a corresponding, reversible oxidation at −0.207 V and an irreversible oxidation at +0.416 V ($E_p{}^a$) also referenced to the Fc$^+$/Fc couple.[7] The quasi-reversible reduction of (dpcat)Pt(dbbpy) at −1.41 V is most likely associated with the dbbpy moiety. Reversible or quasi-reversible reductions at similar potentials were observed for Pt diimine dithiolate complexes, for which the LUMOs are predominantly of diimine character.[10]

Multinuclear Systems. The complex (dpcat)Pt(dbbpy) reacts readily with Pt(PhCN)$_2$Cl$_2$ to yield Cl$_2$Pt(dpcat)Pt(dbbpy) (**5**), eq 4. This complex is very sparingly soluble and therefore extremely difficult to characterize by ^{1}H NMR spectroscopy or electrochemistry. However, excellent elemental analyses and a correct parent ion peak in the mass spectrum were obtained, which serve to define the complex. Cl$_2$Pt(dpcat)Pt(dbbpy) is a good precursor to other binuclear Pt complexes since Cl$^-$ ligands can be replaced by dithiolates and diolates. In this manner, complexes having toluenedithiolate (tdt), di-*tert*-butylcatecholate



5, blue

(4)

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[22] Pierpont, C. G.; Lange, C. W. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons, Inc.: New York, 1994; Vol. 41, pp 331−442.

Table 2. UV/Vis Absorption Maxima and Solubility in CH_2Cl_2 for the dpcat-Bridged Complexes (M = (dpcat)Pt(dbbpy))

complex	UV/vis data (nm)	solubility in CH_2Cl_2
M, **4**	598	very good
Cl_2Pt-M, **5**	543	poor
(tdt)Pt−M, **6**	554, unsymmetrical	poor
(dbcat)Pt−M, **7**	570, unsymmetrical	moderate
(dpcat)Pt−M, **8**	557	very poor
$[(dbbpy)_2Ru-M)](PF_6)_2$, **10**	450[a], 540	very good

[a] This absorption is assigned to the $Ru(diimine)_3^{2+}$ chromophore and results in emission at 615 nm.

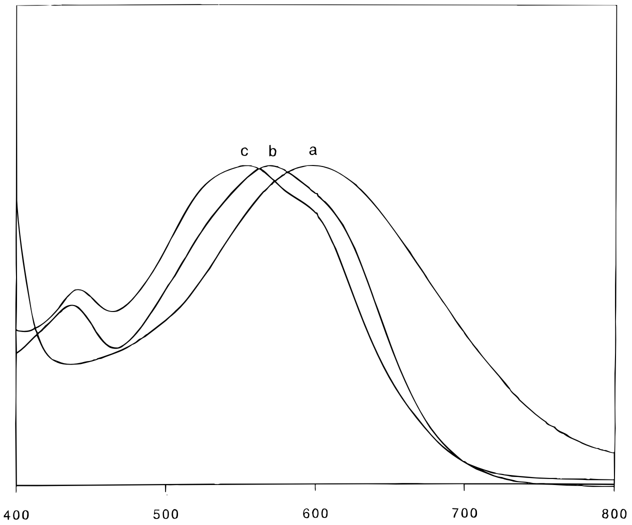
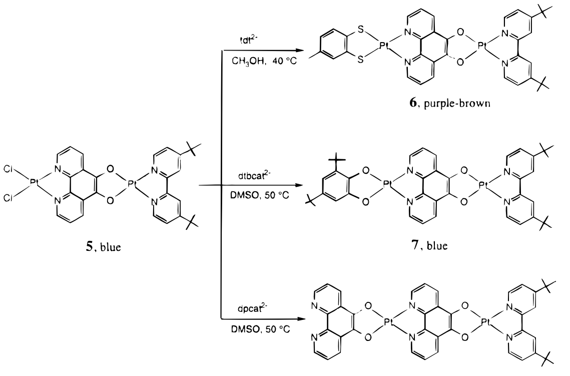


Figure 1. UV/visible spectra of (dpcat)Pt(dbbpy) (a), (dbcat)Pt(dpcat)-Pt(dbbpy) (b), and (tdt)Pt(dpcat)Pt(dbbpy) (c) in CH_2Cl_2.

(dbcat), and dipyridocatecholate (dpcat) as terminal ligands were obtained via eq 5, leading to complexes **6**, **7**, and **8**, respectively.



(5)

The complexes produced in eq 5 were characterized by ^1H NMR, UV/vis, and mass spectroscopies. The mass spectra of these complexes display parent ion peaks with good agreement in isotope patterns between observed and calculated models. The ^1H NMR spectra show shifts of dpcat resonances due to coordination of pyridyl N atoms as well as resonances in the aromatic region that integrate well relative to *t*-Bu and Me resonances. For example, with respect to the former, complex **7** exhibits a resonance for the 2,2′ protons adjacent to the pyridyl N atoms of 8.91 ppm compared with a value of 8.79 ppm for the same protons in **4**. The UV/vis spectra of (tdt)Pt(dpcat)-Pt(dbbpy) and (dbcat)Pt(dpcat)Pt(dbbpy) complexes (Table 2) each show a broad, unsymmetrical band in the visible region (Figure 1). Emission spectra of these complexes are identical to that of the mononuclear complex (dpcat)Pt(dbbpy), which in ambient solution and low temperature glass displays no low-energy (>500 nm) emission but does show an emission around 400 nm that is presumed to be intraligand. This result is interesting in view of the fact that the (tdt)Pt(phen) complex displays an emission at 730 nm assignable to the charge transfer-to-diimine excited state.[10] The present results indicate that any emission associated with the (tdt)Pt(dpcat) chromophore within the binuclear complex (tdt)Pt(dpcat)Pt(dbbpy) is quenched efficiently.

Several quasi-reversible processes are observed in the cyclic voltammogram of (dbcat)Pt(dpcat)Pt(dbbpy). The first oxidation wave at +0.05 V corresponds to the catecholate-to-semiquinone oxidation of the dbcat ligand. This wave is followed by two processes at +0.51 and +0.70 V, one of which is most likely due to the catecholate-to-semiquinone transition of dpcat. The closely related complex $(dbcat)Pt(dpcat)Pt(PPh_3)_2$ displays similar reversible oxidations at −0.260 and +0.250 V referenced to the Fc^+/Fc reduction couple[7] that have been assigned as cat → sq of the dbcat and dpcat ligands, respectively. By analogy, the oxidation of dbcat in (dbcat)Pt(dpcat)Pt(dbbpy) should precede the oxidation of dpcat as well. An additional quasi-reversible oxidation is also seen at +1.17 V. Other irreversible oxidations were also observed for (dbcat)Pt(dpcat)-$Pt(PPh_3)_2$, and they were assigned to semiquinone → quinone transitions. It is not clear why semiquinone → quinone transitions in (dbcat)Pt(dpcat)Pt(dbbpy) would be of higher reversibility. The two reduction processes of (dbcat)Pt(dpcat)-Pt(dbbpy) at −1.45 and −1.78 V are most likely associated with two different diimine moieties.

The redox chemistry of (tdt)Pt(dpcat)Pt(dbbpy) is similar to that of (dbcat)Pt(dpcat)Pt(dbbpy). The complex displays two reversible reductions at −1.61 and −1.91 V that are assumed to be diimine reductions occurring at two different Pt(diimine) centers. The anodic scan shows multiple waves. The process at −0.18 V is thought to be a catecholate-based oxidation by analogy to (dpcat)Pt(dbbpy). However, the reduction current of this couple, i_p^c, is significantly higher than its oxidation counterpart with a shape for the wave that is more symmetrical than a normal, Nernstian wave. In addition, the wave is scan rate dependent. These observations suggest a weak adsorption of the oxidized species.[23] There are two other quasi-reversible oxidation processes observed at +0.24 and +0.49 V. The origin of these quasi-reversible processes is unclear. In view of the fact that Pt(diimine)(dithiolate) complexes do not usually display reversible oxidations, only one reversible oxidation couple (that associated with the catecholate → semiquinone transformation) was expected.

As a diimine equivalent, (dpcat)Pt(dbbpy) reacts with other metal complexes that undergo facile reactions with diimine ligands. These complexes include $Co_4(dbsq)_8$ and $Ru(dbbpy)_2Cl_2$ (eq 6). While the reaction of (dpcat)Pt(dbbpy) with $Co_4(dbsq)_8$ was expected to yield $(dbsq)_2Co(dpcat)Pt(dbbpy)$ in analogy with the reaction of bpy with $Co_4(dbsq)_8$ to yield $(dbsq)_2Co(bpy)$, a trinuclear complex was actually found to form. Specifically, $(dbsq)Co[(dpcat)Pt(dbbpy)]_2$ was identified unambiguously from its mass spectrum. In this reaction, two dbsq ligands at the Co center are replaced by two (dpcat)Pt-(dbbpy) units to give the observed product. In accord with other Co species of this type,[24] the trinuclear $CoPt_2$ complex is paramagnetic.

The complex (dpcat)Pt(dbbpy) can also coordinate to a Ru center by chloride substitution in *cis*-$Ru(dbbpy)_2Cl_2$. The

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(23) Wopschall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1514−1527.

(24) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951−4957.

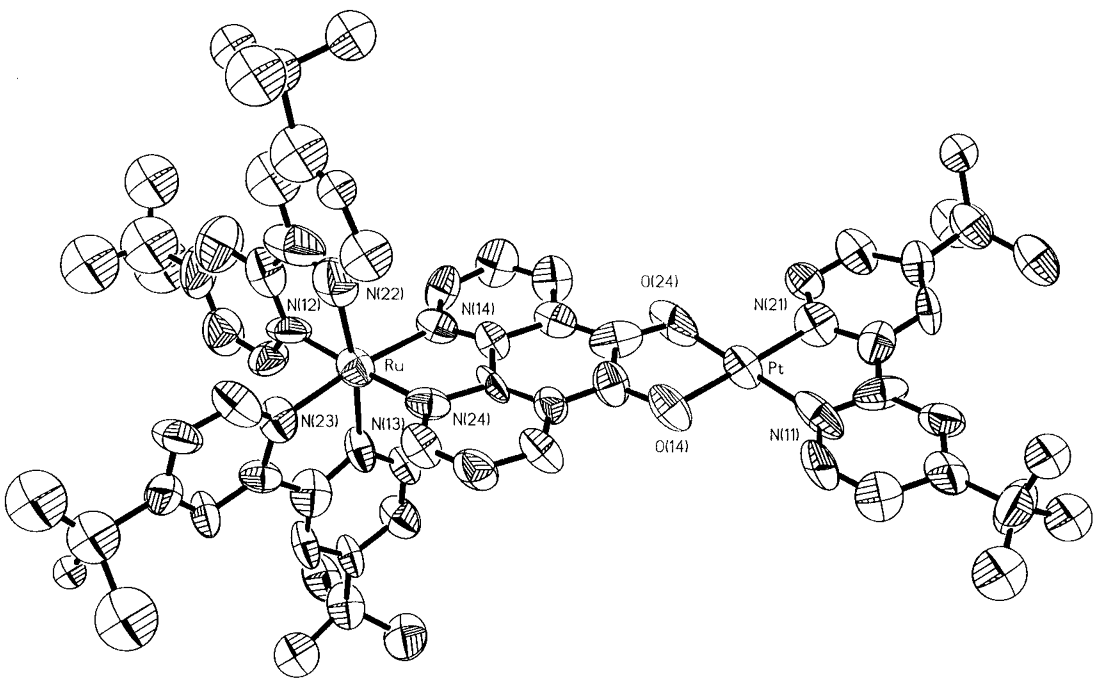


Figure 2. Connectivity structure of the complex cation in $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)](PF_6)_2$ (**10**).

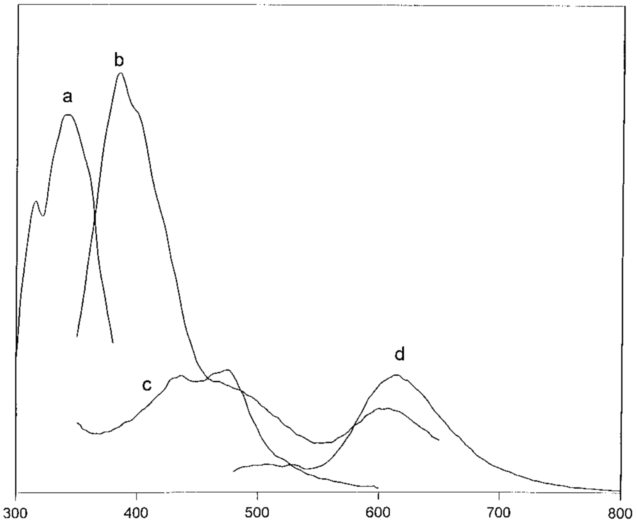
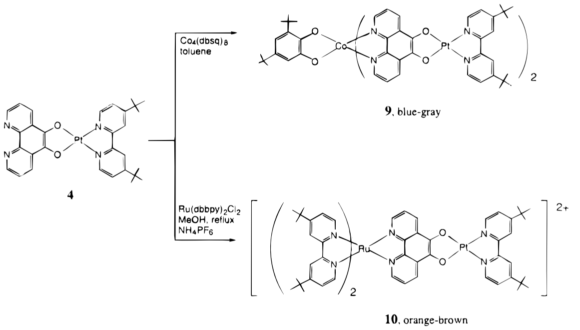


Figure 3. Emission and excitation spectra of $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)](PF_6)_2$ in CH_2Cl_2: (a) excitation spectrum, emission monitored at 400 nm; (b) emission spectrum, excitation at 340 nm; (c) excitation spectrum, emission monitored at 615 nm; (d) emission spectrum, excitation at 460 nm.



(6)

binuclear PtRu complex **10** was synthesized by refluxing of a methanol solution of the two mononuclear components. Its formulation was confirmed by ^1H NMR spectroscopy, elemental analyses, mass spectrometry, and a connectivity structure determination. The X-ray determination was attempted using an area-detector CCD system and microcrystals of **10** obtained by slow evaporation of toluene/CH_2Cl_2 solution. However, the obtained data set did not allow for complete refinement of the structure consistent with current standards of structural analysis. While the results do not allow meaningful analysis of the metrical parameters of **10**, they clearly show the connectivity within the molecule, which were inferred from the spectroscopic data. As shown in Figure 2, the dpcat ligand bridge coordinates to the Ru atom through the N atoms and to the Pt atom through the O atoms. The octahedral environment around the Ru center and the square planar environment around the Pt center are completed by dbbpy ligands.

An attempted synthesis of $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)]^{2+}$ by prior abstraction of Cl^- ligands with Ag^+ [17] did not yield **10** but instead resulted in a blue, sparingly soluble, diamagnetic complex, which was isolated in low yield. The ^1H NMR (CD_2Cl_2) spectrum of this species displayed resonances due to the “(dpcat)Pt(dbbpy)” moiety only: 9.35 (d, 2H, $J = 6.0$ Hz), 8.99 (d, 2H, $J = 8.0$ Hz), 8.74 (s, br, 2H), 7.98 (d, 2H, $J = 2.0$ Hz), 7.74 (dd, 2H, $J = 8.0, 4.4$ Hz), 7.68 (dd, 2H, $J = 6.0, 2.0$ Hz), 1.50 (s, 18H) ppm. The mass spectrum of this product was identical to that of (dpcat)Pt(dbbpy) with a parent ion peak *m*/*e* of 674. The UV/vis absorption spectrum in CH_2Cl_2 shows a band at 534 nm, which suggests an oxidation when compared to the spectrum of (dpcat)Pt(dbbpy), which displays a band at 598 nm. However, independent preparation of the presumed cation $[(dpcat)Pt(dbbpy)]^+$ by oxidation of the neutral complex with $AgPF_6$ yielded a paramagnetic complex that did not have sharp NMR resonances. Reduction of the blue product with Na/Hg yielded (dpcat)Pt(dbbpy) (**4**), as confirmed by ^1H NMR spectroscopy.

The UV/vis spectrum of $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)]^{2+}$ is typical of $Ru(diimine)_3{}^{2+}$ complexes displaying an intense absorption band at *ca.* 450 nm.[25] In addition to this band, a shoulder at 550 nm is observed that is assigned to the MLCT type transition within the (dpcat)Pt(dbbpy) chromophore. The emission spectrum of $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)]^{2+}$ (Figure 3) displays a band that is typical of $Ru(diimine)_3{}^{2+}$-based

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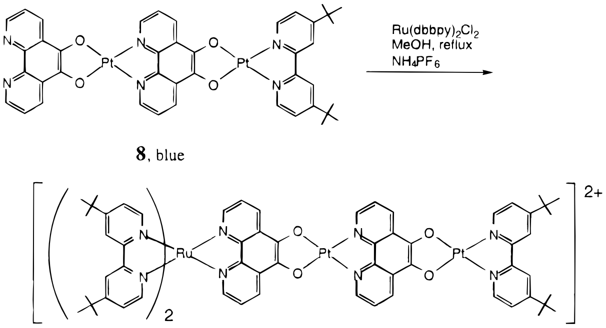
(25) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85−277.

emission and is centered at 615 nm. No other low-energy emission band is observed. However, an intraligand emission band at 400 nm, similar to that observed for other complexes containing the (dpcat)Pt(dbbpy) moiety, is also seen.

The cyclic voltammogram of $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)]^{2+}$ displays processes observed for (dpcat)Pt(dbbpy) at comparable potentials: an oxidation at $+0.37$ V and a reduction at -1.63 V. Additional processes corresponding to a quasi-reversible oxidation at ($+1.08$ V) and quasi-reversible reduction at (-1.8 V) can be assigned to $Ru^{2+/3+}$ and $Ru^{2+/+}$ processes, respectively.

In a manner analogous to that used with (dpcat)Pt(dbbpy), (dpcat)Pt(dpcat)Pt(dbbpy) was reacted with *cis*-$Ru(dbbpy)_2Cl_2$, eq 7. The trinuclear complex $[(dbbpy)_2Ru(dpcat)Pt(dpcat)Pt(dbbpy)]^{2+}$ was identified from the m/e^+ peak for $[(complex)\cdot PF_6]^+$ together with excellent agreement between observed and calculated isotope ratios. However, more detailed studies of this trinuclear complex were hampered by the presence of impurities.



8, blue

11, orange-brown

(7)

Discussion

There have been several previous reports of metal complexes utilizing dipyridocatecholate as a bridging ligand.[7,8] The strategy for the synthesis of these complexes has relied on reacting the dione dpq with metal centers capable of undergoing two-electron oxidative addition to yield a coordinated catecholate. The use of the reduced form of the ligand, $dpcatH_2$, in reaction with Pt(II) yielded complexes having catecholate coordination, but selective binding of the diimine part of dpcat was obviated by this approach. In the present study, a new synthetic approach to the dpcat-bridged complexes has been developed that adds more flexibility to the rational design of multinuclear systems. In this manner, multinuclear complexes can be formed in a stepwise fashion. However, a major synthetic obstacle is the rapid decrease in solubility after introduction of the second metal center. For example, the complex (dpcat)Pt(dbbpy) displays excellent solubility, while the complex (dpcat)Pt(dpcat)Pt(dbbpy) is only very sparingly soluble. As a result, the formation of complexes containing three or more metal centers is difficult and appears possible only if terminal ligands enhance solubility.

Perhaps the most interesting results are obtained from UV/vis absorption and emission measurements of the binuclear complexes: (tdt)Pt(dpcat)Pt(dbbpy), (dbcat)Pt(dpcat)Pt(dbbpy), and $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)]^{2+}$. The absorption spectra of all complexes display unsymmetrical bands that arise from overlapping, independent transitions of separate or isolated chromophores. However, the complex (tdt)Pt(dpcat)Pt(dbbpy) does not display emission that may be due to the (tdt)Pt(dpcat) chromophore, suggesting that the second metal center may serve to quench the emission. Such emission was expected in light of the fact that (tdt)Pt(phen) is a luminescent complex. On the other hand, the $(dbbpy)_2Ru(dpcat)$ chromophore in $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)]^{2+}$ *is* emissive and thus not “quenched” by the same Pt chromophore. The explanation of these observations is unclear at this moment. Evidently, understanding of the excited state structure and dynamics of these complexes is of great importance to the construction of supramolecular systems based on them for light-driven reactions.

Acknowledgment. We 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. We also thank Dr. Rene Lachicotte for the connectivity structure and Dr. Zheng Lu for preliminary studies related to the research reported here.

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