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Kinetics of the methylation of a platinum(II) diimine dithiolate complex

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ABSTRACT

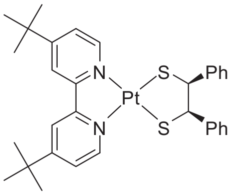
Pt(dbbpy)(bdt) and Pt(tmphen)(bdt) (dbbpy = 4,4′-di-*t*-butyl-2,2′-bipyridine; tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline; bdt^{2-} = 1,2-benzenedithiolate) are reported. Pt(dbbpy)(bdt) reacts with one equivalent of methyl iodide to give the S-methylated product, $[Pt(dbbpy)(CH_3bdt)]I$. The reaction follows second order kinetics with a rate constant of $1.3 \times 10^{-2}\ M^{-1}\ s^{-1}$ at 311 K. The accumulated data are consistent with direct nucleophilic attack by the coordinated bdt^{2-} ligand sulfur atom on the carbon atom of the methyl iodide. Variable-temperature experiments yield an Arrhenius activation energy of 51 ± 3 kJ/mol. Activated complex reaction theory yields an enthalpy and entropy of activation of 48 ± 2 kJ/mol and −125 ± 7 J/(mol K), respectively, consistent with an S_N2 reaction mechanism. The structure of the monosulfinate adduct, $Pt(dbbpy)(bdtO_2)$, also is reported. The fluid-solution luminescence of Pt(tmphen)(bdt) is concentration dependent and characterized by a 1591 ± 41 ns lifetime and 2.6 ± 0.2% quantum yield at infinite dilution. The observed chemical reactivity and self-quenching behavior have important implications for the design of photochemical devices based on the platinum(II) diimine dithiolate chromophore.

1. Introduction

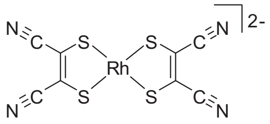
Since Camassei et al. first reported emissions from square-planar platinum(II) diimine complexes [1], there has been considerable interest in the photophysical properties and photochemical reactivity of these systems [2–12], including complexes with dithiolate ligands [2,13–16]. Potential applications include light-emitting diodes [17–20], chemical sensing [7,20,21], and catalysts for light-to-chemical energy conversion schemes [22,23]. The LUMO of these complexes has mainly diimine character. The presence of opposing thiolate donor groups destabilizes the HOMO and results in a lowest excited state with significant thiolate-to-diimine charge-transfer character. The resulting complexes have interesting spectroscopic, electrochemical, chemical, photophysical, and photochemical properties. One example is the fact that the fluid solution emission lifetimes of these complexes are concentration dependent, which is suggestive of dynamic and/or static quenching [8,24]. Surprisingly, this behavior has not always been fully considered [14,25,26], although it is surely relevant to efforts to design molecular devices. Interestingly, the expected dependence of the emission quantum yield on concentration has not yet been verified [24].

An example of photochemical activity is the irradiation of solutions of Pt(bpy)(bdt) (bpy = 2,2′-bipyridine; bdt^{2-} = 1,2-benzenedithiolate) under aerobic conditions to produce singlet oxygen, which reacts with the complex to form mono- and disulfinate products (Scheme 1) [16].

On the other hand, photolysis of Pt(dbbpy)(dpdt) ($dpdt^{2-}$ = *meso*-1,2-diphenyl-1,2-ethanedithiolate) in the presence of oxygen produces the corresponding dithiolene product [15].



Pt(dbbpy)(dpdt)



$Rh(mnt)_2^{2-}$

The nucleophilic S atoms of the bdt^{2-} ligand bonded to platinum(II) also may be alkylated in thermal reactions with alkyl halides [16,27]. However, the preference for oxidation at sulfur rather than the metal is not readily predicted, as there are several

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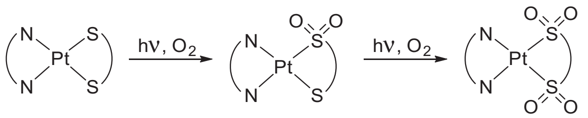
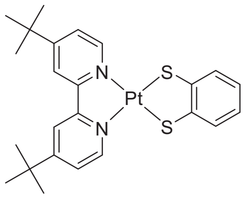


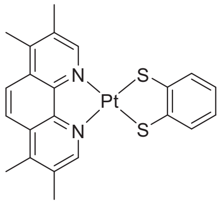
Scheme 1. Photooxidation of Pt(bpy)(bdt).

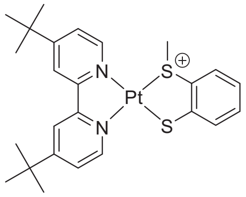
reports of oxidative addition reactions and thiolate alkylation reactions of d^8-electron metal complexes with multiple thiolate donor groups [28–31]. For example, Vlček reported that Rh(mnt)$_2^{2-}$ (mnt^{2-} = maleonitriledithiolate) reacts with methyl iodide without sulfur methylation [32], whereas VanDerveer and Eisenberg found that Rh(L)(mnt)$^-$ (L = 1,5-cyclooctadiene or norbornadiene) is readily methylated at sulfur [33].

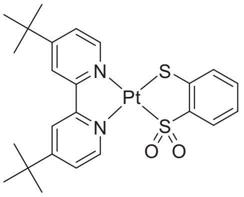
Surprisingly little attention has been given to S-alkylation of platinum complexes. By contrast, several groups have investigated related nickel complexes and determined kinetic parameters of their alkylation reactions [34–38]. More recently, Darensbourg and co-workers have investigated the alkylation of an array of nickel(II) thiolate complexes with various electrophiles [39–42]. Ashby et al. [43] have suggested that the interaction between the occupied dπ nickel orbitals and the p-type sulfur lone pair enhances the nucleophilicity of the coordinated thiolate in such systems.

With the objective of evaluating the relative susceptibilities of the platinum(II) center and thiolate ligands in diimine dithiolate complexes, we have investigated the reaction of Pt(dbbpy)(bdt) (dbbpy = 4–4′-di-*t*-butyl-2,2′-bipyridine) with methyl iodide and found that this yields exclusively the singly S-methylated product, Pt(dbbpy)(CH$_3$bdt)$^+$. We also report the crystal structure of the monosulfinate analogue, Pt(dbbpy)(bdtO$_2$), as well as the concentration dependence of the emission lifetime and quantum yield of the related complex, Pt(tmphen)(bdt).


Pt(dbbpy)(bdt)


Pt(tmphen)(bdt)


Pt(dbbpy)(CH$_3$bdt)$^+$


Pt(dbbpy)(bdtO$_2$)

2. Experimental

2.1. Materials and methods

All reagents were obtained from Aldrich, Pressure Chemical, or Acros. Pt(dbbpy)Cl$_2$ was prepared from K$_2$PtCl$_4$ as previously described [44] and washed with copious amounts of water to remove trace HCl. Deuterated solvents for NMR spectroscopy were obtained from Cambridge Isotope Laboratories. Acetonitrile, dichloromethane and chloroform were distilled from calcium hydride under argon, all other solvents used for synthesis and physical measurements were purged with argon prior to use. Elemental analyses were performed by Atlantic Microlabs. ^{1}H NMR spectra were recorded using a Bruker AC-250 or Bruker 400 MHz instrument; chemical shifts are referenced in ppm versus TMS. In the case of Pt(dbbpy)(bdtO$_2$), spectra were assigned based on 2-dimensional COSY data. Steady-state UV–Vis absorption spectra were recorded using a HP-8453 diode array spectrophotometer. Mass spectra were obtained using an Ionspec HiRes ESI-FTICRMS or a Micromass Q-TOF-II instrument. Observed isotope patterns were in excellent agreement with those calculated based on natural isotopic abundances.

For fluid solution emission studies, solutions of Pt(tmphen)(bdt) were placed in a reservoir connected to a 1-cm quartz cuvette and subjected to three freeze–pump-thaw cycles to give a final pressure over frozen solution of less than <10^{-5} torr. Samples were monitored by UV–Vis absorption spectroscopy, and for any given set of measurements, decomposition was estimated to be less than 3%. Emission and emission lifetime measurements were carried out using previously described instrumentation [45]. The standard deviation (σ) for the experimental decay rates (k') was estimated to be 3% of k'.

Emission quantum yields were determined relative to cresyl violet in MeOH (Acros, spectroscopic grade) (Φ'' = 0.54) [46]. The absorbance of both the standard and the sample at the excitation wavelength were between 0.1 and 0.3 a.u. and were within ±0.01 a.u. of each other. The emission quantum yields, Φ', were calculated using Eq. (1) [47]:

$$\frac{\Phi'}{\Phi''} = \frac{(1-10^{A_r l})\eta_s^2 I_s}{(1-10^{A_s l})\eta_r^2 I_r} \quad (1)$$

where A = absorbance of the platinum diimine dithiolate sample (A_s) or cresyl violet reference (A_r), l = pathlength of the cuvette (1 cm), η = refractive index of the sample (in CHCl$_3$) or reference (in MeOH) solvents, and I = integrated emission intensity of the sample from 650 to 700 nm. Values of the standard deviation (σ) for Φ' were estimated by propagation of the estimated σ for A (0.0035 a.u.), I (2%) and concentration. Φ' was invariant within experimental error for excitation wavelengths from 460 to 610 nm. Details of the analysis of the photophysical data and self-quenching are given in the Supplementary Material. Parameter estimates are reported with ±2σ values.

2.2. Kinetics studies

Time-resolved UV–Vis absorption data were collected using an Applied Photophysics (AP) SX18MV Stopped-Flow instrument fitted with a RISC Acorn PC and A/D converter, 150 W halogen lamp, monochromator, rectangular 2- or 10-mm pathlength quartz cell (20 μL) and photomultiplier tube. The stopped-flow instrument was purged with argon-saturated solvent prior to use, and the Teflon drive syringe pistons were bathed in an argon stream. The drive syringes, flow circuit plumbing and observation cell were thermostated to ±0.1 °C using a Fisher Isotemp 3016 recirculator, running argon-purged coolant (20% aqueous ethanol). Reagent solutions were prepared fresh daily and kept under argon prior to use. The reagents were withdrawn into gastight syringes using stainless steel needles and quickly transferred to the stopped-flow instrument, using three-way valves for the rigorous exclusion of oxygen. Reagent solutions were temperature equilibrated for at least 10 min prior to mixing. Data were typically collected for 100 s and analyzed at single wavelengths or globally (for