# A New Class of Platinum(II) Vapochromic Salts

Levi J. Grove, Jeffrey M. Rennekamp, Hershel Jude, and William B. Connick*

University of Cincinnati, Department of Chemistry, P.O. Box 210172, Cincinnati, Ohio 45221-0172

Received August 6, 2003; E-mail: bill.connick@uc.edu

Vapochromic materials, characterized by pronounced and reversible changes of color and/or emission in the presence of volatile organic compounds (VOCs), are attracting increasing attention because of their utility in chemical sensing applications.[1-3] Stacked square planar d[8] metal complexes with relatively short metal⋯metal interactions have proven especially effective in this capacity,[1,2] because solvent sorption can induce dramatic color response, associated with specific analyte interactions, as well as changes in stacking interactions and dielectric.[1g] Already these compounds have been incorporated into electronic components,[1e-g] and there is growing motivation to expand the repertoire of vapochromic materials and tailor their properties, including selectivity, response time, and strength of analyte binding. Until now, vapochromism in Pt(II) complexes has been confined to two dimeric systems,[2] several stacked neutral complexes,[1h,4] and a series of stacked double salts,[1] which are composed of Pt(II) cations (e.g., [Pt(arylisonitrile)$_4$]$^{2+}$) and M(CN)$_4^{2-}$ (M = Pd, Pt) anions. Conspicuously absent from this list are simple Pt(II) salts consisting of stacked cationic or anionic monomers with nonmetal-containing counterions. These salts are attractive synthetic targets because variation of the counterion is anticipated to provide a wide variety of vapochromic materials and a practical means of tuning the response. Reasoning that a major obstacle to obtaining stacked d[8] cations is electrostatic repulsion, we have focused our attention on ligands, such as 2,2′:6′,2″-terpyridine (tpy), that have strong σ-donating and π-accepting character, because these properties are known to favor Pt⋯Pt stacking interactions.[5,6] Here, we report the Cl$^-$ and PF$_6^-$ salts of Pt(Me$_2$bzimpy)Cl$^+$ (**1**), which are the first examples of simple Pt(II) salts that exhibit vapochromic behavior.
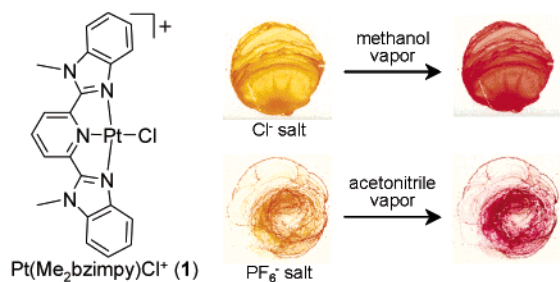
The chloride salt of **1** was prepared by refluxing Me$_2$bzimpy[7] with K$_2$PtCl$_4$. The product retains 2.5 equiv of H$_2$O with tenacity reminiscent of [Pt(tpy)Cl]Cl·2H$_2$O.[8] The PF$_6^-$ salt was prepared by metathesis. Films of the yellow-orange salts were exposed to a series of solvent vapors at room temperature, including diethyl-ether, dichloromethane, methanol, acetone, chloroform, hexanes, carbon tetrachloride, ethanol, benzene, acetonitrile, 2-propanol, and water. The chloride salt only responded to vapors of methanol, chloroform, ethanol, and acetonitrile, undergoing a distinct change in color from yellow to red within seconds. Gravimetric measurements indicate sorption of up to 2 equiv of methanol, though the capacity of samples aged in air for days is somewhat reduced as a
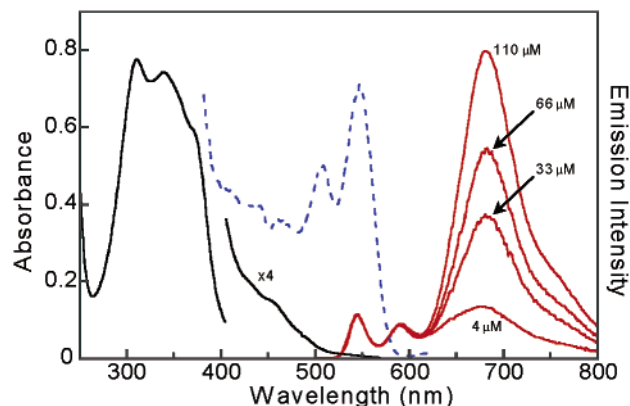
Figure 1. UV−visible absorption spectrum of 10 μM **1**(Cl$^-$)·2.5H$_2$O in room-temperature methanol solution (black lines). 77 K 4:1 EtOH−MeOH glassy solution emission (λ_{ex} = 400 nm; red lines) and excitation (λ_{em} = 670 nm; blue − − −) spectra. Emission spectra are normalized at 545 nm.

consequence of slow water uptake. In contrast, the PF$_6^-$ salt only responded to acetonitrile vapor, changing from yellow to violet within seconds. Uptake was confirmed by the appearance of a band at 2252 cm^{-1} in the FT-IR spectrum. Gravimetric measurements indicate sorption of 1.0 ± 0.1 equiv. For either salt, leaving vapor-exposed samples in air for several days or heating for several minutes restored the original color. The vapochromic response is fully reversible, both in air and under argon atmosphere, and there was no discernible change in behavior after repeated cycling of vapor exposure and heating.

As previously noted for Pt(tpy)Cl$^+$ and Pt(L)Cl$^+$,[5a,9] (L = 2,6-bis(1-octadecylbenzimidazol-2-yl)pyridine, i.e., (C$_{18}$H$_{37}$)$_2$bzmpy) **1**, has a strong tendency to aggregate in solution, suggesting inter-molecular interactions may play a role in the vapochromic response. The UV−visible absorption spectrum of the Cl$^-$ salt in methanol exhibits an intense structured Me$_2$bzimpy π−π* band near 340 nm and two shoulders near 430 and 455 nm, attributable to a metal-to-ligand (π*) charge-transfer transition (Figure 1).[9] The spectrum does not obey Beer's law from 200 nM to 100 μM, as indicated by changes in the apparent molar absorptivity and absorption profile. With increasing concentration, a weak band near 540 nm emerges and is tentatively assigned to a metal-metal-to-ligand charge transfer (MMLCT[dσ* → π*]) transition, where the dσ* derives from the interaction of the d$_{z^2}$(Pt) orbitals of associated complexes. In 77 K 4:1 EtOH−MeOH glassy solution, the emission spectrum of **1** also is strongly concentration-dependent (Figure 1). Excitation of a 4 μM sample at 400 nm results in three emission maxima of comparable intensity near 545, 590, and 680 nm, with a shoulder near 750 nm. The spacing between the 545 and 590 nm features (1400 cm^{-1}) and bandshape are consistent with a vibronically structured π−π* emission originating from a lowest ligand-centered excited state.[9] With increasing concentration, the 680 nm band (~1500 cm^{-1} fwhm) and shoulder gain intensity relative to the short wavelength emission, indicating formation of an emissive aggregate.
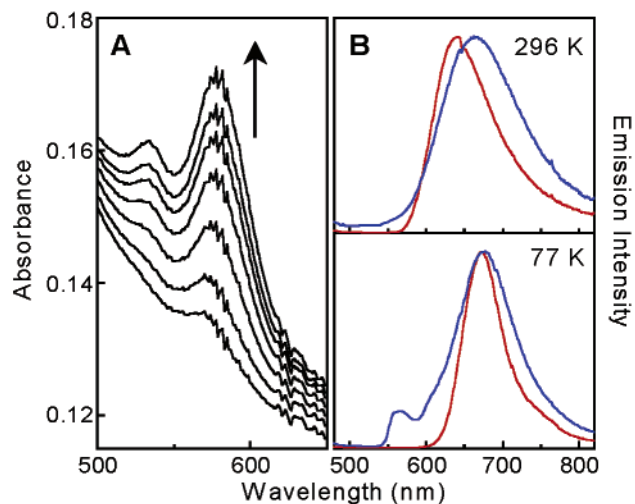
Figure 2. (A) UV—visible absorption spectra of a thin film of **1**(PF$_6^-$) recorded during exposure to acetonitrile vapor. (B) Solid-state emission spectra of **1**(Cl$^-$)·2.5H$_2$O before (blue lines) and after (red lines) exposure to methanol vapor (λ_{ex} = 440 nm).

The ~1400 cm^{-1} vibronic spacing is diagnostic of ligand involvement, and the emission likely originates from a lowest ^{3}MMLCT-[d$\sigma^* \rightarrow \pi^*$] state. The excitation spectrum bears a mirror image relationship to the emission (529, 568 nm; 1300 cm^{-1} spacing), as expected for the corresponding absorption.

To characterize the vapochromic response, UV—visible absorption spectra of films of the salts were recorded (Figure 2A). Dry films exhibit intense absorption from 300 to 400 nm with a weakly structured low-energy tail, suggestive of weak intermolecular ligand···ligand interactions. In contrast, exposure of **1**(PF$_6^-$) to acetonitrile vapor results in a sharply structured absorption with maxima near 532 and 577 nm (1470 cm^{-1} spacing), similar to the MMLCT[d$\sigma^* \rightarrow \pi^*$] transition observed in glassy solution excitation spectra. Removal of the source of solvent vapor results in a gradual decrease in absorbance. Similar results were obtained for films of the chloride salt, though the absorption is shifted to shorter wavelengths (520, 559 nm; 1340 cm^{-1} spacing), suggesting weaker Pt···Pt interactions.

Solid-state emission studies also suggest that vapor sorption increases Pt···Pt interactions, possibly resulting in a change in the orbital character of the lowest emissive state (Figure 2B). The 298 K emission spectrum **1**(Cl$^-$)·2.5H$_2$O consists of a broad band near 670 nm (~2800 cm^{-1} fwhm). Upon cooling to 77 K, the emission slightly narrows and undergoes a small shift (330 cm^{-1}) to a longer wavelength, 685 nm (~2000 cm^{-1} fwhm). Though it is premature to make a definitive assignment, this behavior is not inconsistent with excimeric emission resulting from ligand $\pi-\pi$ interactions between closely interacting complexes as observed for Pt(II) terpyridyl chloride complexes.[5,6b—f,10] Exposure to methanol vapor to give the red form causes the room-temperature emission to sharpen (~2100 cm^{-1} fwhm). Though the emission maximum is blue-shifted with respect to the orange form, the emission onset is distinctly shifted to lower energy. Upon cooling to 77 K, the emission band further narrows (~1300 cm^{-1} fwhm) and red-shifts by 700 cm^{-1}. The bandshapes and thermal effects are characteristic of solid samples of Pt(II) compounds with short Pt···Pt interactions, in which thermal lattice contraction shortens the Pt···Pt spacing, thereby stabilizing the lowest MMLCT states.[6a,c,e,f,11] Similar behavior is observed for samples of **1**(PF$_6^-$) exposed to acetonitrile,

except that the emission maxima occur ~600 cm^{-1} to the red, as expected for stronger Pt···Pt interactions.

Though the mechanistic details of the vapochromic response for these salts are not certain, the available evidence is consistent with a decrease in Pt···Pt separation accompanying vapor sorption. Such behavior would be expected if the formation of favorable Pt···Pt interactions and the inclusion of vapor molecules in lattice voids offset the energy costs of a less efficient packing arrangement of anions and cations.

Supporting Information Available: Experimental details for **1**(Cl$^-$)·2.5H$_2$O and **1**(PF$_6^-$) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Exstrom, C. L.; Sowa, J. R.; Daws, C. A.; Janzen, D.; Mann, K. R.; Moore, G. A.; Stewart, F. F. *Chem. Mater.* **1995**, *7*, 15—17. (b) Daws, C. A.; Exstrom, C. L.; Sowa, J. R., Jr.; Mann, K. R. *Chem. Mater.* **1997**, *9*, 363—367. (c) Exstrom, C. L.; Pomije, M. K.; Mann, K. R. *Chem. Mater.* **1998**, *10*, 942—945. (d) Buss, C. E.; Anderson, C. E.; Pomije, M. K.; Lutz, C. M.; Britton, D.; Mann, K. R. *J. Am. Chem. Soc.* **1998**, *120*, 7783—7790. (e) Kunugi, Y.; Mann, K. R.; Miller, L. L.; Exstrom, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 589—590. (f) Kunugi, Y.; Miller, L. L.; Mann, K. R.; Pomije, M. K. *Chem. Mater.* **1998**, *10*, 1487—1489. (g) Drew, S. M.; Janzen, D. E.; Buss, C. E.; MacEwan, D. I.; Dublin, K. M.; Mann, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 8414—8415. (h) Buss, C. E.; Mann, K. R. *J. Am. Chem. Soc.* **2002**, *124*, 1031—1039. (i) Grate, J. W.; Moore, L. K.; Janzen, D. E.; Veltkamp, D. J.; Kaganove, S.; Drew, S. M.; Mann, K. R. *Chem. Mater.* **2002**, *14*, 1058—1066. (j) Bailey, R. C.; Hupp, J. T. *J. Am. Chem. Soc.* **2002**, *124*, 6767—6774.
(2) (a) Kato, M.; Omura, A.; Toshikawa, A.; Kishi, S.; Sugimoto, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 3183. (b) Lu, W.; Chan, M. C. W.; Cheung, K.-K.; Che, C.-M. *Organometallics* **2001**, *20*, 2477—2486.
(3) (a) Mansour, M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1998**, *120*, 1329—1330. (b) Evju, J. K.; Mann, K. R. *Chem. Mater.* **1999**, *11*, 1425—1433. (c) Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 2763—2772. (d) Cariati, E.; Bu, X.; Ford, P. C. *Chem. Mater.* **2000**, *12*, 3385—3391. (e) Bariáin, C.; Matías, I. R.; Romeo, I.; Garrido, J.; Laguna, M. *Sens. Actuators* **2001**, *B76*, 25—31. (f) Kojima, M.; Taguchi, H.; Tsuchimoto, M.; Nakajima, K. *Coord. Chem. Rev.* **2003**, *237*, 183—196. (g) Fernandez, E. J.; Lopez-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Perez, J.; Laguna, A.; Mohamed, A. A.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 2022—2023.
(4) (a) Bielli, E.; Gidney, P. M.; Gillard, R. D.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1974**, 2133—2139. (b) Shih, K.-C.; Herber, R. H. *Inorg. Chem.* **1992**, *31*, 5444—5449.
(5) (a) Connick, W. B.; Marsh, R. E.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1997**, *36*, 913—922. (b) Aullon, G.; Alvarez, S. *Chem.—Eur. J.* **1997**, *3*, 655—664.
(6) (a) Yip, H.-K.; Cheng, L.-K.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2933—2938. (b) Bailey, J. A.; Hill, M. G.; Marsh, R. E.; Miskowski, V. M.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 4591—4599. (c) Buchner, R.; Cunningham, C. T.; Field, J. S.; Haines, R. J.; McMillin, D. R.; Summerton, G. C. *J. Chem. Soc., Dalton Trans.* **1999**, 711—718. (d) Lai, S.-W.; Chan, M. C. W.; Cheung, K.-K.; Che, C.-M. *Inorg. Chem.* **1999**, *38*, 4262—4267. (e) Field, J. S.; Haines, R. J.; McMillin, D. R.; Summerton, G. C. *J. Chem. Soc., Dalton Trans.* **2002**, 1369—1376. (f) Field, J. S.; Gertenbach, J.-A.; Haines, R. J.; Ledwaba, L. P.; Mashapa, N. T.; McMillin, D. R.; Munro, O. Q.; Summerton, G. C. *J. Chem. Soc., Dalton Trans.* **2003**, 1176—1180.
(7) Addison, A. W.; Burman, S.; Wahlgren, C. G.; Rajan, O. A.; Rowe, T. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1987**, 2621—2630.
(8) Howe-Grant, M.; Lippard, S. J. *Inorg. Synth.* **1980**, *20*, 101—105.
(9) Wang, K.; Haga, M.-a.; Monjushiro, H.; Akiba, M.; Sasaki, Y. *Inorg. Chem.* **2000**, *39*, 4022—4028.
(10) Arena, G.; Calogero, G.; Campagna, S.; Scolaro, L. M.; Ricevuto, V.; Romeo, R. *Inorg. Chem.* **1998**, *37*, 2763—2769.
(11) (a) Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1991**, *30*, 4446—4452. (b) Connick, W. B.; Henling, L. M.; Marsh, R. E.; Gray, H. B. *Inorg. Chem.* **1996**, *35*, 6261—6265. (c) Kato, M.; Kosuge, C.; Morii, K.; Ahn, J. S.; Kitagawa, H.; Mitani, T.; Matsushita, M.; Kato, T.; Yano, S.; Kimura, M. *Inorg. Chem.* **1999**, *38*, 1638—1641.

JA037783J