Inorg. Chem. **2008**, *47*, 1408−1410

Inorganic Chemistry
Communication

Structure of a Crystalline Vapochromic Platinum(II) Salt

Levi J. Grove,[†] Allen G. Oliver,[‡,§] Jeanette A. Krause,[†] and William B. Connick*[,†]

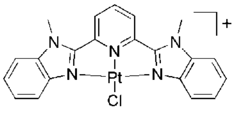
Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, Ohio 45221-0172, and College of Chemistry, University of California—Berkeley, Berkeley, California 94720-1460

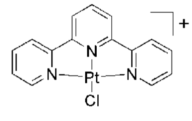
Received July 31, 2007

Square-planar cations of the orange form of [Pt(Me$_2$bzimpy)Cl](PF$_6$)·DMF [Me$_2$bzimpy = 2,6-bis(*N*-methylbenzimidazol-2-yl)pyridine] stack along the *b* axis in a head-to-tail arrangement with short interplanar spacings (3.35 and 3.39 Å). Long intermolecular Pt$\cdots$Pt contacts [4.336(2) and 4.565(2) Å] and comparatively short Me$_2$bzimpy$\cdots$Me$_2$bzimpy distances are consistent with spectroscopic measurements for orange salts of Pt(Me$_2$bzimpy)Cl$^+$. The DMF solvent molecules line channels parallel to *c*, which may provide a conduit for vapor absorption. The crystals are vapochromic, changing from orange to violet upon exposure to acetonitrile vapor. The changes in spectroscopic properties accompanying vapor absorption are consistent with changes in intermolecular interactions between complexes.

Salts of Pt(Me$_2$bzimpy)Cl$^+$ [Me$_2$bzimpy = 2,6-bis(*N*-methylbenzimidazol-2-yl)pyridine] are vapochromic, undergoing a reversible color change upon exposure to certain volatile organic compounds.[1] What distinguishes these materials from other platinum(II) vapochromic systems[2,3] is that the selectivity, color change, and speed of the response are drastically dependent on the counteranion, thereby providing a strategy for tuning the response. For example, [Pt(Me$_2$bzimpy)Cl](PF$_6$) changes from orange to violet when exposed to acetonitrile vapor, whereas the complementary chloride salt changes from orange to red in response to methanol, chloroform, ethanol, and acetonitrile.[1] Absorption and emission spectroscopic data are consistent with the hypothesis that the vapor absorption is accompanied by rearrangement of the Pt(Me$_2$bzimpy)Cl$^+$ cations to give comparatively short Pt$\cdots$Pt interactions (<3.5 Å). Interestingly, the closely related Pt(tpy)Cl$^+$ cation forms a variety of salts with varying intermolecular Pt$\cdots$Pt distances; however, none of these materials has been reported to be vapochromic.[4]

Structural data are expected to provide insight into the factors influencing the vapochromic response of Pt(Me$_2$bzimpy)Cl$^+$ salts. However, obtaining suitable samples for single-crystal X-ray diffraction studies has proven challenging because these compounds tend to form needle-shaped crystals that diffract poorly. Here we report the first structure of a vapochromic Pt(Me$_2$bzimpy)Cl$^+$ salt.


Pt(bzimpy)Cl$^+$


Pt(tpy)Cl$^+$

Orange crystals of [Pt(Me$_2$bzimpy)Cl](PF$_6$)·DMF were obtained by evaporation of an acetonitrile solution mixed with a small amount of DMF.[5] The anions, cations, and solvent pack as discrete molecules, and there are no unusually short intermolecular interactions involving the anion or solvent. We have observed that some Pt(Me$_2$bzimpy)Cl$^+$ salts take up certain vapors without changing color,[6] and therefore the orange color of these solvent-containing crystals is not entirely surprising. However, it is intriguing that orange powder samples of [Pt(Me$_2$bzimpy)Cl](PF$_6$) (solvent free)

---

* To whom correspondence should be addressed. E-mail: bill.connick@uc.edu.

[†] University of Cincinnati.

[‡] Current address: Department of Chemistry & Biochemistry, University of California—Santa Cruz, Santa Cruz, CA 95064.

[§] University of California—Berkeley.

(1) Grove, L. J.; Rennekamp, J. M.; Jude, H.; Connick, W. B. *J. Am. Chem. Soc.* **2004**, *126*, 1594–1595.

(2) (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., 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) 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.

(3) (a) 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. (b) Lu, W.; Chan, M. C. W.; Cheung, K.-K.; Che, C.-M. *Organometallics* **2001**, *20*, 2477–2486. (c) Kato, M.; Omura, A.; Toshikawa, A.; Kishi, S.; Sugimoto, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 3183. (d) Kishi, S.; Kato, M. *Mol. Cryst. Liq. Cryst. A* **2002**, *379*, 303–308. (e) Buss, C. E.; Mann, K. R. *J. Am. Chem. Soc.* **2002**, *124*, 1031–1039. (f) Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C.-m.; He, Z.; Wong, K.-y. *Chem.—Eur. J.* **2003**, *9*, 6155–6166. (g) Wadas, T. J.; Wang, Q.-M.; Kim, Y.-J.; Flaschenreim, C.; Blanton, T. N.; Eisenberg, R. *J. Am. Chem. Soc.* **2004**, *126*, 16841–16849. (h) Kato, M.; Kishi, S.; Wakamatsu, Y.; Sugi, Y.; Osamura, Y.; Koshiyama, T.; Hasegawa, M. *Chem. Lett.* **2005**, *34*, 1368–1369.

(4) (a) Wong, Y.-S.; Lippard, S. J. *Chem. Commun.* **1977**, 824–825. (b) Yip, H.-K.; Cheng, L.-K.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2933–2938. (c) Bailey, J. A.; Hill, M. G.; Marsh, R. E.; Miskowski, V. M.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 4591–4599. (d) Cini, R. D. A.; Giannettoni, R. *Inorg. Chim. Acta* **2001**, *315*, 73–80. (e) Tzeng, B.-C.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem. Commun.* **2003**, *6*, 1341–1343. (f) Sengul, A. *Turk. J. Chem.* **2004**, *28*, 667–672. (g) Angle, C. S.; DiPasquale, A. G.; Rheingold, A. L.; Doerrer, L. H. *Acta Crystallogr.* **2006**, *C62*, m340–m342. (h) Tastan, S.; Krause, J. A.; Connick, W. B. **2007** , to be submitted.

10.1021/ic701523e CCC: $40.75

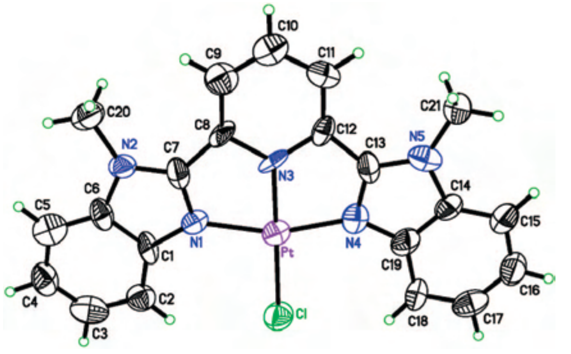


Figure 1. Molecular structure of Pt(Me$_2$bzimpy)Cl$^+$, 50% ellipsoids.

that were precipitated from aqueous solution absorb 1 equiv of DMF and turn violet, whereas the crystals reported here do not respond to DMF vapor. These observations suggest that there are at least two stable polymorphs of the DMF adduct, distinguished by their orange and violet colors.

The coordination geometry of the metal center is approximately square-planar, and the entire Pt(Me$_2$bzimpy)Cl$^+$ unit is planar with a root-mean-square deviation from a best-fit plane of 0.034 Å for 28 non-hydrogen atoms (Figure 1). The Me$_2$bzimpy ligand chelates in a distinctly asymmetric fashion with a very short Pt−N(py) bond length [Pt−N3, 1.906(11) Å] and significantly different Pt−N(im) bond lengths [Pt−N1, 2.011(12) Å; Pt−N4, 1.962(13) Å]. The pattern of a short center Pt−N(py) distance and longer peripheral Pt−N distances is reminiscent of that found for eight structurally characterized Pt(tpy)Cl$^+$ salts [center Pt−N(py), 1.91–1.95 Å; peripheral Pt−N(py), 1.98–2.03 Å].[4] The Pt−N distances are substantially shorter than those reported for related platinum(II) complexes with bidentate N(im)-substituted 2-(2′-pyridyl)benzimidazole ligands and strong trans-influence phenyl or acetylide ancillary ligands [Pt−N(py), 2.08–2.16 Å; Pt−N(im), 2.06–2.13 Å].[7,8] The trans N1−Pt−N4 angle [160.7(5)°] is at the low end of the range reported for Pt(tpy)Cl$^+$ (160.8–163.5°),[4] in keeping with the anticipated relative geometric constraints of the Me$_2$bzimpy five-membered imidazole rings as compared to the six-membered pyridyl rings of tpy. The Pt−Cl distance [2.293(4) Å] lies within the range reported for Pt(tpy)Cl$^+$ salts (2.29–2.32 Å).[4]

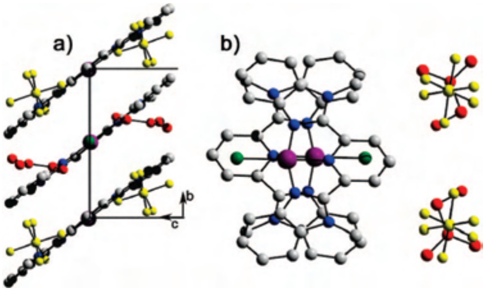


Figure 2. (a) Columnar stacking arrangement, viewed perpendicular to the *bc* plane. (b) Head-to-tail slipped stacking arrangement, viewed down the *b* axis (PF$_6^-$ in yellow; DMF in red).

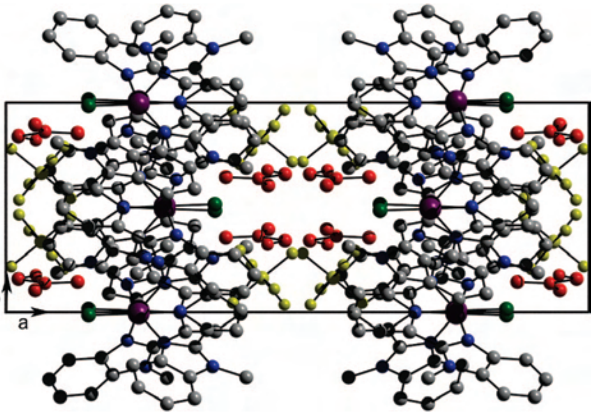


Figure 3. DMF solvent molecule line channels, viewed down the *c* axis (PF$_6^-$ in yellow; DMF in red).

The cations adopt a columnar stacking arrangement in which the planar complexes are canted by ~38° with respect to the stacking axis (*b*; Figure 2a). Consecutive molecules along the stack are related by an inversion center, resulting in a head-to-tail arrangement (Figure 2b) with short interplanar spacings (3.35 and 3.39 Å). Viewed perpendicular to the molecular planes, successive complexes along the stack appear slipped so that each chloride ligand resides in a cavity formed by methyl and pyridyl groups of the two nearest complexes (Figure S1 in the Supporting Information). This arrangement results in relatively long Pt···Pt distances [4.336(2) and 4.565(2) Å], which are entirely consistent with the orange color.[1,3g,4c] By contrast, there are short Pt···C contacts between stacked cations, including Pt···C7 [3.371(15) Å] and Pt···C13 [3.399(16) Å], as well as short Me$_2$bzimpy···Me$_2$bzimpy contacts [N1···C14, 3.351(21) Å; N2···C16, 3.358(21) Å; N3···C1, 3.395(21) Å]. For comparison, Pt(tpy)Cl$^+$ salts pack with the cations typically forming dimers, chains, or chains of dimers with comparable interplanar spacings (3.18–3.52 Å) but shorter Pt···Pt separations. Excluding the structure of the adenosine-5′-monophosphate salt (Pt···Pt, 3.70 Å), the average of the shortest Pt···Pt distances for the remaining seven Pt(tpy)Cl$^+$ compounds (including [Pt(tpy)Cl](PF$_6$)·CH$_3$CN)[4g] is 3.34(4) Å.[4]

Anions and solvent molecules fill the voids between the columns of cations, with the solvent molecules lining zigzag channels along *c*, suggesting a possible conduit for diffusion of vapors in and out of the crystals (Figures 3 and S2 in the Supporting Information). Upon exposure to acetonitrile vapor, the color of the crystals changed from orange to violet. The color change, which began in the interior of individual crystals and at the center of clusters of crystals, was complete

---

(5) Crystallographic data for orange [Pt(Me$_2$bzimpy)Cl](PF$_6$)·DMF: [C$_{21}$H$_{17}$N$_5$ClPt]PF$_6$·HCON(CH$_3$)$_2$, MW = 788.00, T = 183 K, λ = 0.775 00 Å, monoclinic, *C*2/*c*, a = 26.983(8) Å, b = 8.530(2) Å, c = 25.018(7) Å, β = 118.059(7)°, Z = 8, V = 5081(2) Å^3, R1 = 0.0464, wR2 = 0.1078 for data with $I > 2\sigma(I)$ (R1 = 0.0837, wR2 = 0.1166 for all data). Data were collected using a Bruker Platinum200 CCD detector at Beamline 11.3.1 (ALS) using synchrotron radiation. The structure was solved by direct methods and the difference Fourier technique and refined by full-matrix least squares on F^2 (1 Å resolution) with anisotropic displacement parameters (ADPs) for all non-hydrogen atoms of the cation and anion. The ADP of C13 was constrained to be equal to that of the better behaved C7. Hydrogen atoms were located directly or calculated and treated with a riding model. The complex crystallizes with a DMF molecule, appearing cleanly in the initial maps. However, it misbehaves upon refinement, requiring constraints and restraints (see the Supporting Information for details).

(6) For example, the orange nitrate salt absorbs up to ~0.7 equiv of methanol and does not change color.

(7) Shavaleev, N. M.; Bell, Z. R.; Easun, T. L.; Rutkaite, R.; Swanson, L.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **2004**, 3678–3688.

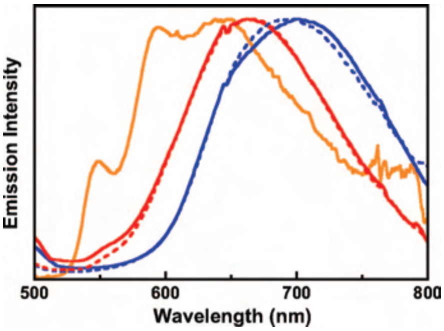


Figure 4. Emission spectra (λ_{ex} = 440 nm) of orange crystals of Pt(Me$_2$bzimpy)Cl]PF$_6$·DMF (yellow solid line), after exposure to acetonitrile vapor (blue solid line), after heating at 100 °C for 10 min (red solid line), after a second exposure to acetonitrile vapor (blue dashed line), and after heating again at 100 °C for 10 min (red dashed line). Spectra have been scaled to the same maximum intensity.

within ~60 min. Although the crystals retained their shape and clarity, X-ray diffraction measurements yielded only powder rings. These results suggest that vapor absorption disrupts the microcrystalline structure of the crystals despite their macroscopic stability. Under similar conditions, powder samples of [Pt(Me$_2$bzimpy)Cl](PF$_6$) (solvent free) absorb 1 equiv of acetonitrile within ~2 min, changing from orange to violet. Violet-colored samples, formed by exposure of the solvent-free powder to DMF vapor, completely exchange DMF for acetonitrile within ~30 min. The slower response of the orange [Pt(Me$_2$bzimpy)Cl](PF$_6$)·DMF crystals may reflect the influence of the particle size on diffusion, as well as differences in the energy barrier for transformation from the orange to violet form.

The emission spectrum of ~60 orange crystals adhered to the crystallization vial shows progressively intense maxima at 554, 599, and 650 nm (Figure 4). The band profile is suggestive of overlapping structured unimolecular $\pi-\pi^*$ emission[1] and a broader unstructured emission maximizing near 650 nm. The latter is slightly blue-shifted from that of orange powder samples of [Pt(Me$_2$bzimpy)Cl](PF$_6$) [solvent-free; λ_{max} = 676 nm; full width at half-maximum (fwhm)~2900 cm^{-1}], which has been attributed to an excimeric excited state characterized by localization of the excitation on interacting Me$_2$bzimpy ligands of adjacent chromophores.[1] After exposure of the crystals to acetonitrile vapor, the emission spectrum consists of a band at 704 nm (fwhm ~ 3000 cm^{-1}; Figure 4). Somewhat similar long-wavelength emissions from vapor-exposed powder samples of Pt(Me$_2$bzimpy)Cl$^+$ salts have been assigned to a low-energy metal–metal-to-ligand charge-transfer (MMLCT [dσ^* → π^*(Me$_2$bzimpy)]) transition, where the dσ^* orbital derives from the antibonding combination of the 5d$_{z^2}$ Pt orbitals of adjacent complexes.[1] Heating the crystals for 10 min at 100 °C drives off the solvent, as verified by gas chromatography–mass spectrometry, and results in the original orange color and a broad excimeric-like emission band maximizing at 665 nm (fwhm ~ 3100 cm^{-1}). Re-exposure to acetonitrile vapor resulted in a low-energy emission maximizing at 694 nm (fwhm ~ 3000 cm^{-1}). Heating the sample restored the orange color and the 665 nm emission (Figure 4). Despite qualitatively similar behavior, powder samples do not yield the same emission spectra as those obtained for the crystals. The agreement between the violet-colored samples is poor, with the emission band for the vapor-exposed powder appearing narrower and shifting to shorter wavelengths (652 nm; fwhm ~ 2400 cm^{-1}; Figure S3 in the Supporting Information); the precise structural reasons for these differences are not yet fully understood.

The results presented here confirm the presence of π-stacking interactions and the absence of strong metal–metal interactions in the orange crystals. The structure also reveals a channel along which vapors may diffuse. Although our inability to reproduce this particular crystal form has prevented more detailed spectroscopic investigations, it is apparent that the violet color of the acetonitrile-exposed crystals and the accompanying changes in emission are consistent with stabilization of a low-energy MMLCT [dσ^* → π^*] transition. As was found for several other vapochromic platinum(II) systems,[3] it is likely that vapor absorption is accompanied by rearrangement of the platinum complexes, which in this case results in short Pt···Pt distances (<3.5 Å). It is tempting to imagine that the transformation occurs by the simplest imaginable deformation, namely, slipping of adjacent cations by 1.35 Å along antiparallel vectors that lie parallel to the plane of each complex to give dimers with 3.39 Å Pt···Pt contacts. However, translation/libration/screw analysis using the U_{ij} of the non-hydrogen atoms of the cation lends no support to this notion because the largest translational component is not aligned along this deformation pathway. Regardless of the mechanistic details, it would appear that the vapochromic behavior of Pt(Me$_2$bzimpy)Cl$^+$ salts is connected with their tendency to adopt packing arrangements spanning a wide range of metal–metal distances and Me$_2$bzimpy···Me$_2$bzimpy interactions.

Acknowledgment. We thank the NSF (Grant CHE-0134975) and the Arnold and Mabel Beckman Foundation for support. L.J.G. thanks the Department of Chemistry University of Cincinnati (UC) for the Procter & Gamble Fellowship. The X-ray sample was submitted through the SCrALS (Service Crystallography at Advanced Light Source) program, and data were collected at Beamline 11.3.1 at the Advanced Light Source (ALS). The ALS is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract DE-AC03-76SF00098. We thank Drs. F. Hollander (University of California–Berkeley), L. Sallans (UC), and R. Marsh, as well as L. Henling (Caltech), for technical assistance and helpful discussions.

Supporting Information Available: Complete crystallographic data in CIF format and experimental details for X-ray crystallography, emission spectroscopy, and gas chromatography. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701523E

---

(8) Liu, Q.-D.; Jia, W.-L.; Wang, S. *Inorg. Chem.* **2005**, *44*, 1332–1343.