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A Comparison of Isomers: *trans*- and *cis*-Dicyanobis(*para*-ethylisocyanobenzene)Platinum

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We report the synthesis and characterization of *trans*-Pt(*p*-CN−C_6H_4−C_2H_5)$_2$(CN)$_2$ and compare the properties to the previously reported *cis* isomer, *cis*-Pt(*p*-CN−C_6H_4−C_2H_5)$_2$(CN)$_2$. These geometric isomers exhibit textbook differences in spectroscopic and vapochromic properties, especially in the solid-state.

Introduction

We recently reported the synthesis and vapochromic sensing capability of *cis*-Pt(*p*-CN−C_6H_4−C_2H_5)$_2$(CN)$_2$.[1] This neutral complex was formed from the thermal rearrangement of the isomeric double-salt complex [Pt(*p*-CN−C_6H_4−C_2H_5)$_4$][Pt(CN)$_4$]. We are investigating these types of platinum complexes due to their vapochromic properties,[2] which have potential for use in chemical sensors and other optoelectronic devices.[3] Here we report the synthesis and characterization of the trans isomer of Pt(*p*-CN−C_6H_4−C_2H_5)$_2$(CN)$_2$ and compare it to the previously reported *cis*-Pt(*p*-CN−C_6H_4−C_2H_5)$_2$(CN)$_2$. This is the first well-characterized trans isomer of the Pt(isocyanide)$_2$(CN)$_2$ family of compounds[4] and presents a textbook example of the differences in properties that geometric isomers can exhibit.

Experimental Section

General Considerations and Materials. All solvents used were ACS reagent grade and dried over molecular sieves prior to use. [Pt(*p*-CN−C_6H_4−C_2H_5)$_4$][Pt(CN)$_4$] was prepared by a modification of the method reported by Buss and Mann.[1] The sample of *cis*-Pt-(*p*-CN−C_6H_4−C_2H_5)$_2$(CN)$_2$ (***cis*-PtC$_2$**) was available from a previous study.[1]

***trans*-Pt(CN-*p*-C_6H_4−C_2H_5)$_2$(CN)$_2$ (*trans*-PtC$_2$).** A mixture of [Pt(*p*-CN−C_6H_4−C_2H_5)$_4$][Pt(CN)$_4$] (0.201 g, 0.197 mmol) and hydrocarbon-stabilized $CHCl_3$ (25 mL, 0.31 mol) was stirred at reflux under a nitrogen atmosphere for 5 h. The remaining solid was removed by filtration, and the soluble product was purified by chromatography (silica gel, 85:15 CH_2Cl_2/$CH_3CO_2C_2H_5$). The first fraction was collected and rotary evaporated to afford a reddish-purple powder (0.080 g, 0.157 mmol, 79.9%). mp 174 °C (dec). ^{1}H NMR (300 MHz, rt, CD_2Cl_2): δ 7.54 (d, J = 8.4 Hz, 2 H, Ph), 7.37 (d, J = 8.4 Hz, 2 H, Ph), 2.74 (q, J = 7.7 Hz, 2 H, CH_2), 1.26 (t, J = 7.7 Hz, 3 H, CH_3). ^{13}C NMR (75 MHz, rt, CD_2Cl_2): δ 149.9 (isocyanide; Ph), 129.9 (isocyanide; Ph), 127.7 (isocyanide; Ph), 122.8 (isocyanide; Ph), 112.7 (m, $J_{^{195}\mathrm{Pt}-^{13}\mathrm{C}} = 490$ Hz), 29.4 (isocyanide; CH_2), 15.4 (isocyanide; CH_3). ^{195}Pt NMR (64.5 MHz, rt, CD_2Cl_2, external reference K_2PtCl_4 in D_2O, δ −1624): δ −4698 (m, $J_{^{195}\mathrm{Pt}-^{14}\mathrm{N}} = 94$ Hz). FTIR (ATR, ZnSe crystal): ν_{CNR} 2231 cm^{-1} (vs); ν_{CN} 2142 cm^{-1} (m). UV−vis (ATR, cubic zirconia crystal, film cast from dichloromethane solution): $\lambda_{\max} = 568$ nm. Emission (thin film, $\lambda_{\mathrm{exc}} = 397.6$ nm) $\lambda_{\max} = 668$ nm. HRFAB-MS: (calculated) 532.1077; (found) 532.1066 (M + Na)$^+$.

Infrared Spectroscopy. Infrared spectra were obtained by the ATR (attenuated total reflectance) method using a Nicolet Magna-FTIR System 550 spectrometer. The sample films were deposited on a ZnSe trough HATR crystal purchased from PIKE Technologies. The films were cast from either CH_2Cl_2 or $CHCl_3$ solutions. Data were processed using OMNIC ESP v 4.1 software.

NMR Spectroscopy. NMR spectra were acquired on a Varian Inova 300 MHz spectrometer operating at 64.457 MHz for ^{195}Pt. The ^{195}Pt spectra were obtained at room temperature and externally referenced to K_2PtCl_4 in D_2O, δ −1624.0 ppm. A typical set of parameters for the ^{195}Pt experiments included: acquisition time = 0.164 s, relaxation delay = 0.300 s, sweep width = 400.0 kHz and a 45° pulse. The ^{1}H and ^{13}C spectra were obtained at room temperature using standard parameters and referenced to the residual protonated solvent peaks (CH_2Cl_2 ^{1}H 5.32 ppm; ^{13}C 54.0 ppm).

Visible Absorption Spectroscopy. Solid-state visible absorption spectra were acquired at room temperature using a modification of the apparatus reported by Drew, Mann, Marquardt, and Mann.[5] Thin

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(1) Buss, C. E.; Mann, K. R. *J. Am. Chem. Soc.* **2002**, *124,* 1031.

(2) (a) Nagel, C. C. U.S. Patent 4,834,909, 1989. (b) Mann, K. R.; Daws, C. A.; Exstrom, C. L.; Janzen, D. E.; Pomije, M. U.S. Patent 5,766,952, 1998.

(3) Selected sensor references: (a) Drew, S. M.; Janzen, D. E.; Mann, K. R. *Anal. Chem.* **2002**, *74*, 2547. (b) Albert, K. J.; Walt, D. R.; Gill, D. S.; Pearce, T. C. *Anal. Chem.* **2001**, *73*, 2501. (c) Rakow, N. A.; Suslick, K. S. *Nature* **2000**, *406*, 710. (d) Seker, F.; Meeker, K.; Kuech, T. F.; Ellis, A. B. *Chem. Rev.* **2000**, *100*, 2505. (e) Dickinson, T. A.; White, J.; Kauer, J. S.; Walt, D. R. *Nature* **1996**, *382*, 697. (f) Bohrer, F. I.; Sharoni, A.; Colesniuc, C.; Park, J.; Schuller, I. K.; Kummel, A. C.; Trogler, W. C. *J. Am. Chem. Soc.* **2007**, *129*, 5640. (g) Mansour, M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1998**, *120*, 1329. (h) Bailey, R. C.; Hupp, J. T. *J . Am. Chem. Soc*. **2002**, *124*, 6767. (i) Li, B.; Sauvé, G.; Iovu, M. C.; Jeffries-EL, M.; Zhang, R.; Cooper, J.; Santhanam, S.; Schultz, L.; Revelli, J. C.; Kusne, A. G.; Kowalewski, T.; Snyder, J. L.; Weiss, L. E.; Fedder, G. K.; McCullough, R. D.; Lambeth, D. N. *Nano Lett.* **2006**, *6,* 1598. Selected electronic device applications references: (j) Kunugi, Y.; Mann, K. R.; Miller, L. L.; Exstrom, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 589. (k) Kunugi, Y.; Miller, L. L.; Mann, K. R.; Pomije, M. K. *Chem. Mater.* **1998**, *10*, 1487. (l) Kunugi, Y.; Mann, K. R.; Miller, L. L.; Exstrom, C. L. U.S. Patent 6,160,267, 2000. (m) Kunugi, Y.; Mann, K. R.; Miller, L. L.; Pomije, M. K. U.S. Patent 6,137,118, 2000.

(4) A thorough search of the Cambridge Structural Database (CSD version 5.28, January 2007) reveals no examples of crystallographically characterized *trans*-Pt(isocyanide)$_2$(CN)$_2$ structures. (a) *trans*-Pt(isocyanide)$_2$-(CN)$_2$ isomers were reported based on KBr pellet IR spectra by Isci, H.; Mason, W. R. *Inorg. Chem.* **1975**, *14,* 913. (b) *trans*-Pt(CNCH$_3$)$_2$(CN)$_2$ isomer was detected by ^{195}Pt NMR but not isolated or otherwise characterized in a report by Martellaro, P. J.; Hurst, S. K.; Larson, R.; Abbott, E. H.; Peterson, E. S. *Inorg. Chim. Acta,* **2005**, *358*, 3377.

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10.1021/om7008167 CCC: $37.00

films of the samples were cast from either CH_2Cl_2, $CH_2Cl_2/CH_3CO_2C_2H_5$ or CH_2Cl_2/THF solutions and were deposited on a custom-built cubic zirconia trough HATR crystal. The spectrum was collected using an Ocean Optics S2000 spectrophotometer and corrected for ATR penetration depth effects.

Emission Spectroscopy and Solid-State Quantum Yields. The solid-state emission spectra were acquired using a modification of the apparatus described previously.[5] A bifurcated (six around one) fiber optic probe with an angle tip was used to bring light into and out of the sample. Spectra were corrected for detector response with an Ocean Optics CCD spectrophotometer that was calibrated with a standard light source. The raw intensity values at each wavelength were multiplied by the appropriate correction factor as determined with the standard lamp and then by λ^3 so that the resulting intensity units are proportional to photons/wavenumber.[6] For vapochromic studies, a thin film of the sample was deposited on the tip of a Delrin plug that was fitted into a sample compartment outfitted to accommodate VOC saturated vapors to flow over the film. A bifurcated fiber optic cable was used to excite the sample with an LED at $\lambda = 397.6$ nm and also to collect the spectrum using an Ocean Optics S2000 spectrophotometer. Solid-state quantum yields were obtained by a modification of the method described by Wrighton et al.[7] The diffuse reflectance was captured from a "perfectly" scattering surface to give (after integration and correction for instrument response) a quantity proportional to the incident light intensity (I_0, units of photons/wavenumber). The scatterer was then replaced with the sample and the emission from the sample (I_{emit}, the emitted light), and the remaining scattered intensity from the light source (I, the reduced light source intensity) were captured and corrected. These two measurements allow the solid-state emission quantum yield to be calculated from:

$$\phi = \frac{I_{\mathrm{emit}}}{I_0 - I}$$

For the studies presented here, we have decreased a major source of error in Wrighton's method by replacing the powdered MgO scatterer (which has a surface that is very difficult to reproduce) with a 1 × 1 cm piece of Fluorilon scattering target.[8] The Fluorilon target is a NIST standard of fused powdered Teflon with a greater than 99% scattering coefficient across the entire spectral region of interest (350−1000 nm). The procedure consists of measuring the diffuse reflectance of the Fluorilon target followed by rubbing the freshly grown crystals into the pores of the target with a metal spatula. The light (unabsorbed excitation beam and emission) from the target with the sample embedded in the surface is then collected, and the necessary calculations are carried out with an Excel spreadsheet.

X-Ray Structure Determination. A single-crystal X-ray structure was obtained for *trans*-Pt(*p*-CN$-C_6H_4-C_2H_5)_2(CN)_2$.[9] A red crystal (approximate dimensions 0.5 × 0.08 × 0.03 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART Platform CCD diffractometer for a data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 77 reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 10 s and a detector distance of 4.971 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.30° steps in ω at four different φ settings and a detector position of $-28°$ in 2θ. The intensity data were corrected for absorption and decay (SADABS).[10] Final cell constants were calculated from the *xyz* centroids of 899 strong reflections from the actual data collection after integration (SAINT).[11]

The structure was solved using SIR-97[12] and refined using SHELXL-97.[13] The space group *Pccn* was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated that provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed that located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least-squares refinement converged to $R_1 = 0.0407$ and $wR_2 = 0.1007$ (F^2, all data).

Results and Discussion

The neutral *trans*-Pt(*p*-CN$-C_6H_4-C_2H_5)_2(CN)_2$ (***trans*-PtC$_2$**) compound is synthesized in high yield by heating the isomeric double salt complex to reflux in chloroform. An FTIR spectroscopy study of the column chromatography fractions obtained from this reaction clearly illustrates that a minor byproduct (<10%) of the synthesis is the cis isomer.[1] The main product, a reddish-purple solid, was characterized by single-crystal X-ray diffraction, ^{1}H, ^{13}C, and ^{195}Pt NMR, ATR-FTIR, solid UV−visible absorption, and emission and high-resolution FAB mass spectroscopy methods. Solid samples of the trans isomer appear stable in the laboratory environment for at least 1 year based on infrared characterization;[14] thus, no special precautions were taken during these studies. Since we had samples of the previously characterized cis complex and now the trans isomer in hand, we set out to systematically compare first, their interconversion, and then their solution and solid-state properties.

We had already used the solid-state isomeric transformation of the double salt complexes of the form $[Pt(CNR)_4][Pt(CN)_4]$ by a bulk melting process[1] to produce the isomeric *cis*-Pt(CNR)$_2$(CN)$_2$, so we set out to determine whether the interconversion of the trans to cis neutral complex was possible. Heating a solid sample of pure ***trans*-PtC$_2$** under an active argon atmosphere to 200 °C in an oil bath for 20 min followed by slowly cooling to room temperature gives a deep-red solid. During this experiment, the solid never appears to melt but does become an orange-red color at approximately 160 °C. An infrared spectrum of the deep-red product confirms it is ***cis*-PtC$_2$.**[1] Conversion of ***cis*-PtC$_2$** back to ***trans*-PtC$_2$** was never observed in our hands.

A comparison of the IR spectra of ***cis*-PtC$_2$** and ***trans*-PtC$_2$** is shown in Figure 1. As expected, the ***cis*-PtC$_2$** displays two cyanide stretches at 2156 and 2150 cm^{-1} and two isocyanide

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[6] Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

[7] Wrighton, M. S.; Ginley, D. S.; Morse, D. L. *J. Phys. Chem.* **1974**, *78*, 2229.

[8] Avian Technolgies: Wilmington, OH; http://www.aviantechnologies.com/faq.html.

[9] Crystal data for ***trans*-PtC$_2$**: $C_{20}H_{18}N_4Pt$, orthorhombic, space group *Pccn*, $a = 14.729(4)$ Å, $b = 20.074(5)$ Å, $c = 6.2507(16)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1848.2(8)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.831$ mg/m^3, $m = 7.601$ mm^{-1}, final *R* indices [$I > 2\sigma(I)$], $R1 = 0.0407$, $wR2 = 0.0944$, *R* indices (all data), $R1 = 0.0616$, $wR2 = 0.1007$.

[10] (a) *SADABS*, v. 2.03; Sheldrick, G., 2002. (b) Blessing, R. *Acta Cryst.* **1995**, *A51*, 33.

[11] *SAINT*, v. 6.2; Bruker Analytical X-ray Systems: Madison, WI, 2001.

[12] SIR97 - Altomare A.; Burla M. C.; Camalli M.; Cascarano G. L.; Giacovazzo C.; Guagliardi A.; Moliterni A. G. G.; Polidori G.; Spagna R. *J. Appl. Cryst*. **1999**, *32*, 115.

[13] *SHELXTL*, v. 6.10; Bruker Analytical X-ray Systems: Madison, WI, 2000.

[14] A film cast from a chloroform solution containing a 13 month-old solid sample of ***trans*-PtC$_2$** (used previously to acquire the NMR data) was analyzed by FTIR and found to contain only ***trans*-PtC$_2$**.

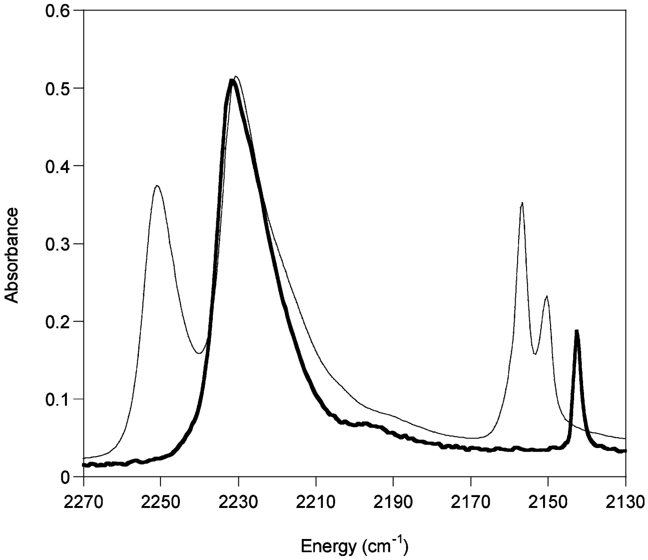

Figure 1. Solid-state ATR-IR spectra of ***cis*-PtC$_2$** (light line) and ***trans*-PtC$_2$** (bold line).

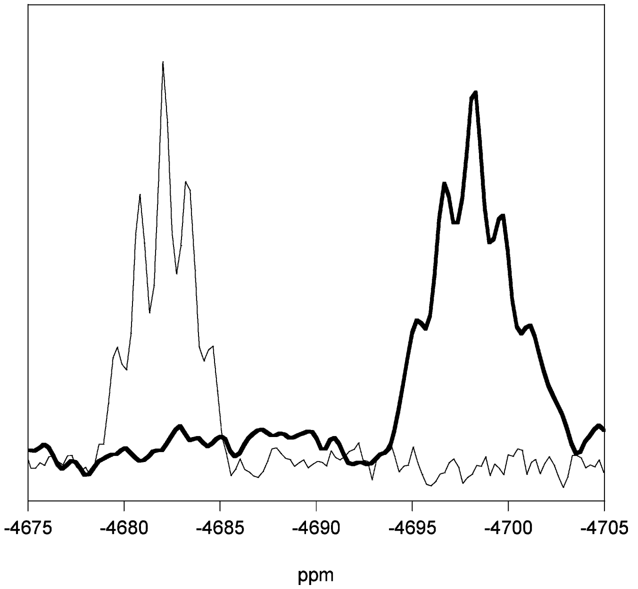

Figure 2. ^{195}Pt NMR spectra of ***cis*-PtC$_2$** (light line) and ***trans*-PtC$_2$** (bold line) (64.5 MHz, 298 K, CD$_2$Cl$_2$).

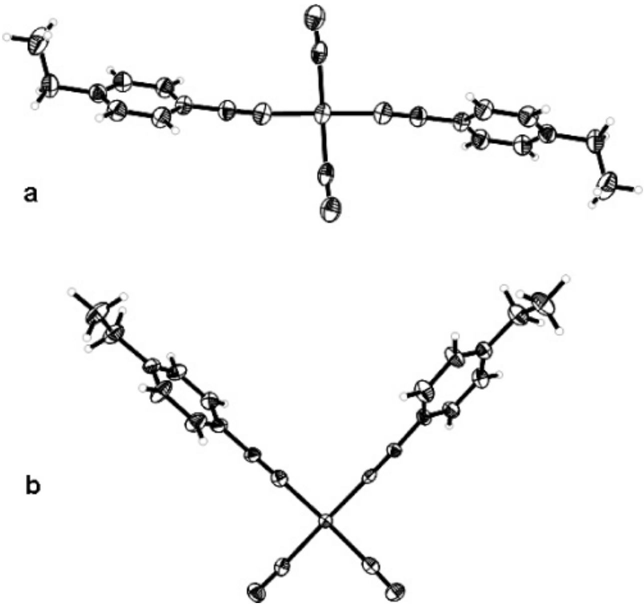

Figure 3. ORTEP diagrams (50% ellipsoids) of (a) ***trans*-PtC$_2$** and (b) ***cis*-PtC$_2$**.

stretches at 2230 and 2251 cm^{-1}. This is consistent with the cis arrangement (local C_{2v} symmetry) of the cyanide ligands and the isocyanide ligands, resulting in two IR active stretches of each type. The ***trans*-PtC$_2$** (local D_{2h} symmetry) displays one cyanide stretch at 2142 cm^{-1} and one isocyanide stretch at 2231 cm^{-1}. This is consistent with the trans arrangement of the cyanide ligands and isocyanide ligands, resulting in one IR active stretch of each type.

We also characterized ***trans*-PtC$_2$** in solution with ^{1}H and ^{13}C NMR spectroscopy. Not surprisingly, the respective spectra of ***trans*-PtC$_2$** and ***cis*-PtC$_2$**, acquired under identical conditions, give nearly identical chemical shifts for the proton and carbon nuclei.[15] The most notable difference is in the observed coupling between the ^{195}Pt and the ^{13}C nuclei of the cyanide ligand (***trans*-PtC$_2$**: $J_{^{195}\mathrm{Pt}-^{13}\mathrm{C}} = 490$ Hz versus ***cis*-PtC$_2$**: $J_{^{195}\mathrm{Pt}-^{13}\mathrm{C}} = 560$ Hz). The similarity of the respective ^{1}H and ^{13}C NMR spectra is not entirely surprising due to the remoteness of these nuclei from the ^{195}Pt. However, the ^{195}Pt NMR spectra exhibit differences because of the significant differences in the Pt-ligand bonding in the two isomers. The ^{195}Pt spectra in Figure 2 illustrate not only different chemical shifts (***trans*-PtC$_2$**: $\delta = -4698$ ppm versus ***cis*-PtC$_2$**: $\delta = -4682$ ppm) but also different ^{195}Pt$-$^{14}N coupling constants (***trans*-PtC$_2$**: $J_{^{195}\mathrm{Pt}-^{14}\mathrm{N}} = 94$ Hz versus ***cis*-PtC$_2$**: $J_{^{195}\mathrm{Pt}-^{14}\mathrm{N}} = 80$ Hz).[16]

Although the solution properties of the cis and trans isomers show small differences in the ligand environment, they hint that larger differences are present in the electronic environment at the platinum center. These electronic differences at the metal lead to large spectroscopic differences, as a consequence of the structural and packing differences of the cis and trans isomers in the solid state.

We were fortunate to obtain X-ray quality single crystals of ***trans*-PtC$_2$** grown by evaporation of a dichloromethane solution. As can be seen from Figure 3a, the molecular structure consists of a neutral square planar Pt atom coordinated to two cyanide ligands and two *p*-CN$-$C$_6$H$_4$$-C_2H_5$ ligands. The ligands of the same types are oriented in a trans fashion, which is unprecedented for compounds of the general type Pt(CNR)$_2$(CN)$_2$.[4] The packing consists of columns of stacked planar neutral molecules with only one Pt$-$Pt distance (3.1253(8) Å) within a stack, which corresponds to half of the unit cell *c*-axis length. Interestingly, a short intermolecular $\pi-\pi$ distance of 3.36 Å between the phenyl rings of independent platinum stacks is present (Figure S1, Supporting Information). This intermolecular $\pi-\pi$ interaction between the phenyl rings occurs in sheets perpendicular to the stacking axis and forms a second dimensional interaction network throughout the structure (Figure S2, Supporting Information). No solvent molecules or disorder are present in the structure.

A structural comparison between ***trans*-PtC$_2$** and ***cis*-PtC$_2$** illustrates many interesting differences. As noted previously,[1]

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(15) NMR data for ***cis*-PtC$_2$**: ^{1}H NMR (300 MHz, rt, CD$_2$Cl$_2$): δ 7.52 (d, $J = 8.4$ Hz, 2 H, Ph), 7.36 (d, $J = 8.4$ Hz, 2 H, Ph), 2.74 (q, $J = 7.6$ Hz, 2 H, CH$_2$), 1.25 ($J = 7.6$ Hz, 3 H, CH$_3$). ^{13}C NMR (75 MHz, rt, CD$_2$Cl$_2$): δ 149.5 (isocyanide; Ph), 129.8 (isocyanide; Ph), 127.6 (isocyanide; Ph), 123.3 (isocyanide; Ph), 110.7 (m, $J_{^{195}\mathrm{Pt}-^{13}\mathrm{C}} = 560$ Hz, cyanide ligand), 29.3 (isocyanide; *C*H$_2$), 15.4 (isocyanide; *C*H$_3$). ^{195}Pt NMR (64.5 MHz, rt, CD$_2$Cl$_2$, external reference K$_2$PtCl$_4$ in D$_2$O, δ -1624): δ -4682 (m, $J_{^{195}\mathrm{Pt}-^{14}\mathrm{N}} = 80$ Hz).

(16) A ^{195}Pt$-$^{14}N ^2J coupling constant for the compound *cis*-Pt(CN)$_2$(CNCH$_3$)$_2$ is reported as 80 Hz. Martellaro, P. J.; Hurst, S. K.; Larson, R.; Abbott, E. H.; Peterson, E. S. *Inorg. Chim. Acta*, **2005**, *358*, 3377.

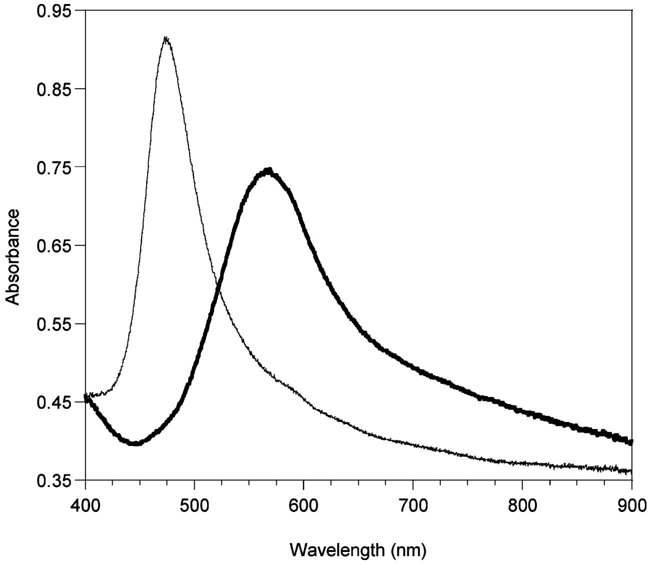

Figure 4. Solid-state absorbance spectra of ***cis*-PtC$_2$** (light line) and ***trans*-PtC$_2$** (bold line) (298 K, ATR corrected).

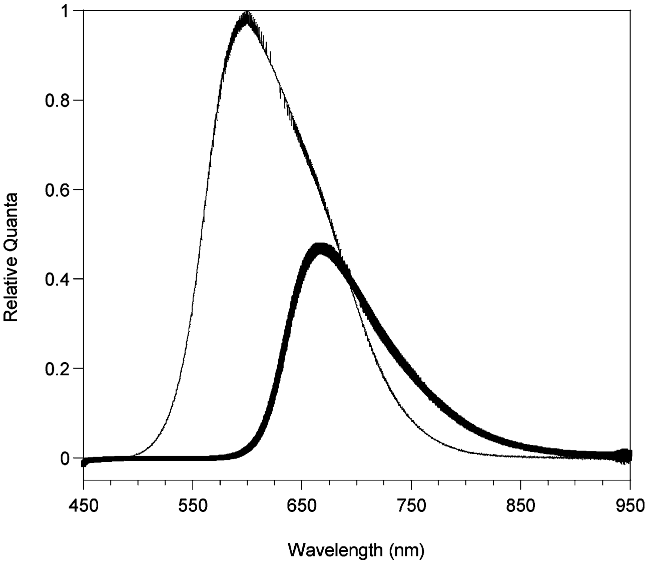

Figure 5. Solid-state emission spectra of ***cis*-PtC$_2$** (light line) and ***trans*-PtC$_2$** (bold line) (298 K, λ_{exc} = 397.6 nm, corrected for detector response).

we also have two crystal structures of solvates of the orange morph of ***cis*-PtC$_2$**, ***cis*-PtC$_2$**·0.5(toluene), and ***cis*-PtC$_2$**·*x*(hexanes). In both cis isomer structures, the ***cis*-PtC$_2$** molecules stack in one-dimensional columns. However, the ***cis*-PtC$_2$** structures have two different Pt−Pt distances alternating between a "long" and "short" distance. For ***cis*-PtC$_2$**·0.5(toluene), these distances are 3.281 and 3.300 Å with an average of 3.2905(2) Å, whereas for ***cis*-PtC$_2$**·*x*(hexanes), these distances are 3.278 and 3.296 Å with an average of 3.287(2) Å. Notably, all of these Pt−Pt distances are longer than the 3.1253(8) Å distance in ***trans*-PtC$_2$**. The 3.1253(8) Å distance in ***trans*-PtC$_2$** is one of the shortest that we have characterized in our vapochromic materials.[1,17]

The significant differences in the Pt−Pt distances give rise to large electronic differences in these solid-state materials. The solid-state absorption spectra of the cis and trans isomers are shown in Figure 4. The cis isomer shows a strong absorption at 476 nm, whereas the trans isomer absorbs at 568 nm, consistent with a considerably shorter Pt−Pt distance in the trans isomer.[18] Both compounds also exhibit strong solid-state luminescence at room temperature (Figure 5). Consistent with the absorption spectra, the cis isomer emits at higher energy (601 nm) than the trans isomer (647 nm). We also measured the absolute solid-state luminescence quantum yield for the cis and trans isomers to be 0.45 and 0.21, respectively, under a nitrogen atmosphere.

To assess the vapochromic potential of ***trans*-PtC$_2$**, we conducted several series of emission experiments exposing films of ***trans*-PtC$_2$** to various vapor-phase VOCs such as acetone, chloroform, methanol, and toluene. In each experiment, the emission spectra show large, irreversible changes in the intensity and the crude shape of the emission band. However, the spectra also clearly show that λ_{max} is barely affected by VOC exposure. Further, we were not able to reproduce the original film spectrum intensity after repeated exposure to VOCs. These observations are consistent with partial dissolution of the film followed by recasting rather than a"true" vapochromic response. We concluded from these experiments that ***trans*-PtC$_2$** does not exhibit vapoluminescent behavior. This conclusion is in direct contrast to ***cis*-PtC$_2$**, which exhibits vapoluminescent behavior with a variety of aromatic VOCs as well as ethanol.[1]

These large isomeric differences in solid-state vapoluminescent behavior led us to examine the packing differences of the cis and trans isomers more carefully. A unique feature of ***trans*-PtC$_2$** is the presence of the intermolecular $\pi-\pi$ interactions between isocyanide ligands of different stacks; neither ***cis*-PtC$_2$**·0.5(toluene) nor ***cis*-PtC$_2$**·*x*(hexanes) have interactions of this type. The short intermolecular $\pi-\pi$ interactions between the isocyanide ligands give rise to a second-dimensional ordering of the Pt−Pt stacks for ***trans*-PtC$_2$**. We believe this combination of packing forces (Pt−Pt stacking as well as intermolecular $\pi-\pi$ interactions) gives rise to a relatively close-packed structure. Comparison of the overall packing efficiency of each using the Kitaigorodskii packing coefficients[19] illustrates that ***trans*-PtC$_2$** (0.678) packs significantly more efficiently than ***cis*-PtC$_2$** (0.620).

A comparison of space-filling representations for the packing of these structures is shown in Figure 6. This figure illustrates that the geometric isomerization leads to large differences in the molecular shape, which in turn results in completely different packing. In the ***trans*-PtC$_2$** packing view shown in Figure 6a, the lack of voids or channels is clearly evident, whereas in the ***cis*-PtC$_2$** packing view in shown Figure 6b, the presence of the channels is equally apparent. We believe that the voids and channels found in ***cis*-PtC$_2$** and in other vapochromic compounds play a fundamental role in facilitating the vapochromic response. We also believe the two-dimensional packing motif is a strong factor contributing to the lack of vapochromic behavior of ***trans*-PtC$_2$**.

In summary, we have synthesized and characterized the trans isomer of Pt(p-CN−C_6H_4−C_2H_5)$_2$(CN)$_2$ and compared it with the cis analog. Our comparisons illustrate how the geometric isomerization leads to minor changes in the ligand environment

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[17] (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. (b) Buss, C. E. Ph.D. Dissertation, University of Minnesota, Minneapolis, MN, 2002. (c) Anderson, C. E. MS Dissertation, University of Minnesota, Minneapolis, MN 1997.

[18] Gliemann, G.; Yersin, H. *Struct. Bonding* **1985**, 62, 87 and references therein.

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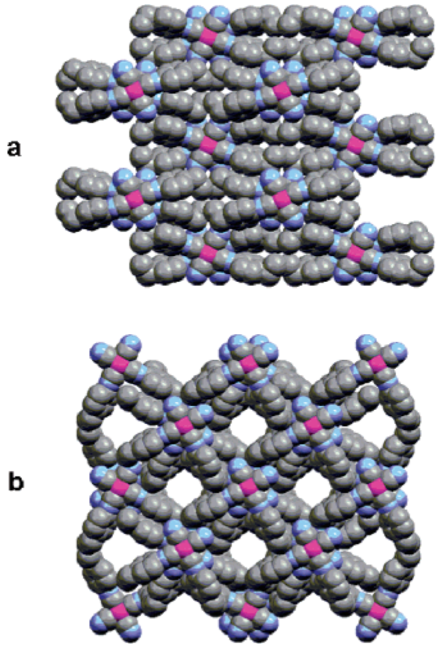

Figure 6. Solid-state packing diagrams of (a) ***trans*-PtC$_2$** and (b) ***cis*-PtC$_2$** (view parallel to the Pt−Pt stacking axis).

in solution but results in large changes in the solid-state packing. The solid-state packing differences influence the solid-state electronic properties, which are dominated by intermolecular interactions. We believe that ***trans*-PtC$_2$** does not exhibit vapochromic behavior due to a unique combination of factors. The efficient packing and short $\pi-\pi$ interactions between isocyanide ligands of ***trans*-PtC$_2$** precludes channels or voids for VOC sorption and disfavors reorganization of the structure to accommodate VOCs with concomitant modulation of the Pt−Pt interactions.[17a]

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Supporting Information Available: Additional crystallographic figures for ***trans*-PtC$_2$** and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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