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Selection and Discovery of Polymorphs of Platinum Complexes Facilitated by Polymer-Induced Heteronucleation

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Polymer-induced heteronucleation was utilized for the selective crystallization of the color polymorphic platinum complexes $Pt(bpy)Cl_2$ and $Pt(phen)Cl_2$. Crystal structures of two polymorphs of $Pt(phen)Cl_2$ were determined and reveal that, as in the case of $Pt(bpy)Cl_2$, this compound has one form with Pt⋯Pt interactions (orange crystals) and another lacking these contacts (yellow crystals). Free energy measurements reveal that the polymorphs of $Pt(bpy)Cl_2$ and $Pt(phen)Cl_2$ without Pt⋯Pt interactions are more stable in both cases by 0.67(2) and 0.53(1) kJ/mol, respectively, and this finding is consistent with the principle of close packing. Furthermore, a search of the Cambridge Structural Database reveals that, for polymorphic platinum complexes, shorter intermolecular Pt⋯Pt interactions generally result in less dense structures.

Introduction

Polymorphism, the existence of a substance as two or more crystalline phases that differ solely in arrangements and/or conformations of the molecules in the crystal lattice, exerts a profound effect on the properties of materials.[1,2] The vast majority of polymorphism investigations have been conducted on pharmaceuticals because of the potential for bioavailability to vary based on crystalline form and the resultant quality control and intellectual property rights issues.[2,3] Pigments[4] and explosives are two other classes of compounds much investigated because of the profound effect that polymorphism can have on their properties, and certainly the phenomenon of polymorphism touches on a variety of other compound classes; platinum complexes often crystallize as multiple crystal phases, both polymorphs and solvates, that show striking color differences among forms and have potential applications as photosensitizers,[5] vapor sensors,[6−8] and antimalarial agents.[9] The prototypical example $Pt(bpy)Cl_2$ (bpy = 2,2′-bipyridine) has yellow and red polymorphs (designated here as forms I and II, respectively) that have been studied for decades.[10] Both crystal structures have been determined by single-crystal X-ray diffraction on crystals grown from various solvents,[11,12] and thorough studies in the literature have related the color properties of these two polymorphs to the absence or presence of Pt⋯Pt interactions in the solid state.[5,13−16]

Structural data from single crystals of platinum complexes allow the examination of the close connection between solid-state packing and properties. Traditional methods of crystallization, which include changing solvent, temperature, and concentration conditions, often do not lead to crystals suitable

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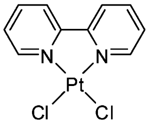
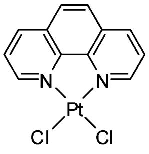
for structure determination. However, it has been shown that polymer-induced heteronucleation facilitates the production of single crystals.[17−19] This approach is also successful at selectively producing known and new crystal phases of several small organic molecules and extended networks, based on the polymer employed, making it amenable for polymorph selection and discovery for the model Pt(diimine)-Cl_2 system. Additionally, for the most insoluble complexes investigated here, one can pick a single solvent and simply vary the polymer heteronucleant to gain diversity during crystallization and selectively produce the desired phase as a high quality single crystal.

Experimental Section

Cross-linked Polymer Synthesis. Polymer libraries were synthesized in 96-well polypropylene microtiter plates by a previously published procedure.[17] Briefly, six 1:1 (v/v) monomer solutions in ethanol were dispensed as 90 pairwise combinations and six pure monomer solutions by a Gilson 215 liquid handler to a volume of 100 μL. To each of these 96 solutions was added 50 μL of a 1:1 (v/v) solution of divinylbenzene (DVB) in ethanol containing 2 mol % 2,2′-azobisisobutyronitrile (AIBN) with respect to DVB. The solutions were photopolymerized in a nitrogen gas atmosphere and then annealed at 85 °C under vacuum to yield cross-linked polymer libraries. The components used to build the libraries are as follows. Library A: 4-acetoxystyrene (AOS), *n*-butyl methacrylate (*n*-BuMA), *tert*-butyl methacrylate (*t*-BuMA), benzyl methacrylate (BzMA), methyl methacrylate (MMA), and styrene (STY) with DVB. Library B: 2-vinylpyridine (2VP), 4-vinylpyridine (4VP), 2-dimethylaminoethyl methacrylate (DMAEMA), *N,N*-dimethylmethacrylamide (DMMAA), *N*-methacryloylmorpholine (MAM), and methacrylonitrile (MAN) with DVB. Library C: acrylic acid (AA), 2-ethoxyethyl methacrylate (EEMA), ethylene glycol methacrylate phosphate (EGMAP), 2-hydroxyethyl methacrylate (HEMA), methacrylic acid (MAA), and methyl methacrylate (MMA) with DVB.

Syntheses. Pt(bpy)Cl_2 was prepared by the literature procedure.[9] Pt(phen)Cl_2 (phen = 1,10-phenanthroline) was synthesized by the same general method, substituting phen for bpy.


Pt(bpy)Cl_2


Pt(phen)Cl_2

Crystallization of Pt(bpy)Cl_2 and Pt(phen)Cl_2. Pt(bpy)Cl_2 (50 mg) was dissolved in dimethyl sulfoxide (DMSO; 10 mL), and the entire solution was dispensed evenly among the 96 wells of each microtiter plate containing cross-linked polymers. Heating at 90 °C overnight led to evaporation of the solvent and the formation of crystals. Pt(bpy)Cl_2 was redissolved by the addition of DMSO (10 mL) evenly among the 96 wells of each plate for an additional two trials to gauge reproducibility. Pt(phen)Cl_2 (25 mg) was dissolved in warm DMSO (20 mL). The entire solution was dispensed, and the solvent was evaporated as described above. Three separate trials were performed to determine reproducibility.

Raman Spectroscopy. Raman spectra were obtained using a Renishaw inVia Raman Microscope equipped with a Leica microscope, RenCam CCD detector, 785 nm diode laser, 1200 lines/mm grating, and 50 μm slit. Spectra were collected in extended scan mode in the range of 100−3200 cm^{-1} and analyzed using the WiRE 2.0 software package. Calibration was performed using a silicon standard. Pt(bpy)Cl_2 form I: 154, 176, 200, 260, 271, 295, 336, 345, 386, 416, 430, 456, 488, 456, 648, 657, 675, 720, 767, 798, 1028, 1046, 1060, 1112, 1163, 1178, 1243, 1270, 1286, 1324, 1346, 1499, 1563, 1606 cm^{-1}. Pt(bpy)Cl_2 form II: 175, 198, 213, 258, 270, 295, 335, 387, 431, 647, 657, 676, 772, 790, 899, 1030, 1046, 1057, 1075, 1119, 1165, 1269, 1281, 1293, 1329, 1503, 1563, 1614 cm^{-1}. Pt(phen)Cl_2 form I: 132, 147, 172, 191, 216, 259, 288, 322, 338, 354, 431, 444, 504, 512, 549, 567, 612, 658, 728, 751, 781, 797, 823, 852, 887, 928, 950, 960, 1038, 1056, 1094, 1115, 1143, 1154, 1207, 1224, 1252, 1310, 1322, 1340, 1349, 1411, 1435, 1457, 1517, 1582, 1608, 1629, 1639, 2147 cm^{-1}. Pt(phen)Cl_2 form II: 154, 180, 203, 218, 255, 287, 347, 399, 442, 461, 473, 501, 512, 551, 565, 660, 728, 752, 886, 929, 1040, 1061, 1151, 1209, 1229, 1255, 1309, 1347, 1435, 1460, 1523, 1584, 1608, 1632, 1642, 2132, 2145 cm^{-1}.

Thermomicroscopy. Samples were heated using a Mettler Toledo FP82HT hot stage connected to a FP90 control processor and viewed under a Leica DMLP microscope, which was equipped with crossed polarizers. Heating rates were typically between 1.0 and 5.0 °C/min.

Powder X-ray Diffraction. Powder X-ray diffraction (PXRD) data were collected at ambient temperature on ground powders using a Bruker AXS D8 Advance powder diffractometer equipped with a Cu Kα source (λ = 1.5406 Å) and scintillation detector. Pt(bpy)-Cl_2 form I: d = 9.056 (1.8), 8.698 (1.6), 7.852 (100), 5.939 (1.2), 5.394 (6.3), 4.548 (24.7), 3.941 (4.3), 3.880 (4.7), 3.713 (1.2), 3.616 (1.1), 3.547 (1.1), 3.482 (4.9), 3.361 (2.7), 3.038 (2.1), 2.982 (10.3), 2.768 (5.1), 2.630 (5.1), 2.479 (3.2), 2.326 (1.2), 2.280 (8.2), 2.189 (7.0), 2.101 (4.9), 1.909 (2.4) Å (I/I_0). Pt(bpy)Cl_2 form II: d = 8.785 (48.4), 8.036 (100), 4.927 (21.9), 4.401 (4.6), 4.030 (18.7), 3.990 (3.9), 3.764 (5.1), 3.466 (5.1), 3.394 (82.0), 3.285 (7.7), 3.166 (28.2), 3.129 (25.2), 2.796 (12.2), 2.688 (9.9), 2.598 (5.8), 2.499 (6.3), 2.467 (6.8), 2.428 (4.7), 2.361 (3.7), 2.314 (6.2), 2.295 (9.0), 2.175 (3.8), 2.108 (2.7), 1.997 (4.9), 1.975 (4.5), 1.934 (2.8), 1.903 (5.0) Å (I/I_0). Pt(phen)Cl_2 form I: d = 8.428 (12.0), 7.880 (100), 5.326 (1.3), 5.211 (1.8), 4.787 (3.8), 4.480 (12.0), 4.338 (10.6), 4.247 (6.8), 3.844 (1.7), 3.633 (1.7), 3.582 (1.6), 3.529 (1.4), 3.255 (1.3), 3.183 (4.0), 3.066 (1.8), 2.998 (2.0), 2.954 (4.8), 2.841 (3.6), 2.716 (1.6), 2.439 (2.2), 2.406 (3.3), 2.353 (3.0), 2.260 (4.8), 2.234 (3.2), 2.033 (2.5) Å (I/I_0). Pt(phen)Cl_2 form II: d = 9.129 (100), 8.217 (70.9), 6.468 (10.2), 5.075 (28.2), 4.569 (15.5), 4.459 (11.8), 4.096 (7.3), 3.672 (12.6), 3.524 (8.0), 3.475 (16.8), 3.394 (39.6), 3.250 (19.4), 3.202 (13.3), 3.058 (28.6), 2.901 (6.0), 2.861 (7.0), 2.740 (9.2), 2.646 (5.2), 2.539 (6.4), 2.523 (12.3), 2.287 (8.1), 2.228 (9.2), 2.157 (7.6), 2.051 (6.8), 1.903 (6.6) Å (I/I_0).

Single-Crystal X-ray Diffraction. Single-crystal X-ray diffraction data were recorded on a Bruker SMART 1K CCD-based X-ray diffractometer equipped with an LT-2 low-temperature device and a normal focus Mo-target X-ray tube (λ = 0.71073 Å) operated at 2000 W power (50 kV, 40 mA). The data were corrected for absorption, and the structures were solved and refined using the Bruker SHELXTL software package (version 6.12). All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated at idealized positions and refined as riding atoms with individual isotropic displacement parameters.

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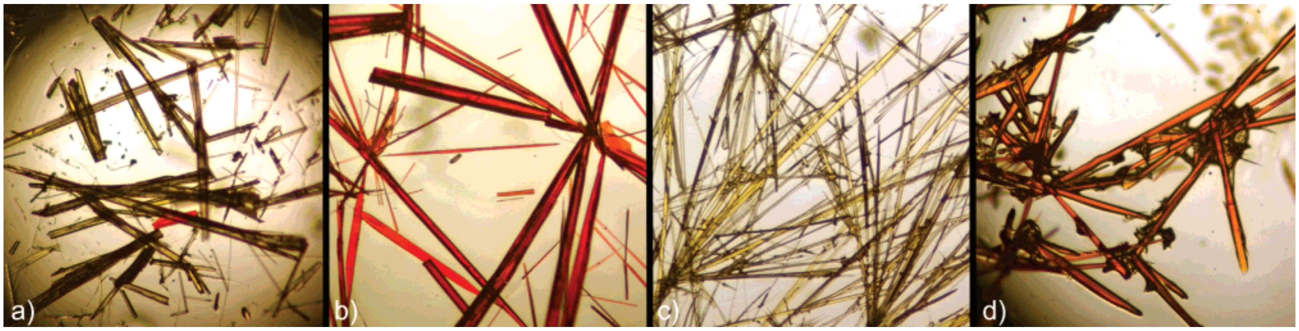

Figure 1. Photomicrographs of Pt(bpy)Cl_2 and Pt(phen)Cl_2 polymorphs grown in the presence of cross-linked polymers: (a) Pt(bpy)Cl_2 form I (2VP/DMMAA/DVB terpolymer), (b) Pt(bpy)Cl_2 form II (AOS/*n*-BuMA/DVB terpolymer), (c) Pt(phen)Cl_2 form I (MMA/STY/DVB terpolymer), and (d) Pt(phen)Cl_2 form II (AOS/MMA/DVB terpolymer).

Equilibrium Solubility Experiments. UV−vis spectra of saturated solutions of Pt(bpy)Cl_2 and Pt(phen)Cl_2 polymorphs were recorded on a Cary Bio 300 UV−visible spectrophotometer. Saturated solutions of Pt(bpy)Cl_2 polymorphs were prepared by stirring in ethyl acetate for several days, while saturated solutions of Pt(phen)Cl_2 polymorphs were prepared by stirring in tetrahydrofuran for several days. Optical and Raman microscopy confirmed the polymorphic identity of the residual solid in each vial, indicating that no transformation to another crystal form occurred during the experiment.

Results and Discussion

Pt(bpy)Cl_2. The dimorphic complex Pt(bpy)Cl_2 was chosen to explore the ability of insoluble polymers to selectively produce forms I (yellow) and II (red). Cross-linked polymers were chosen such that solvent from which crystal growth takes place does not dissolve the polymer; this ensures a heteronucleation process. When crystallization was carried out by evaporation of DMSO solutions at 90 °C in the absence of added polymers, forms I and II were found to crystallize in approximately equal amounts. Both concomitant formation and pure phases of both forms were observed in the 96 control crystallizations. However, selective crystallization of Pt(bpy)Cl_2 polymorphs was achieved in the presence of cross-linked polymer libraries (Figure 1a and b). For example, from the 192 polymers in the aryl/nonpolar library A and the nitrogen-containing library B, a greater than 5:1 majority of the less thermodynamically stable (vide infra) form II was produced. When incorporated into the cross-linked polymers, certain monomers had a high propensity for facilitating the production of form II, with occurrence rates of at least 90% of observed crystalline material over all trials. These include the aryl monomers 4VP, STY, and AOS, the amides DMMAA and MAM, the aliphatic-substituted methacrylates MMA and *t*-BuMA, and the amino-substituted methacrylate DMAEMA. Furthermore, all 12 combinations of cross-linked polymers containing 4VP/MAM and 4VP/MAN yielded 100% of form II over all trials, indicating a very strong selectivity for this polymorph by these aryl/nitrogen-containing functionalities. The only polymers that had a significantly higher selectivity for form I versus the control experiment contained the highly polar and acidic monomer EGMAP. However, several polymers containing this monomer did not yield well-formed crystals.

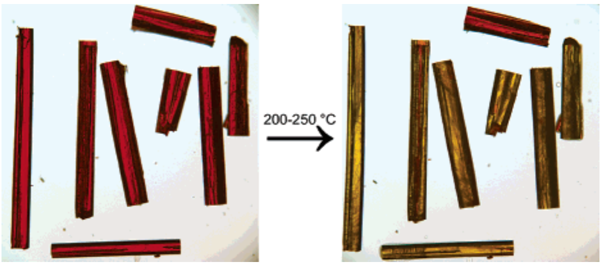

Figure 2. Photomicrograph of the transformation of Pt(bpy)Cl_2 form II to form I between 200 and 250 °C.

Each polymorph was subjected to analysis by Raman spectroscopy, PXRD, and thermomicroscopy. Raman spectra and PXRD data, which are in excellent agreement with the predicted patterns from single-crystal structures, show several characteristic differences between forms (see Experimental Section). Thermomicroscopy experiments revealed an irreversible nearly single crystal-to-single crystal transformation of form II to form I from ∼200 to 250 °C (Figure 2). However, not all form II crystals transform after holding at 250 °C for 5 h, with mechanical contact at this temperature, or with additional heating to 350 °C. Though this peculiar behavior is consistently observed, it can be said that form I is more stable than form II above 200 °C. To better understand the thermodynamic relationship between forms at room temperature, forms I and II were stirred as a slurry in CH_2Cl_2. This resulted in a complete conversion to yellow form I crystals after 1 h, signaling that form I is also more stable than form II at room temperature. Equilibrium solubility experiments revealed that form II is 30% more soluble than form I at 299 K, and from these measurements a difference in free energy of 0.67(2) kJ/mol between the two polymorphs can be derived.[20] This also corresponds to the stability relationship predicted from the principle of close packing[21,22] because the room-temperature densities of forms I and II are 2.61 and 2.56 g/cm^3, respectively.[11,12] A distinguishing feature in the packing between polymorphs is a lengthy Pt···Pt distance of 4.52 Å for form I, which is

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(20) The difference in free energy was calculated from UV−visible absorbance by the equation $\Delta G = RT \ln K$, with K = (abs form I)/(abs form II). The free energy difference was calculated for the absorption at 286 nm for Pt(bpy)Cl_2 and at 262 nm for Pt(phen)Cl_2.

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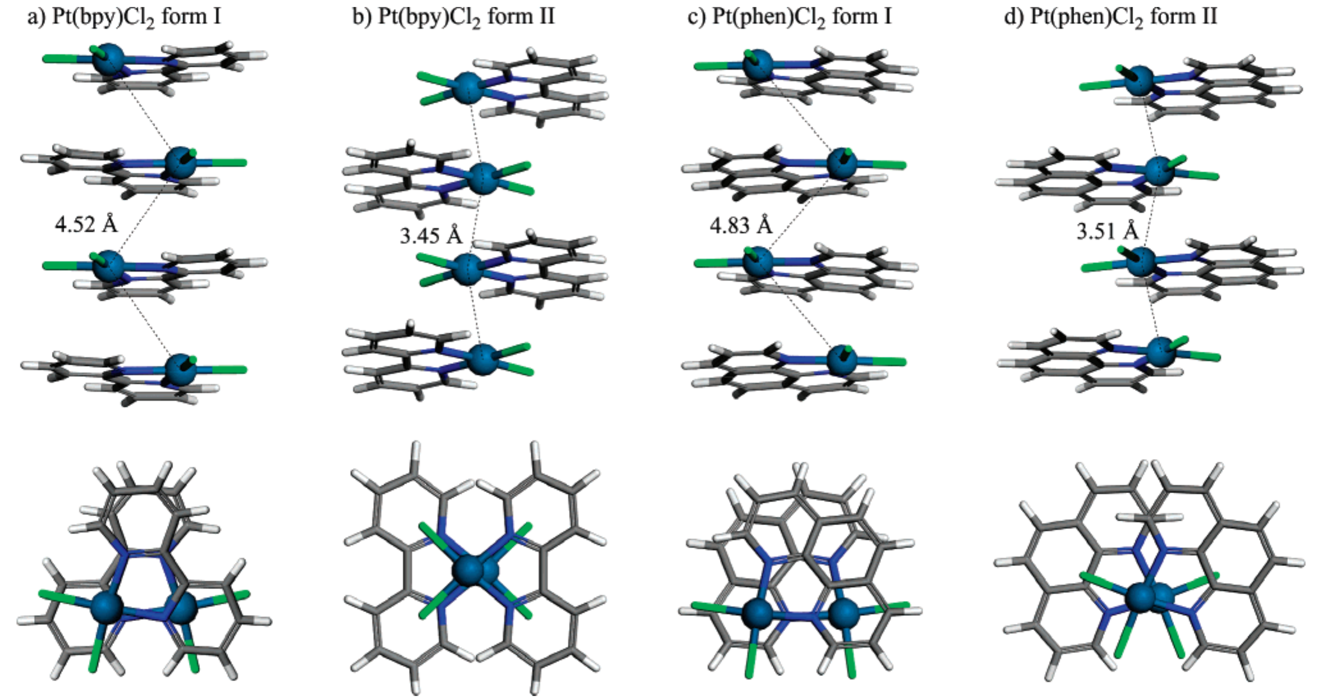

Figure 3. Packing diagrams showing the Pt···Pt distances for the polymorphs of Pt(bpy)Cl$_2$ and Pt(phen)Cl$_2$.

reduced to 3.45 Å in form II (Figure 3). Thus, the small energy difference between forms indicates that the molecules can pack with intermolecular Pt···Pt interactions, but this stronger interaction[23] occurs at the expense of the van der Waals interactions in the less closely packed structure that make the overall crystal higher in energy.

Pt(phen)Cl$_2$. Having demonstrated that polymer libraries affect selective polymorph production of platinum complexes with the Pt(bpy)Cl$_2$ system, Pt(phen)Cl$_2$ was investigated with the aim of producing new polymorphs and obtaining crystal structures of this compound whose solid-state structure has eluded researchers. Suitable crystals of this compound were not obtained from supersaturated solutions in DMSO in glass vials or by evaporation of DMSO solutions at 90 °C in polypropylene microtiter plates in the absence of added polymers. In both cases, the result was very fine yellow needles (form I) that are essentially identical to those that precipitate during the synthesis of the material. However, cross-linked polymer libraries facilitated the growth of single crystals suitable for X-ray diffraction studies upon evaporation of DMSO solutions (Figure 1c). This revealed a monoclinic unit cell (Table 1) consisting of columnar stacks of nearly planar Pt(phen)Cl$_2$ molecules related by a glide plane with a distance of 3.50 Å between molecular planes and a close C···C contact distance of 3.30 Å. However, the closest Pt···Pt distance, similar to the case of form I of Pt(bpy)Cl$_2$, is a distant 4.83 Å (Figure 3). The other close interactions are two C−H···Cl contacts which connect adjacent columns at 2.69 and 2.82 Å.[24]

Table 1. Crystallographic Information for Forms I and II of Pt(phen)Cl$_2$

	form I	form II
color	yellow	orange
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$Pca2_1$
temp	293(2)	123(2)
a (Å)	9.602(10)	18.257(10)
b (Å)	17.119(5)	9.167(5)
c (Å)	7.339(5)	6.866(4)
α (deg)	90	90
β (deg)	109.437(13)	90
γ (deg)	90	90
Z	4	4
V (Å^3)	1137.6(15)	1149.0(10)
ρ (g/cm^3)	2.605	2.579
data/parameters/restraints	5508/156/0	3185/159/1
R_1	0.0358	0.0251
wR^2	0.0827	0.0561

In addition to form I, an orange crystal form (form II), not reported in the previous investigations of this compound, was observed to grow in the presence of several polymers (Figure 1d), with the highest selectivity from polymers containing the relatively polar monomers EGMAP and MMA. The production of form II was successfully scaled up by crystallization employing MMA/AOS/DVB cross-linked polymers, a composition identified during initial screening experiments, to afford sufficient material for bulk characterization. Form II not only differs in color from form I, but it also has a characteristic PXRD pattern and Raman spectrum (see Experimental Section). Single crystals of form II were also obtained from several different cross-linked polymers, and the structure was determined by X-ray diffraction (Table 1). Similar to form I, the structure of form II consists of columns of alternating Pt(phen)Cl$_2$ molecules related by a glide plane. The interplanar spacing between the nearly planar molecules is 3.36 Å, and there is a single

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(23) DFT calculations predict a ~4 kcal/mol stability gain for the Pt···Pt dimer of platinum biphenyl dicarbonyl. Stoyanov, S. R.; Villegas, J. M.; Rillema, D. P. *Inorg. Chem.* **2003**, *42*, 7852−7860.

(24) All carbon−hydrogen bonds were normalized to 1.083 Å for measuring close contacts. For van der Waals radii, see: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

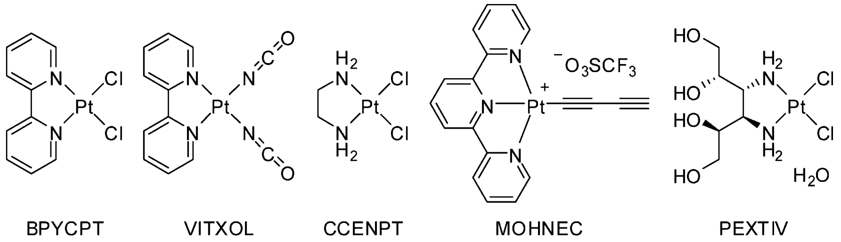

Figure 4. Structure and REFCODE of the five platinum complexes currently in the CSD with more than one structure and an intermolecular Pt···Pt distance of <3.5 Å for at least one polymorph.

close C···C contact of 3.40 Å and two close C···Cl contacts of 3.37 and 3.43 Å. The molecular orientation is such that a zigzag chain of Pt atoms with a Pt···Pt distance of 3.51 Å exists, similar to the interaction observed in Pt(bpy)Cl_2 form II (Figure 3). Addtionally, two close C−H···Cl contacts of 2.59 and 2.73 Å link neighboring columns of molecules. Despite these interactions, form II is actually less closely packed than form I with densities of 2.579 and 2.627 g/cm^3, respectively, determined from X-ray data collected at the same temperature (123 K) for comparative analysis.[25] Slurry conversion of form II to form I was observed in a saturated CH_2Cl_2/DMSO solution after extended equilibration, indicating that form I is more stable. However, in contrast to the case of Pt(bpy)Cl_2, a high kinetic barrier to the transformation between polymorphs of Pt(phen)Cl_2 exists because thermomicroscopy showed no transitions for either form with heating to 350 °C. Solubility measurements reveal that form II is 23% more soluble, which corresponds to form II being 0.53(1) kJ/mol less stable than form I at room temperature. Thus, the existence of the Pt···Pt interaction appears to be interfering with the ability of Pt(bpy)Cl_2 and Pt(phen)Cl_2 to close pack, contributing to the formation of less dense and less stable structures. This is indeed the trend for other platinum complexes with at least two reported polymorphs in the Cambridge Structural Database (CSD). With the addition of Pt(phen)Cl_2, there will be 63 polymorphic platinum complexes in the CSD,[26] six of which have at least one polymorph with an intermolecular Pt···Pt interaction of <3.5 Å (Figure 4). For five of these six complexes, the form with the shorter Pt···Pt distance is less dense, with the exception being PEXTIV. This complex possesses extensive hydrogen bonding, which is known to cause deviations from traditional density/stability relationships.[27] Thus, polymorphs with closer intermolecular Pt···Pt interactions in the solid state are likely to be higher in energy, although the energy difference may be quite small, less than 1 kJ/mol for the two determined here, between polymorphs.

Conclusions

Polymer-induced heteronucleation was employed for the selective crystallization of polymorphs of platinum complexes as single crystals directly in the presence of the polymers. This allowed the first structural characterization of two Pt(phen)Cl_2 polymorphs, one of which was previously unknown. Furthermore, this approach identified conditions suitable for the scale up of each polymorph of Pt(bpy)Cl_2 and Pt(phen)Cl_2. This made the elucidation of the relationship between solid-state structure and stability possible. The free energy difference between the polymorphs of both compounds was determined for the first time, and it was found that the polymorph with close Pt···Pt contacts is less dense and less stable in both cases, which is in accord with the principle of close packing.

Acknowledgment. This work was supported by the Beckman Foundation. The authors thank Dr. Jeff W. Kampf for crystal structure determination.

Supporting Information Available: Results from all crystallizations of Pt(bpy)Cl_2 and Pt(phen)Cl_2 from polymer libraries A−C, Raman spectra and PXRD patterns of Pt(bpy)Cl_2 and Pt(phen)Cl_2 polymorphs, and crystallographic information files (CIF) for Pt(phen)Cl_2 polymorphs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) The unit cell of Pt(phen)Cl_2 form I at 123(2) K was determined to be $a = 9.547(2)$ Å, $b = 17.102(4)$ Å, $c = 7.274(2)$ Å, $\beta = 109.004(4)°$, $V = 1122.9(5)$ Å^3, $\rho = 2.627$ g/cm^3. This unit cell shows the expected lattice contractions associated with lower temperature data collection, indicating that no change in structure has occurred. However, an increase in mosaicity was observed at low temperature, resulting in an unacceptable structure model.

(26) A search of the November 2005 version of the CSD for "Pt" and "polymorph" or "form" with 3D coordinates yielded 203 hits, of which 66 compounds were determined to have at least two unique structures based on unit cell parameters and packing motif. CCDC, 12 Union Road, Cambridge, U.K.

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