thermal parameters are listed in Table VII.

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Registry No. **2** (R = R′ = H), 117227-49-3; $\mathbf{2}^{+}$ (R = R′ = H), 117227-54-0; $\mathbf{2}^{-}$ (R = R′ = H), 117227-59-5; **2** (R = Me, R′ = H), 117227-50-6; $\mathbf{2}^{+}$ (R = Me, R′ = H), 117227-55-1; $\mathbf{2}^{-}$ (R = Me, R′ = H), 117227-60-8; **2** (R = H, R′ = Me), 117227-51-7; $\mathbf{2}^{+}$ (R = H, R′ = Me), 117227-56-2; $\mathbf{2}^{-}$ (R = H, R′ = Me), 117227-61-9; **2** (R = R′ = Me), 117227-52-8; $\mathbf{2}^{+}$ (R = R′ = Me), 117227-57-3; $\mathbf{2}^{-}$ (R = R′ = Me), 117227-62-0; **2** (R = H, R′ = Et), 117227-53-9; $\mathbf{2}^{+}$ (R = H, R′ = Et), 117227-58-4; $\mathbf{2}^{-}$ (R = H, R′ = Et), 117227-63-1; **4** (X = *n*-Bu), 117227-68-6; $\mathbf{4}^{-}$ (X = *n*-Bu), 117227-74-4; **4** (X = Ph), 117227-79-9; $Ru(bpy)_2CO_3$, 59460-48-9; $[Ru(sal)_2(MeCN)_2]PF_6$, 117227-65-3; $Ru(sal)_2(py)_2$, 117227-71-1; $Ru(sal)_2(PPh_3)_2$, 117227-72-2; $Ru(sal)_2(bpy)$, 117227-73-3; $[Ru(sal)(bpy)_2]ClO_4$, 117227-70-0; $[Ru(sal)_2(bpy)]ClO_4$, 117227-67-5; $Ru(sal)_2(MeCN)_2$, 117227-75-5; $[Ru(sal)_2(py)_2]^+$, 117227-76-6; $[Ru(sal)_2(PPh_3)_2]^+$, 117227-77-7; $[Ru(sal)_2(bpy)]^+$, 117227-66-4; $[Ru(sal)(bpy)_2]^{2+}$, 117227-78-8; salicylaldehyde, 90-02-8; *n*-butylamine, 109-73-9; aniline, 62-53-3; ceric ammonium sulfate, 7637-03-8.

Supplementary Material Available: Complete results of the EPR analysis of RuL_3 (Table VIII) and, for the crystal structure of $Ru(sal)_3$, hydrogen atom positional parameters (Table IX), complete bond distances (Table X) and angles (Table XI), anisotropic displacement parameters (Table XII), torsional angles (Table XIII), least-squares planes (Table XIV), and complete crystallographic data (Table XV) (15 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Concurrent and Reversible Changes of Color and of Phase in an Aqueous Solution of the (2,6-Pyridinedicarboxylato)chloroplatinate(II) Complex. Spectroscopic and Crystallographic Studies of the Discrete Monomer and Evidence of a Stacked Polymer

Xia-Ying Zhou and Nenad M. Kostić*

Received June 30, 1988

The title complex, $[Pt(dipic)Cl]^-$, was prepared in a reaction between dipicolinate salts and $[PtCl_4]^{2-}$. The variation in temperature or in concentration of its aqueous solution causes two changes—of color and of phase—which are sudden, concurrent, and reversible. At higher temperatures or lower concentrations the complex is yellow and monomeric, whereas at lower temperatures or attempted higher concentrations it is red and probably polymeric. The red form is microcrystalline and probably composed of stacked $[Pt(dipic)Cl]^-$ units. Unlike other square-planar complexes that form stacks, the yellow form of $[Pt(dipic)Cl]^-$ remains monomeric over a wide range of concentration and temperature until the sudden onset of the supposed polymerization. The nucleation and growth of the red form are easily monitored owing to the concomitant color change. The monomeric salt $(n\text{-}Bu)_4N[Pt(dipic)Cl]\cdot 0.5H_2O$ crystallizes in the monoclinic (*C*-centered) space group $C2/m$ with the following lattice properties: $a = 19.385$ (6) Å, $b = 27.965$ (9) Å, $c = 19.562$ (3) Å, $\beta = 93.38$ (2)°, $V = 10\,587$ (8) Å^3, and $Z = 8$. The structure was refined to $R_w = 0.0454$. The $[Pt(dipic)Cl]^-$ ion is essentially planar and contains a Pt(II) atom, a tridentate dipicolinate dianion that forms a strained chelate, and a unidentate Cl^- ligand. The Pt–N distance, on the average 1.89 Å, is uncommonly short. Since the layers of the complex anions are 7.0 Å apart and are separated by the bulky $(n\text{-}Bu)_4N^+$ cations, no intermolecular interactions exist. The putative polymeric form of $K[Pt(dipic)Cl]$ exhibits an X-ray powder pattern different from that of the monomeric $(n\text{-}Bu)_4N^+$ salt. The UV–vis spectrum of the red $K[Pt(dipic)Cl]$ in the solid state contains a low-energy absorption band diagnostic of the stacking. This band disappears when the red polymer dissolves in water to give a yellow monomeric solution. The $[Pt(dipic)Cl]^-$ salts, like thermochromic materials, hold promise as temperature indicators.

Introduction

Discovery and improvement of materials are important aims of chemical research. For example, stacking of planar molecules gives rise to one-dimensional materials, some of which exhibit anisotropic electrical conductivity, cooperative magnetic interactions, metal–insulator transitions, and even superconductivity.[1-4] Study of these properties has brought together chemists, physicists, and materials scientists.

Square-planar complexes of transition metals, particularly those of platinum(II), are notorious for columnar stacking.[1,5-8] When partially oxidized, these stacks become metallic conductors. Most reports on these one-dimensional materials justifiably deal with their properties in the solid state, because it is the solids that are conductive. But the solutions from which these solids are obtained are interesting as well. More should be known about precursors of the one-dimensional polymers,[9] about the mechanism of stacking and polymerization in solution, and about nucleation and growth of the polymers. This knowledge is necessary for a purposeful design and synthesis of new one-dimensional materials.

The first evidence of stacked aggregates, which are precursors for one-dimensional polymers, often is an unusual color dependent on the composition and temperature of the solution. The color variability resembles thermochromism of transition-metal complexes, a phenomenon generally observed in the solid state.[10]

We report here on the unusual behavior of a square-planar platinum(II) complex in solution. It undergoes sudden trans-

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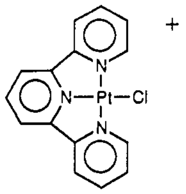
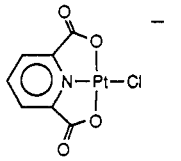
formation into a colloid-like phase, possibly by stacking polymerization, and the resulting material has interesting macroscopic properties. The phase change is easily monitored owing to the concomitant color change. Both changes are reversible.

This study grew out of an unexpected observation in our research on labeling of metalloproteins with the two similar Pt(II) chloro complexes





which differ in selectivity toward cytochrome *c* because the terpyridine and dipicolinate (dipic) ligands differ in their steric properties.[11-13] During a routine evaporation, the yellow aqueous solution of the [Pt(dipic)Cl]$^-$ complex turned suddenly into a red, immobile, gel-like substance. The striking transformation was easily reversed by dilution or heating. This is the report on its manifestations and causes.

Materials and Methods

Chemicals. The compounds $K_2[PtCl_4]$, $(n\text{-Bu})_4NCl$, Ph_4AsCl, D_2O, and $CDCl_3$ were obtained from Aldrich, dipicolinic acid (2,6-pyridinedicarboxylic acid) was obtained from Sigma, and cation exchangers CM 52 and Amberlite CG 50 were obtained from Whatman and Aldrich, respectively. Distilled water was demineralized further.

NMR Spectroscopy. The ^1H NMR spectra of solutions in D_2O and in $CDCl_3$ were recorded at 300 MHz with Nicolet NT300 and Bruker WM300 spectrometers, with use of DSS and residual protons as internal standards. The relaxation times T_1 over 3–50 °C were determined by the conventional method of inversion recovery with the Bruker instrument, whose temperature controller has an accuracy of ±0.5 °C. The recovery time was varied from 0.1 to 30 s, and the intensity was fitted exponentially. The activation energy was calculated from the plot of ln T_1^{-1} versus T^{-1}. The ^{195}Pt NMR spectra of a 30 mM solution of K[Pt(dipic)Cl] in a mixture containing 30% D_2O and 70% H_2O were recorded at 64.4 MHz with the Bruker instrument equipped with a 20-mm probe. Each spectrum was acquired in 8K data points with the following spectral width, pulse duration, tilt angle, and delay time: 100 kHz, 80 μs, 60°, and 500 ms. A solution of $K_2[PtCl_4]$ saturated with NaCl was kept in a coaxial inset tube as an external reference (0 ppm). The peaks were sought between +850 and −2000 ppm.

UV–Vis and IR Spectrophotometry. The UV–vis spectra were recorded with an IBM 9430 spectrophotometer. Optical paths were from 10 to 0.05 mm. The IR spectra between 4000 and 200 cm^{-1} were recorded with an IBM IR98 Fourier-transform instrument. The IR samples were dried in a desiccator for several weeks and under vacuum for 1 h, and the Nujol mulls were smeared on CsI or NaCl plates.

Formula Mass. This property (often called molecular weight) was determined with a Knauer vapor-pressure osmometer, a Utopia digital meter, and a universal thermistor probe. The cell and head temperatures were 36.0 and 38.0 °C, respectively. Both the calibration solutions (NaCl) and the sample solutions spanned the range of 5–30 mM. Thermal equilibrium was always attained, and the base line was checked regularly.

Colors and Phases. The temperatures at which the first red spots appeared on cooling and those at which the last red spots disappeared on heating were recorded with a Forma 2067 bath filled with a mixture of water and ethylene glycol. The temperature was changed by 1 °C between −20 and +50 °C, and equilibration lasted for 20–60 min.

$(NH_4)_2$dipic. To a suspension of 1.00 g (6.0 mmol) of dipicolinic acid in 1 mL of water was added 20 mL (a large excess) of concentrated aqueous ammonia. The mixture was heated at 60–70 °C and dried without charring. The white residue was dissolved repeatedly in 5 mL of water and dried at 60–70 °C until NH_3 was removed; yield 1.10 g (91%). Proton NMR spectrum (δ values) in D_2O: 8.62, t; 8.41, d; ^3J(H–H) = 7.8 Hz.

K_2dipic. A solution containing 0.109 g (0.65 mmol) of dipicolinic acid and 0.071 g (1.27 mmol) of KOH in 3 mL of water was dried at 60–70 °C to yield a white residue. An excess of base was avoided lest it might subsequently cause side reactions with Pt complexes. Proton NMR spectrum (δ values) in D_2O: 8.18, t; 8.10, d; ^3J(H–H) = 7.6 Hz.

K[Pt(dipic)Cl]. A solution containing 0.402 g (2.0 mmol) of $(NH_4)_2$dipic in 40 mL of water was added dropwise to a stirred solution containing 0.830 g (2.0 mmol) of $K_2[PtCl_4]$ in 10 mL of water. The reaction is best carried out in the dark, or in dilute (ca. 0.25 M) HCl instead of water, in order to suppress side reactions. The mixture was heated at 80 °C for 4 h, and its color changed from red to orange. The UV band at 272 nm, due to the free dipicolinate anion, decreased while a broad one at ca. 330 nm, due to the chelate complex, increased. The orange reaction mixture was cooled to room temperature, and the NH_4^+ ions were replaced with K^+ ions on a 2.5 × 14 cm CM 52 column. Both the prior equilibration and the elution were done with 0.10 M KCl. Two bands formed. The first one was red and contained the unspent $K_2[PtCl_4]$; the second one was yellow and contained K[Pt(dipic)Cl]. The yellow solution was concentrated in a rotary evaporator. The red or orange solid that formed was filtered off, washed with ethanol and acetone, and dried in a desiccator. The average weight of the first crop was 0.30 g; the yield (36%) was sacrificed to purity. Anal. Found (calcd for $C_7H_3NO_4ClKPt$): C, 19.31 (19.34); H, 0.99 (0.70); N, 3.12 (3.22). (All elemental analyses were done by Galbraith Laboratories, Inc.) Proton NMR spectrum (δ values) in D_2O: 8.45, t; 7.92, d; ^3J(H–H) = 8.0 Hz. Infrared bands (cm^{-1}) in Nujol mull: for the red salt, 3539 w, 3053 w, 2912 s, 1697 m, 1680 s, 1664 m, 1653 m, 1636 m, 1317 s mult, 1151 m, 1103 m, 914 w, 831 w, 770 m, 752 m, 675 m, 596 w, 462 m, 368 vw, 331 m, 319 m, 300 m; for the orange salt, 3086 w, 3074 w, 2926 s, 1686 s, 1668 s, 1323 s, 1150 m, 1136 m, 1111 m, 1106 m, 916 w, 831 w, 768 m, 752 m, 675 m, 599 w, 463 m, 457 m, 370 vw, 332 m, 322 m, 301 m, 263 vw, 247 vw, 223 vw.

Concentrated HNO_3 was added, in small drops, to the red gel-like substance obtained by cooling of an aqueous solution of K[Pt(dipic)Cl]. The color changed to purplish and stayed so indefinitely. An excess of HNO_3, however, dissolved the solid and yielded a yellow solution.

$(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$ and $Ph_4As[Pt(dipic)Cl]$. These salts were prepared directly from the orange solution obtained in the reaction between 0.118 g (0.284 mmol) of $K_2[PtCl_4]$ and 0.057 g (0.284 mmol) of $(NH_4)_2$dipic (see above). Solid $(n\text{-Bu})_4NCl$ was added gradually to the stirred orange solution at room temperature until precipitation ceased. The needlelike yellow crystals were filtered and washed with cold water. The yield was 0.098 g (54%) with respect to $K_2[PtCl_4]$; mp 100–101 °C. Anal. Found (calcd for $C_{23}H_{39}N_2O_4ClPt\cdot 0.5H_2O$): C, 42.85 (42.68); H, 6.28 (6.24); N, 4.29 (4.33). Proton NMR spectrum (δ values) in $CDCl_3$: 8.14, t; 7.73, d. Infrared bands (cm^{-1}) in Nujol mull: 3585 w, 3501 w, 2926 s, 1699 m, 1664 s, 1491 w, 1408 w, 1304 s, 1151 m, 1101 m, 908 w, 881 w, 825 w, 775 m, 748 m, 675 w, 595 w, 572 w, 543 w, 526 w, 453 m, 421 w, 345 m, 331 m, 292 m. Similarly, a concentrated aqueous solution of Ph_4AsCl was added dropwise to the stirred orange solution at room temperature until precipitation ceased. The yellow solid was filtered and washed with cold water; yield: 0.086 g (39%) with respect to $K_2[PtCl_4]$. A red precipitate formed upon addition of the concentrated $[Co(NH_3)_6]Cl_3$ solution to the stirred orange reaction mixture. It was presumed to be $[Co(NH_3)_6][Pt(dipic)Cl]_3$ but was not investigated further.

The salt $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$ is soluble at room temperature in acetone, chloroform, *N*,*N*-dimethylformamide, ethanol, methanol, and methyl ethyl ketone; it is somewhat soluble in acetonitrile, 2-propanol, 1,1,1-trichloroethane, 1,4-dioxane, and ethyl acetate; it is slightly soluble or insoluble in diethyl ether, hexanes, benzene, carbon tetrachloride, and water. The salt $Ph_4As[Pt(dipic)Cl]$ is soluble in *N*,*N*-dimethylformamide, acetonitrile, chloroform, and methanol; it is somewhat soluble in acetone, methyl ethyl ketone, and ethanol; it is slightly soluble or insoluble in 1,4-dioxane, ethyl acetate, diethyl ether, hexanes, 1,1,1-trichloroethane, benzene, carbon tetrachloride, ethanol, 2-propanol, and water.

Salts $M^{x+}[Pt(dipic)Cl]_x$. The cations K^+ and NH_4^+ in the orange reaction mixture were replaced with H^+, Li^+, Na^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, and Al^{3+} on the columns of Amberlite CG 50 cation exchanger that were previously equilibrated with 0.10 M solutions of the corresponding Cl^- or NO_3^- salts and washed with water. The resin was in excess of that required for the complete exchange. Elution with the equilibrating solution in each case produced the red band of the unspent $K_2[PtCl_4]$, which moved first, and the yellow band of the [Pt(dipic)Cl]$^-$ salt, which moved second. Only the yellow one was collected.

***trans*-$K_2[Pt(dipic)_2]$.** A solution of 10.0 mg (0.04 mmol) of K_2dipic in 4.15 mL of D_2O was added to the solution of 17.9 mg (0.04 mmol) of K[Pt(dipic)Cl] in 4.15 mL of D_2O. The mixture changed from yellow to colorless after 1 day at room temperature. Proton NMR spectrum (δ values) in D_2O: 8.33, t; 7.91, d; 7.72, d; ^3J(H–H) = 7.8 Hz; ^4J(H–H) = 1.5 Hz.

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Table I. Crystallographic Data for $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$

chem formula: $PtC_{23}H_{40}N_2O_{4.5}Cl$
$a = 19.385\ (6)$ Å
$b = 27.965\ (9)$ Å
$c = 19.562\ (3)$ Å
$\beta = 93.38\ (2)°$
$V = 10587\ (8)$ Å^3
$Z = 8$
fw = 647.12
space group: $C2/m$ (No. 12)
$T = 22 \pm 1$ °C
$\lambda = 0.71073$ Å
$\rho_{calcd} = 1.623$ g cm^{-3}
$\mu = 54.88$ cm^{-1}
transmission coeff: 0.9971–0.7576
$R(F_o \text{ or } F_o^2) = 0.0379$
$R_w(F_o \text{ or } F_o^2) = 0.454$

Crystallographic Analysis of $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$. This yellow salt was dissolved in $CHCl_3$, and a 4-fold volume of anhydrous diethyl ether was laid slowly on the solution. Pinacoidal single crystals, which formed after 1 day, were removed and kept in air. The technical details are summarized in Table I.

The positions of three independent platinum atoms were obtained by a Patterson interpretation method.[14] Two of them sit on the *x*, 0, *z* mirror plane, and the third one is in a general position. The $(n\text{-Bu})_4N^+$ ion sits on the 2-fold axis. After the non-hydrogen atoms were located in difference-Fourier and least-squares refinements, the oxygen atom of a water molecule was found. All the non-hydrogen atoms in the Pt complexes and the nitrogen atoms in the $(n\text{-Bu})_4N^+$ ions were refined anisotropically, but the butyl carbon atoms were left with isotropic thermal parameters. Hydrogen atoms in calculated positions were used only for the calculation of structure factors. The C–H bond length was fixed at 0.95 Å, and the hydrogen isotropic thermal parameter, *B*, was fixed at 5.0 Å^2. Standard scattering factors were used.[15] Anomalous dispersion effects were included in F_c;[16] the values for f' and f'' were the standard ones.[17] The work was done with the Enraf-Nonius CAD4-SDP package.

X-ray Diffraction from Powders. The patterns were recorded with a Guinier camera produced by Enraf-Nonius; the Cu Kα wavelength was 1.5406 Å. The following three samples were examined: ground single crystals of yellow $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$, microcrystals of K[Pt(dipic)Cl] obtained by evaporation of its aqueous solution under reduced pressure, and microcrystals of K[Pt(dipic)Cl] obtained by cooling of its solution and drying of the red gel-like substance. The *d* spacings and the line intensities are listed in the supplementary material.

Formation of the Complexes and Their Properties

Dipicolinic acid ($dipicH_2$) and its dinegative anion (dipic) are versatile ligands.[18] Most commonly, dipic is a meridional tridentate ligand.[19-21] The facial coordination of dipic,[22,23] meridional coordination of $dipicH_2$,[24] bridging of two metal atoms,[25] and polymerization of chelate complexes by coordination of the carbonyl oxygen atoms[26] are also known. Only one case of bidentate, N,O-coordination has been described[27] prior to this report on $[Pt(dipic)_2]^{2-}$. The dipicolinate complexes described herein are among the few that contain a third-row metal and are the first ones with platinum.

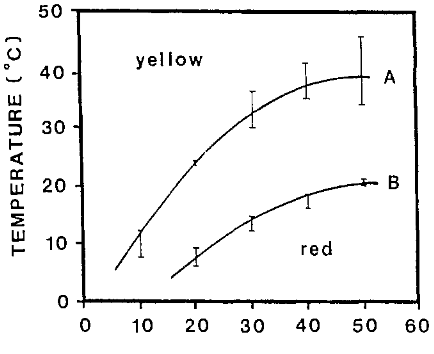
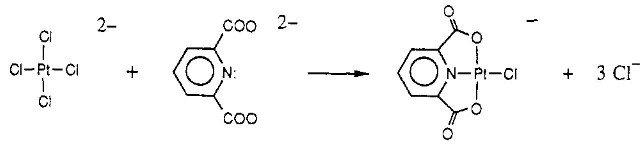


Figure 1. Color change and phase change in the aqueous solution of K[Pt(dipic)Cl]: (A) dissolution of the last red particle, the solution becoming uniformly yellow; (B) appearance of the first red particle in the yellow solution.

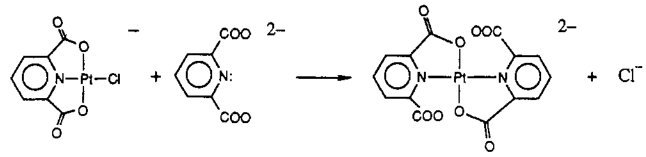
Since $dipicH_2$ is sparingly soluble in water, the substitution reactions were carried out with $(NH_4)_2$dipic and K_2dipic. The reaction shown in eq 1 is slow at room temperature but relatively fast at 80 °C. Various $[Pt(dipic)Cl]^-$ salts were prepared by cation exchange and by precipitation.



(1)

The simple ^1H NMR spectrum of the $[Pt(dipic)Cl]^-$ complex proves the tridentate coordination of the ligand. The red and orange K^+ salts yield identical yellow solutions in D_2O and exhibit identical ^1H NMR spectra. Such a spectrum of the yellow $(n\text{-Bu})_4N^+$ salt in $CDCl_3$ is very similar to the other two, except for the small effects of the cation and of the solvent on the chemical shifts.

The bis(bidentate) complex *trans*-$[Pt(dipic)_2]^{2-}$ is formed according to eq 2. The coupling between the H^3 and H^5 atoms is of the expected magnitude.[28] Since the bidentate picolinate moiety of the dipic ligand is planar,[29] the cis configuration would bring the ligands prohibitively close to each other. Structures of various square-planar Pt(II) complexes prove that two cyclic ligands in the cis positions evidently cannot be coplanar.[30-32] Indeed, planar picolinate-like ligands adopt a trans configuration in bis(bidentate) complexes of platinum(II).[33,34]



(2)

Color and Phase of $[Pt(dipic)Cl]^-$

Behavior of Solution. The aqueous solution of the $[Pt(dipic)Cl]^-$ complex is remarkable for the simultaneous changes of color and

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of phase that are induced by changing temperature or concentration (see Figure 1). Regardless of the color in the solid state—yellow, orange, or red—[Pt(dipic)Cl]$^-$ salts give a pale yellow solution in water. When the solution is cooled at a moderate rate (10–20 K min^{-1}), without freezing, it turns into a red colloidal suspension, which is actually microcrystalline (see below). At the beginning of the transition, red nuclei appear in the yellow solution and then grow and coalesce into an immobile, gel-like substance. Although the transformations can be reversed by heating, some hysteresis is evident in Figure 1.

Variation of the solution concentration (at constant temperature) causes the same changes as the variation of its temperature (at constant concentration). During evaporation, the yellow aqueous solution turns into the same red gel-like substance as when it is cooled. The red substance gives a yellow aqueous solution upon dilution or heating. Evidently, the two changes can be effected by either vertical or horizontal transitions in the phase diagram (Figure 1). These changes are akin to first-order phase transitions.

Qualitative experiments with 30 mM solutions of K[Pt(dipic)Cl] in buffers spanning the pH range 2.0–9.6 showed that the two changes occur in the weakly acid and neutral solutions alike. The behavior of the [Pt(dipic)Cl]$^-$ complex is unaffected by the presence of other ions, an indication that the phase change is not merely flocculation of a sol. The solution of pure K[Pt(dipic)Cl] and the reaction mixture, which contained NH_4^+, Cl^-, and $[PtCl_4]^{2-}$ ions as well, gave similar phase diagrams. The [Pt(dipic)Cl]$^-$ salts with the monovalent, divalent, and trivalent cations changed color, and most of them also formed the gel-like phase, upon cooling. The Na^+ and Ca^{2+} salts behaved atypically in yielding precipitates rather than gel-like materials at low temperatures.

Nonaqueous solutions of the K^+, $(n\text{-Bu})_4N^+$, and Ph_4As^+ salts remain yellow under the conditions shown in Figure 1. Experiments with mixtures of water with ethanol, methanol, *N*,*N*-dimethylformamide, and acetone were hampered by the incomplete solubility of the complex salts in some of these mixtures. It is nevertheless clear that the interesting transition occurs only in solvents that are mostly aqueous in composition. This fact and the presence of carboxylate groups in the dipic ligand point to hydrogen bonding as a possible cause of the gel-like state. In this state a small quantity of the complex (typically ca. 30 mM) apparently organizes a great amount of water (ca. 55 M). Although this solute-to-water molar ratio is nearly 1:2000, the red gel-like substance obtained by cooling of the solution is immobile. This immobility is strikingly evident when the red substance on the bottom of a test tube remains still even after the test tube is inverted!

UV-Vis Spectra. The sparingly soluble yellow salt $(n\text{-Bu})_4N$[Pt(dipic)Cl] and the soluble red and orange forms of the solid K[Pt(dipic)Cl] all give yellow aqueous solutions with virtually identical spectra. The band positions (λ_{max}, in nm) and absorptivities (ϵ_{max} in parentheses, in M^{-1} cm^{-1}) of the K^+ salt are as follows: 328 (2900), 250 sh (8000), 228 (11 000); see Figure 2A. The spectra of the $(n\text{-Bu})_4N^+$ salt in nonaqueous solutions are very similar to one another and somewhat different from its spectrum in aqueous solution. The absorption bands (λ_{max} in nm; ϵ_{max} in parentheses, in M^{-1} cm^{-1}) are as follows: in *N*,*N*-dimethylformamide, 355 (1900), 300 (2000), 265 (2100); in chloroform, 354 (1900), 300 (2000), 253 (4400); in absolute ethanol, 352 (3100), 298 (3300), 252 (7600). The band at the lowest energy can be assigned to the MLCT transition Pt(II) → pyridine, and the band at the highest energy to a $\pi \rightarrow \pi^*$ transition in the pyridine chromophore.[35] The dependence of the λ_{max} values on solvent polarity is too small and too irregular to be termed solvatochromism.[35]

A suspension of the solid K[Pt(dipic)Cl] in Nujol, however, exhibits a prominent new absorption band at higher wavelengths, as Figure 2B shows. The λ_{max} values (in nm) are as follows: yellowish orange K[Pt(dipic)Cl], *476*, 310 (sh), 256, 230; reddish orange K[Pt(dipic)Cl], *520*, 320 (sh), 252, 229. The solution and the solid produce similar spectra in the UV region. Clearly, it is the new band in the visible region (at 476 and 520 nm) that causes the deeper color.

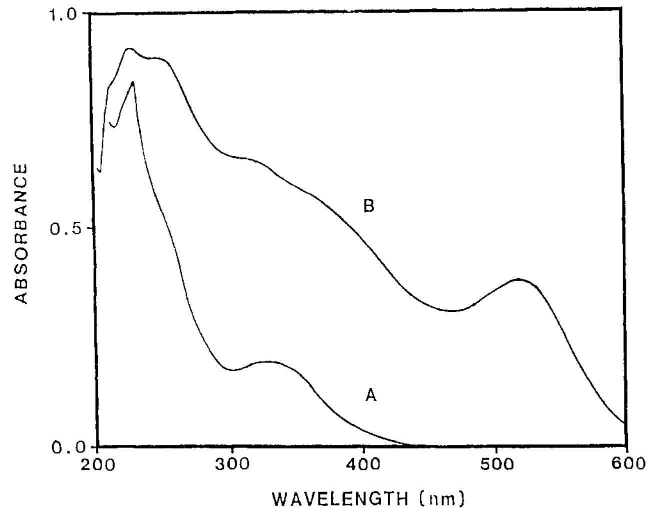

Figure 2. Ultraviolet-visible spectra of K[Pt(dipic)Cl]: (A) yellow 1.8 × 10^{-4} M solution of the red solid in water; (B) suspension of the red solid in Nujol.

The new absorption band at lower energies is diagnostic of one-dimensional stacking of square-planar metal complexes in the solid state.[36-38] The variability of color, from yellowish orange to reddish orange, of K[Pt(dipic)Cl] precipitates probably is due to the variable extent of stacking, provided that the interplanar distance is constant.

Most square-planar complexes that form columnar stacks in the solid state aggregate already in solution, but [Pt(dipic)Cl]$^-$ remains monomeric in solution over a range of concentration and temperature. Solutions of the K^+ salt in water up to 30 mM and of the $(n\text{-Bu})_4N^+$ salt in *N*,*N*-dimethylformamide, which was examined only up to 0.5 mM, obey Beer's law throughout the UV–vis region, and relative intensities of the bands remain unchanged.

Formula Mass. The absence of oligomerization is confirmed by the osmometric experiments. The calculated formula mass of K[Pt(dipic)Cl] is 435 g mol^{-1}. Measurements of the vapor pressure over its 5, 10, 15, 20, and 25 mM solutions in water at 36.0 °C yielded a constant value of 403 ± 40 g mol^{-1}.

The reliability of this osmometric method[39,40] was confirmed in experiments with [Pt(trpy)Cl]Cl, a complex that is similar to K[Pt(dipic)Cl] and that is known to dimerize in aqueous solution.[28] The calculated formula mass of [Pt(trpy)Cl]Cl is 499 g mol^{-1}, but its 5–20 mM solutions yielded an average value of 924 ± 130 g mol^{-1}. Complexes that oligomerize in solution not only exhibit increased formula mass but also violate Beer's law. The [Pt(dipic)Cl]$^-$ complex, which remains monomeric and obeys Beer's law, is an exception.

NMR Spectroscopy. The ^1H NMR spectrum of the yellow solution of K[Pt(dipic)Cl] in D_2O at room temperature is independent of concentration over the entire range studied, 5–30 mM. This, too, is evidence against association. The spectrum of $(n\text{-Bu})_4N$[Pt(dipic)Cl] in a different solvent, $CDCl_3$, exhibits slightly different chemical shifts. The yellow 30 mM solution of the K^+ salt in D_2O at 50 °C, the red gel-like substance at 3 °C, and the samples at intermediate temperatures all gave the same signals, namely (in δ units) 7.91 d and 8.44 t.

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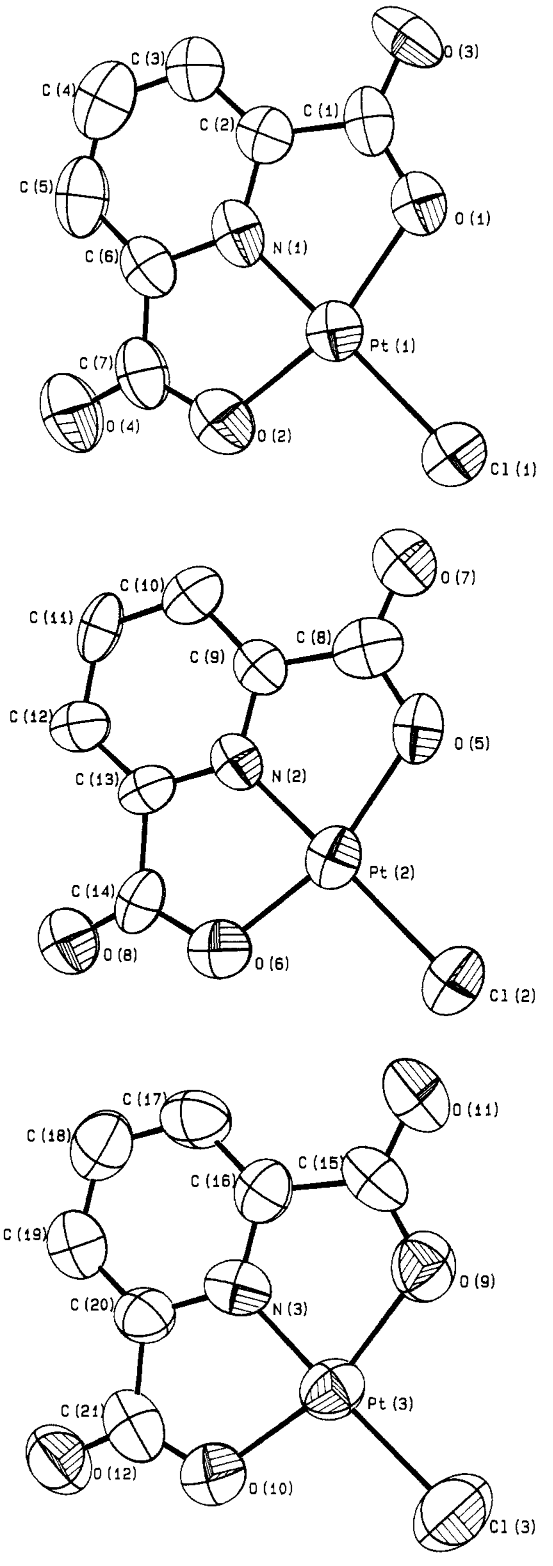

Figure 3. Molecular structures (ORTEP drawings) of the three types of complex anion, designated I (top), II (middle), and III (bottom), that coexist in the crystal of $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot0.5H_2O$. The ellipsoids enclose 50% of the electron density.

The relaxation times T_1 for both the triplet and the doublet resonances of the 30 mM K[Pt(dipic)Cl] solution in D_2O and of the DSS resonance changed smoothly with temperature over the range 3–50 °C. The constancy of the activation energy for the spin–lattice relaxation in the complex (11.3 ± 1.4 kJ regardless of the resonance monitored) indicates that the phase change, which was evident in the NMR tube and was reversible, does not affect abnormally the mobility of the complex. The activation energy for DSS, which is mobile, is 10.8 ± 0.4 kJ.

Table II. Important Bands (cm^{-1}) in the IR Spectra of the Dipicolinate Anion and of Its Complexes

compd	ν_{OH}	ν_{COO} asym	ν_{COO} sym	ν_{PtO}	ν_{PtCl}
K_2dipic		1612	1431		
		1582	1377		
yellow $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot0.5H_2O$	3585	1664	1304	345	292
	3501			331	
red K[Pt(dipic)Cl]	3539	1680	1317	331	300
				319	

Table III. Coordinates of the Non-Hydrogen Atoms in the Complex Anion of the Salt $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot0.5H_2O$[a]

atom	x	y	z
		Type I	
Pt(1)	0.27791 (4)	0.000	0.48337 (4)
Cl(1)	0.3753 (2)	0.000	0.5567 (3)
O(1)	0.2035 (6)	0.000	0.5530 (5)
O(2)	0.3252 (6)	0.000	0.3946 (6)
O(3)	0.0891 (6)	0.000	0.5594 (6)
O(4)	0.2997 (8)	0.000	0.2829 (6)
N(1)	0.1977 (7)	0.000	0.4220 (6)
C(1)	0.1406 (9)	0.000	0.5254 (8)
C(2)	0.1341 (8)	0.000	0.4502 (8)
C(3)	0.0771 (9)	0.000	0.4049 (9)
C(4)	0.084 (1)	0.000	0.335 (1)
C(5)	0.149 (1)	0.000	0.3095 (9)
C(6)	0.2081 (9)	0.000	0.3533 (8)
C(7)	0.282 (1)	0.000	0.3401 (9)
		Type II	
Pt(2)	0.21555 (4)	0.000	0.93026 (4)
Cl(2)	0.1865 (3)	0.000	1.0423 (2)
O(5)	0.3214 (5)	0.000	0.9441 (5)
O(6)	0.1182 (5)	0.000	0.8854 (6)
O(7)	0.4144 (5)	0.000	0.8850 (6)
O(8)	0.0644 (6)	0.000	0.7827 (6)
N(2)	0.2375 (6)	0.000	0.8380 (6)
C(8)	0.3519 (9)	0.000	0.8876 (9)
C(9)	0.3034 (7)	0.000	0.8239 (8)
C(10)	0.3231 (9)	0.000	0.7569 (8)
C(11)	0.2702 (9)	0.000	0.7039 (7)
C(12)	0.2014 (8)	0.000	0.7212 (9)
C(13)	0.1873 (8)	0.000	0.7873 (8)
C(14)	0.1167 (9)	0.000	0.8181 (8)
		Type III	
Pt(3)	0.46689 (3)	0.75923 (2)	0.25807 (3)
Cl(3)	0.5816 (2)	0.7532 (2)	0.2896 (2)
O(9)	0.4332 (4)	0.7566 (3)	0.3534 (4)
O(10)	0.4696 (4)	0.7629 (3)	0.1558 (4)
O(11)	0.3356 (5)	0.7541 (4)	0.4065 (4)
O(12)	0.3990 (5)	0.7698 (4)	0.0609 (4)
N(3)	0.3716 (5)	0.7637 (3)	0.2348 (5)
C(15)	0.3653 (7)	0.7576 (5)	0.3545 (6)
C(16)	0.3272 (5)	0.7612 (4)	0.2840 (6)
C(17)	0.2587 (6)	0.7626 (5)	0.2679 (7)
C(18)	0.2339 (6)	0.7654 (5)	0.2005 (7)
C(19)	0.2808 (7)	0.7672 (5)	0.1497 (6)
C(20)	0.3498 (6)	0.7661 (4)	0.1677 (6)
C(21)	0.4101 (7)	0.7658 (5)	0.1223 (6)

[a] Three types of the anion, designated I–III, coexist in the crystal.

The ^{195}Pt NMR spectrum, also, was invariable with temperature—both the yellow 30 mM solution of K[Pt(dipic)Cl] at 40 °C and the red substance obtained from it at 3 °C gave a single peak at 189 and 216 ppm, respectively. These values fall in the range characteristic of Pt(II) complexes with the NO_2Cl set of donors.[41,42] When corrected for temperature dependence,[43,44] the spectra of the yellow and red forms become virtually indis-

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Table IV. Important Bond Distances (Å) in the Complex Anion of $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$[a]

type I		type II		type III	
Pt(1)–Cl(1)	2.302 (5)	Pt(2)–Cl(2)	2.296 (5)	Pt(3)–Cl(3)	2.279 (4)
Pt(1)–O(1)	2.04 (1)	Pt(2)–O(5)	2.05 (1)	Pt(3)–O(9)	2.014 (8)
Pt(1)–O(2)	2.01 (1)	Pt(2)–O(6)	2.03 (1)	Pt(3)–O(10)	2.008 (8)
Pt(1)–N(1)	1.91 (1)	Pt(2)–N(2)	1.88 (1)	Pt(3)–N(3)	1.881 (9)
O(1)–C(1)	1.30 (2)	O(5)–C(8)	1.28 (2)	O(9)–C(15)	1.32 (1)
O(2)–C(7)	1.32 (2)	O(6)–C(14)	1.31 (2)	O(10)–C(21)	1.30 (1)
O(3)–C(1)	1.23 (2)	O(7)–C(8)	1.22 (2)	O(11)–C(15)	1.20 (2)
O(4)–C(7)	1.19 (2)	O(8)–C(14)	1.19 (2)	O(12)–C(21)	1.21 (1)

[a] See footnote *a* of Table III.

Table V. Important Bond Angles (deg) in the Complex Anion of $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$[a]

type I		type II		type III	
Cl(1)–Pt(1)–O(1)	99.8 (3)	Cl(2)–Pt(2)–O(5)	99.9 (3)	Cl(3)–Pt(3)–O(9)	96.4 (2)
Cl(1)–Pt(1)–O(2)	98.0 (4)	Cl(2)–Pt(2)–O(6)	98.0 (3)	Cl(3)–Pt(3)–O(10)	101.0 (2)
N(1)–Pt(1)–O(1)	80.7 (5)	N(2)–Pt(2)–O(5)	81.1 (5)	N(3)–Pt(3)–O(9)	81.9 (4)
N(1)–Pt(1)–O(2)	81.5 (6)	N(2)–Pt(2)–O(6)	80.9 (4)	N(3)–Pt(3)–O(10)	80.7 (3)
O(1)–C(1)–C(2)	116 (1)	O(5)–C(8)–C(9)	114 (1)	O(9)–C(15)–C(16)	115 (1)
O(2)–C(7)–C(6)	116 (1)	O(6)–C(14)–C(13)	115 (1)	O(10)–C(21)–C(20)	113.6 (9)
N(1)–C(2)–C(1)	112 (1)	N(2)–C(9)–C(8)	113 (1)	N(3)–C(16)–C(15)	110.9 (9)
N(1)–C(6)–C(7)	112 (1)	N(2)–C(13)–C(14)	110 (1)	N(3)–C(20)–C(21)	111.2 (9)

[a] See footnote *a* of Table III.

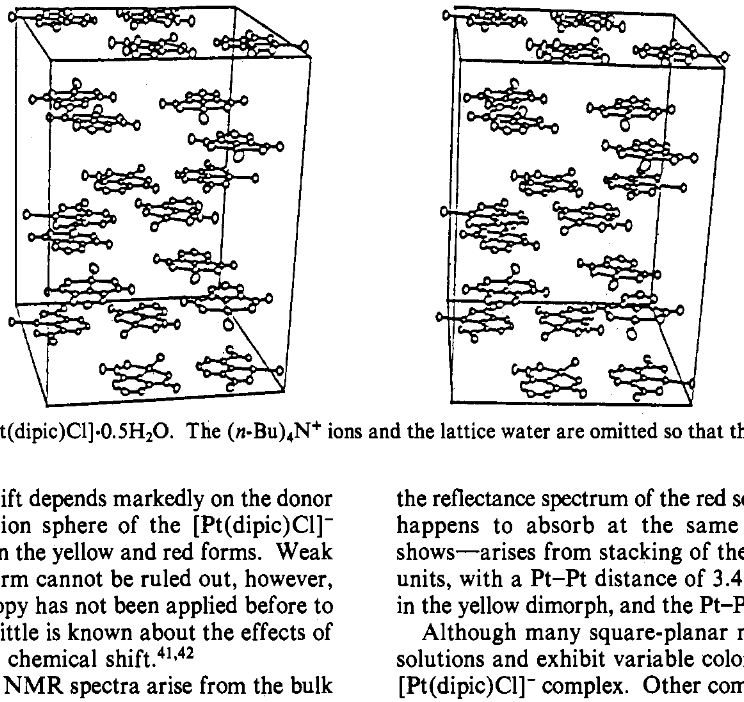

Figure 4. Unit cell of $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$. The $(n\text{-Bu})_4N^+$ ions and the lattice water are omitted so that the packing of the complex anions can be seen clearly.

tinguishable. Since the ^{195}Pt shift depends markedly on the donor atoms,[41,42] the first coordination sphere of the [Pt(dipic)Cl]$^-$ complex probably is the same in the yellow and red forms. Weak axial interactions in the red form cannot be ruled out, however, because ^{195}Pt NMR spectroscopy has not been applied before to columnar stacks and because little is known about the effects of axial interactions on the ^{195}Pt chemical shift.[41,42]

It is assumed above that the NMR spectra arise from the bulk sample at all temperatures and, in particular, that the low-temperature spectrum is not that of the residual yellow solution. Indeed, the low-temperature sample appears uniform, and no yellow liquid is visible in it.

IR Spectra. The principal stretching vibrations of the yellow and red forms of K[Pt(dipic)Cl] are listed in Table II. These findings are fully consistent with the molecular structure discussed above and with the spectra of other relevant compounds.[45–49]

Comparison with Other Complexes. The red and yellow forms of [Pt(bpy)Cl$_2$],[50] like such forms of [Pt(dipic)Cl]$^-$, differ from each other in the solid state, but their yellow solutions in CHCl$_3$ exhibit identical UV–vis spectra.[51] The new band at 520 nm in the reflectance spectrum of the red solid[51]—the red K[Pt(dipic)Cl] happens to absorb at the same wavelength, as Figure 2B shows—arises from stacking of the square-planar [Pt(bpy)Cl$_2$] units, with a Pt–Pt distance of 3.45 Å.[52] There is no stacking in the yellow dimorph, and the Pt–Pt distance is long, ca. 4.5 Å.[53]

Although many square-planar metal complexes associate in solutions and exhibit variable colors, none of them are like the [Pt(dipic)Cl]$^-$ complex. Other complexes oligomerize gradually and violate Beer's law, their color changes generally require considerable temperature changes, and their differently colored forms are all soluble. In contrast to these usual properties, the [Pt(dipic)Cl]$^-$ complex reported here obeys Beer's law almost until it aggregates, it changes color over a relatively narrow temperature range, and its red form is insoluble in water without changing into the yellow form. We know of just one other compound, pseudoisocyanine chloride, that resembles [Pt(dipic)Cl]$^-$ in its behavior in solution; it forms so-called J-aggregates and changes color upon concentration and cooling.[54]

Structure of the Red Form

The gel-like substance apparently can be oxidized by HNO$_3$. Because partial oxidation of the Pt(II) stacks usually yields deep colors,[1,5–8] the purple color of this product is consistent with a mixed-valence compound. By extension of this reasoning, it may be inferred that the red, gel-like material contains proximate Pt

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atoms, i.e, stacked complex anions.

Diffraction patterns of the powdered microcrystalline samples proved that the orange and red forms of K[Pt(dipic)Cl] (which cannot be obtained as single crystals) are identical with each other and different from the yellow $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$. The former solid, obtained by slow evaporation at room temperature or by cooling of the solution, has a richer diffraction pattern than the latter solid, obtained by precipitation with a bulky countercation. The former solid differs from the latter one in having a larger unit cell, a lower space symmetry, or both. The spectroscopic evidence indicates that the orange and red solids are stacked, whereas the yellow one is not (see above).

Structure of the Yellow Form

Since the K^+ and $(n\text{-Bu})_4N^+$ salts have identical spectral properties, the structure of the yellow form is studied with the latter salt. Coexisting in the crystal of the yellow $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$ are three slightly different types of the complex anion, designated I–III and shown in Figure 3. The first two are virtually planar, whereas the third is slightly puckered. In particular, the N and Cl atoms in complex III lie 0.05 Å away from the average plane on the opposite sides of it. The atomic coordinates and principal dimensions are listed in Tables III–V.

The exceptionally short Pt–N distance of 1.88–1.91 Å indicates partial multiplicity, a property consistent with the assignment of the absorption band at 328–355 nm in the UV–vis spectrum of $[Pt(dipic)Cl]^-$ to a Pt(II) → pyridine MLCT transition (see above). The average value of 11 Pt–N distances in Pt(II) complexes with pyridine, picolinic acid, and similar pyridine derivatives is 2.03 Å.[29,30,33,34,55] The M–N distances in the dipic chelates with first-row transition metals, whose atoms are much smaller than the Pt atom, span the range of 1.88–2.17 Å.[19–21,24] The other molecular dimensions are ordinary.[19–22,24,55–57] The O–Pt–N "bite" angles of 80.7–81.9° indicate strain in the chelate complex. The difference of ca. 0.10 Å between the two C–O distances in the same carboxylate group indicates considerable localization of the π electrons in the exocyclic group.

The typical interlayer distances in columnar Pt(II) complexes are 3.2–4.2 Å,[58–60] and in such Pd(II)[61] and Rh(I)[62] complexes they are approximately 3.4 Å. In the salt reported herein, the $(n\text{-Bu})_4N^+$ cations are interposed between the layers of the $[Pt(dipic)Cl]^-$ anions that are 7.0 Å apart in the *b* direction. The first layer in Figure 4 consists of two anions of type I in the middle and one anion of type II on either side. The second layer consists of four anions of type III. The third layer is like the first one, and so on. The lattice water does not form hydrogen bonds. The yellow salt is similar to the yellow form of $[Pt(bpy)Cl_2]$, discussed above,[53] because neither exhibits stacking.

Acknowledgment. This work was financed by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under contract W-7405-ENG-82. We thank Lee M. Daniels of the ISU Molecular Structure Laboratory for the crystal structure of $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$, Clark D. Carlson and Robert E. McCarley for the X-ray powder patterns, Eva M. A. Ratilla for help with NMR measurements, Robert J. Angelici for use of the osmometer, and Jesse H. Day and Roger D. Willett for consultations. We are especially grateful to Gordon K. Anderson, Alan L. Balch, Arthur J. Frank, and W. Roy Mason for their comments on the manuscript.

Supplementary Material Available: For the crystal and molecular structures of $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$, types I–III, tables giving details of the crystallographic method, all bond distances and bond angles, the least-squares plane for type III and deviations from it, coordinates of non-hydrogen atoms with *B* values, general displacement parameters *U* and *B*, amplitudes of thermal vibrations for non-hydrogen atoms, and calculated coordinates of hydrogen atoms, and, for the X-ray diffraction from powders, tables giving patterns for K[Pt(dipic)Cl] obtained by evaporation and for the ground single crystals of $(n\text{-Bu})_4N[Pt(dipic)Cl]\cdot 0.5H_2O$ (31 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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