Inorg. Chem. **2004**, *43*, 72–78

Inorganic Chemistry

Article

Synthesis of $\mathrm{Pt(dpk)Cl_4}$ and the Reversible Hydration to $\mathrm{Pt(dpk\text{-}O\text{-}OH)Cl_3 \cdot H\text{-}phenCl}$: X-ray, Spectroscopic, and Electrochemical Characterization

Katherine N. Crowder, Stephanie J. Garcia, Rebekah L. Burr, J. Micah North, Mike H. Wilson, Brian L. Conley, Phillip E. Fanwick,[†] Peter S. White,[‡] Karl D. Sienerth,* and Robert M. Granger, II*

Chemistry Department, Elon University, Elon, North Carolina 27244, and Department of Chemistry, Sweet Briar College, Sweet Briar, Virginia 24595

Received September 18, 2003

We report on the synthesis of a platinum(IV) compound containing a di-2-pyridyl ketone (dpk) ligand that is stable both in its anhydrous form $[\mathrm{Pt(dpk)Cl_4}]$ (**1**) and in its hydrated form $[\mathrm{Pt(dpk\text{-}O\text{-}OH)Cl_3}]\cdot$H-phenCl (**2**). The crystal structure of the hydrated form shows that one of the hydroxide groups from the resulting *gem*-diol has undergone a cyclometalation/condensation reaction resulting in an oxygen atom directly coordinated to the Pt(IV) center and the formation of H-phenCl. We correlate our physical data with predictions made by molecular modeling, and we propose an explanation for the unusual activity found for this dpk ketone. Spectroscopic and solubility studies are presented here, as well. Electrochemical studies of **1** indicate that it undergoes a highly irreversible reduction at a potential of about –0.45 V vs $\mathrm{Ag^+/Ag}$ in $\mathrm{CH_3CN}$ and that the irreversibility is likely due to an EC mechanism, the nature of which is currently under further investigation. Another distinct redox pair, apparently reversible, appears at a potential of about –1.1 V vs $\mathrm{Ag^+/Ag}$.

Introduction

Investigation into the properties of the ligand di-2-pyridyl ketone (hereafter called dpk) was first reported in 1967 by Osborne and McWhinnie. Their work focused on the coordination of dpk in copper(II) halide and perchlorate complexes.[1] In the time since this first study, metal ion complexes with dpk have been reported for nickel(II),[2−10] iron(II) and iron(III),[2,4,6] manganese(II),[2,8] uranium(VI),[10] cobalt(II) and cobalt(III),[2,4,6,8,11] zinc(II),[2,8,10,12] cadmium(II),[12] mercury(II),[12] copper(I) and copper(II),[2,8−10,13−18] chromium(III),[14] ruthenium(II),[14,19] rhenium(I) and rhenium(V),[20,21] silver(I),[22] antimony(III),[23] palladium(II),[24] gold(III),[24] and

---

* To whom correspondence should be addressed. Electrochemical and spectroscopic studies matters should be addressed to K.D.S. at Elon University. E-mail: sienerth@elon.edu. Tel: 336-278-6217. Fax: 336-278-6258. Synthesis matters should be addressed to R.M.G. at Sweet Briar College. E-mail: rgranger@sbc.edu. Tel: 434-381-6403. Fax: 434-381-6488.

[†] Author to whom questions regarding the X-ray structure of compound **2** should be addressed at Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907-2084.

[‡] Author to whom questions regarding the X-ray structure of compound **1** should be addressed at Department of Chemistry, CB#3290 Venable Hall, University of North Carolina, Chapel Hill, NC 27599-3290.

(1) Osborne, R. R.; McWhinnie, W. R. *Inorg. Phys. Theor.* **1967**, 2075−2078.
(2) Feller, M. C.; Robson, R. *Aust. J. Chem.* **1968**, *21*, 2919−2927.
(3) Feller, M. C.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 1997−2003.
(4) Bakker, I. J.; Feller, M. C.; Robson, R. *J. Inorg. Nucl. Chem.* **1971**, *33*, 747−754.
(5) Ortego, J. D.; Perry, D. L. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3031−3034.
(6) Rattanaphani, V.; McWhinnie, W. R. *Inorg. Chim. Acta* **1974**, *9*, 239−244.
(7) Perry, D. L.; Vaz, C.; Wendlandt, W. W. *Thermochim. Acta* **1974**, *9*, 76−78.
(8) Fischer, B. E.; Sigel, H. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2127−2132.
(9) Wang, S.; Richardson, J. W., Jr.; Briggs, S. J.; Jacobson, R. A.; Jensen, W. P. *Inorg. Chim. Acta* **1986**, *111*, 67−72.
(10) Ishaq, M.; Baghlaf, A. O.; Al-Mouty, A.; Al-Dousry, M. *J. Chem. Soc. Pak.* **1992**, *14*, 115−117.
(11) Ortego, J. D.; Waters, D. D.; Steele, C. S. *J. Inorg. Nucl. Chem.* **1974**, *36*, 751−756.
(12) Ortego, J. D.; Upalawanna, S.; Amanollahi, S. *J. Inorg. Nucl. Chem.* **1979**, *41*, 593−595.
(13) Basu, A.; Saple, A. R.; Sapre, N. Y. *J. Chem. Soc., Dalton Trans.* **1987**, 1797−1799.
(14) Sommerer, S. O.; Jensen, W. P.; Jacobson, R. A. *Inorg. Chim. Acta* **1990**, *172*, 3−11.
(15) Bhaduri, S.; Sapre, N. Y.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1991**, 2539−2543.
(16) Kavounis, C. A.; Tsiamis, C.; Cardin, C. J.; Zubavichus, Y. *Polyhedron* **1996**, *15*, 385−390.
(17) Goher, M. A. S.; Al-Salem, N. A.; Mak, T. C. W. *Polyhedron* **2000**, *19*, 1465−1470.
(18) Parker, O. J.; Aubol, S. L.; Breneman, G. L. *Polyhedron* **2000**, *19*, 623−626.
(19) Basu, A.; Kasar, T. G.; Sapre, N. Y. *Inorg. Chem.* **1988**, *27*, 4539−4542.

10.1021/ic035102f CCC: $27.50

platinum(II),[24,25] and to date, there has been only one study on M(IV), which focused on tin(IV).[26] Initially, it was believed that the ligand dpk had the ability to coordinate as a bidentate ligand to the metal ion via one of two modes: either through the two nitrogen atoms located in the pyridine rings or through one pyridyl nitrogen and the carbonyl oxygen. Although Osborne and McWhinnie reported that their complexes bound through one ring nitrogen and the carbonyl oxygen,[1] research by Feller and Robson since has concluded that the coordination was actually through the two nitrogen atoms.[2,3] Current evidence suggests that in aqueous solution coordination through the pyridyl ring nitrogens is favored, and the majority of metal complexes with dpk are coordinated in this way. By N,N-coordination, π-back-bonding is possible through electron delocalization onto the pyridine rings and the electronegative oxygen atom of the ketone group. After the initial coordination with the metal ion, the dpk ligand is subject to nucleophilic attack by water in the presence of many different metal ions, including but not limited to Ni(II), Co(III), Cu(II), Cr(III), Sb(III), Pd(II), Au(III), and Pt(II).[22] It is thought that the oxidation state of the metal has an effect on the hydrolysis of the dpk ligand, as complexes with Ag(I) exist in the ketone form only[22] whereas dpk compounds containing metals in higher oxidation states often contain the hydrated form of the ligand.[2,3,6,8,16,18,20,25] The addition of water can form a *gem*-diol on the carbonyl carbon of the dpk ligand.[2−4,9,11,14,16,18] Also several transition metal complexes have been reported that exist in either the hydrate form[1−5,8,9,11,12,15,18−20,24] or as the resulting oxo anion from the deprotonation of the hydrated form.[2,4,8] While several groups have reported on the synthesis of complexes containing one dpk ligand, little focus has been devoted to properties and characteristics of these 1:1 metal to ligand compounds.[1,2,6,8,10,12,21−24] However, a great deal of attention has been given to the bis complexes due to some unusual behavior of the dpk ligand.[1−6,8−12,14,19−20,22,24] In most reported solid-state structures of metal−dpk complexes where the ratio of metal to ligand is 1:2, the structures show that one of the oxygen atoms from the newly formed *gem*-diol on the ligand cyclometalates with the metal center, making the ligand anionic and tridentate (N,O,N′) in character.[2−4,6,9,11,12,14,18,20,23,24] The dimensions of the ligand and the tetrahedral angle about the *gem*-diol carbon requires that the six-membered ring formed from the carbonyl carbon, two carbons, and two nitrogens from the pyridine rings and the metal center be stabilized in either the chair or boat type configuration. The observed boat configuration places one of the oxygen atoms from the *gem*-diol carbon close to the fifth position of an octahedral stereochemistry about the metal atom. The second dpk ligand on the metal center functions in the same way to complete the distorted octahedral trans N_4O_2 coordination sphere around the central metal atom.[14,18,20,25] We report the synthesis and structures of the first dpk complexes involving a transition metal in the +4 oxidation state; only one other dpk complex with a metal (Sn) in the +4 state has been reported.[26] Furthermore, we were able to obtain crystal structures for both the anhydrous form and the hydrated form of the Pt(IV) dpk compound, thus allowing us to compare directly the two structures. Last, we have an X-ray structure of a cyclometalated tridentate (N,O,N′) dpk ligand for a complex in which the metal to ligand ration was 1:1 instead of the more prevalent 1:2 ratio found in the literature.

We have also conducted preliminary investigations of the electrochemistry of the Pt(IV) dpk compound in acetonitrile. A substantial amount of research has been devoted to the study of platinum complexes as homogeneous catalysts[27−31] and as possible future anticancer agents against cisplatin-resistant tumors.[32−35] Much research has focused on reductive eliminations from six-coordinate Pt(IV) complexes resulting in the formation of new C−C, C−O, and C−H bonds.[28−31] Similarly, the broad range of anticancer activity of Pt(IV) complexes, while not thoroughly studied or understood, appears to relate to the range of coordinating behavior of the ligands (e.g., axial vs equatorial). Moreover, the specific cytotoxicity of a Pt(IV) complex is generally believed to be dependent upon preliminary reduction to Pt(II) prior to undergoing cytotoxic behavior.[32−35] Therefore, the redox chemistry of Pt(IV) complexes is of great interest because understanding such behavior can help elucidate the mechanism of catalytic reactions involving Pt(IV) as well as the mechanisms of cytotoxicity for in-vitro and in-vivo reactions. Electrochemistry is a valuable tool for gaining insight into redox behavior of electroactive species, but surprisingly, there are few reports of electrochemical measurements with the known dpk complexes.[21,36] We report some preliminary electrochemical results and compare them to those found in the literature.

---

(20) Bandoli, G.; Dolmella, A.; Gerber, T. I. A.; du Preez, J. G. H.; Kemp, H. J. *Inorg. Chim. Acta* **1994**, *217*, 141−147.

(21) (a) Bakir, M.; McKenzie, J. A. M. *J. Electroanal. Chem.* **1997**, *425*, 61−66. (b) Bakir, M.; McKenzie, J. A. M. *J. Chem. Soc., Dalton Trans.* **1997**, 3571−3578.

(22) Yang, G.; Zheng, S.-L.; Chen, X.-M.; Lee, H. K.; Zhou, Z.-Y.; Mak, T. C. W. *Inorg. Chim. Acta* **2000**, *303*, 86−93.

(23) Alonzo, G.; Bertazzi, N.; Maggio, F.; Benetollo, F.; Bombieri, G. *Polyhedron* **1996**, *15*, 4269−4273.

(24) Annibale, G.; Canovese, L.; Cattalini, L.; Natile, G.; Biagini-Cingi, M.; Manotti-Lanferdi, A. *J. Chem. Soc., Dalton Trans.* **1981**, 2280−2287.

(25) Ferreira, A. D. Q.; Bino, A.; Gibson, D. *Inorg. Chim. Acta* **1997**, *265*, 155−161.

(26) Perry, D. L.; Margrave, J. L.; Bonnell, D. W. *Inorg. Chim. Acta* **1985**, *101*, L1−L4.

(27) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley-Interscience: New York, 1992.

(28) Crumpton, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2000**, *122*, 962−963.

(29) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 1456−1465.

(30) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576−2587.

(31) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **2002**, *124*, 2839−2852.

(32) Choi, S.; Filotto, C.; Bisanzo, M.; Delaney, S.; Lagasee, D.; Whitworth, J. L.; Jusko, A.; Li, C.; Wood, N. A.; Willingham, J.; Schwenker, A.; Spaulding, K. *Inorg. Chem.* **1998**, *37*, 2500−2504.

(33) Choi, S.; Mahalingaiah, S.; Delaney, S.; Neale, N. R.; Masood, S. *Inorg. Chem.* **1999**, *38*, 1800−1805.

(34) Wong, E.; Giandomenico, C. M. *Chem. Rev.* **1999**, *99*, 2451−2466.

(35) Lee, Y.; Lee, S. S.; Kim, K. M.; Lee, C. O.; Sohn, Y. S. *J. Med. Chem.* **2000**, *43*, 1409−1412.

(36) Tong, M.-L.; Lee, H. K.; Tong, Y.-X.; Chen, X.-M.; Mak, T. C. W. *Inorg. Chem.* **2000**, *39*, 4666−4669.

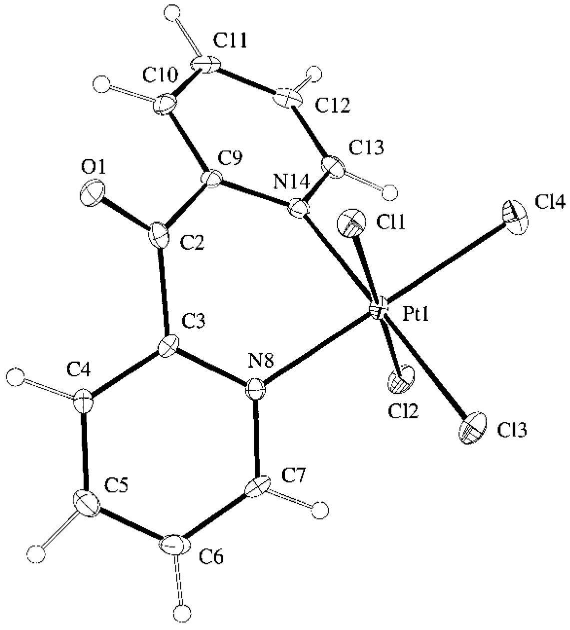

Figure 1. Ortep of compound **1**. Select bond angles: N(14)−Pt−N(8) 88.62°; C(3)−C(2)−C(9) 120.00°. Selected bond length: C(2)−O(1) 1.225 Å.

Table 1. Elemental Analysis (%) of Compound **1**

element	predicted	obtained
C	25.35	25.32
H	1.55	1.53
N	5.38	5.37
Pt	37.44	37.22

Experimental Section

Synthesis of Tetrachloro(di-2-pyridyl ketone)platinum(IV), [Pt(dpk)Cl$_4$]. The complex [Pt(dpk)Cl$_4$] **(1)** was isolated as a bright yellow solid from an aqueous solution of K_2PtCl_6 and a 1.2 molar excess of the ligand dpk (dpk = di-2-pyridyl ketone) with an 89% yield based on K_2PtCl_6. Compound **1** was presumably synthesized in its hydrated form, but it is readily dehydrated by recrystalization from anhydrous ether and anhydrous acetone followed by drying under vacuum at 75 °C. Elemental microanalysis[37] of **1**, after recrystallization from anhydrous acetone and ether, confirmed the formula [Pt(dpk)Cl$_4$]. See Table 1 for elemental results. The structure of **1** was determined by X-ray crystallography (see Figure 1). Crystals suitable for X-ray diffraction were obtained by slow diffusion from anhydrous DMSO and anhydrous ether. The DMSO was dried over 3 Å sieves and transferred to freshly dried 3 Å sieves twice more before use. The slow diffusion chamber was set up in a drybox and sealed before moving it to a storage cabinet free of vibrations.

Synthesis of Trichloro(hydroxy-di-2-pyridylmethoxy)platinum(IV) Hydrochloride, [Pt(dpk-O-OH)Cl$_3$]·H-phenCl. In an attempt to produce [Pt(dpk)(phen)Cl$_2$][Cl]$_2$, compound **1** was placed in DMSO with 1,10-phenanthroline. Initial spectroscopic data had indicated that a compound with the formula [Pt(dpk)(phen)Cl$_2$][Cl]$_2$ had indeed been produced; however, when crystals of this compound were analyzed by X-ray diffraction, the complex [Pt(dpk-O-OH)Cl$_3$]·H-phenCl (**2**-phen) was indicated. Alternatively, [Pt(dpk-O-OH)Cl$_3$] ·HCl (**2**) is obtained as a bright yellow solid from an aqueous solution of K_2PtCl_6 and the ligand dpk, or **2** can be produced by exposing compound **1** to water, with a yield of approximately 90%. Note, crystals of **2**-phen suitable for X-ray diffractions were obtained by slow diffusion from DMSO and ether in which no care had been taken to dry the DMSO. We speculate that we were successful in obtaining an X-ray structure of **2**-phen because the presence of the H-phen moiety inhibited the establishment of an equilibrium between the hydrated and anhydrous forms of this Pt−dpk complex. The X-ray structure of **2**-phen along with selected bond angles and bond lengths is seen in Figure 2.

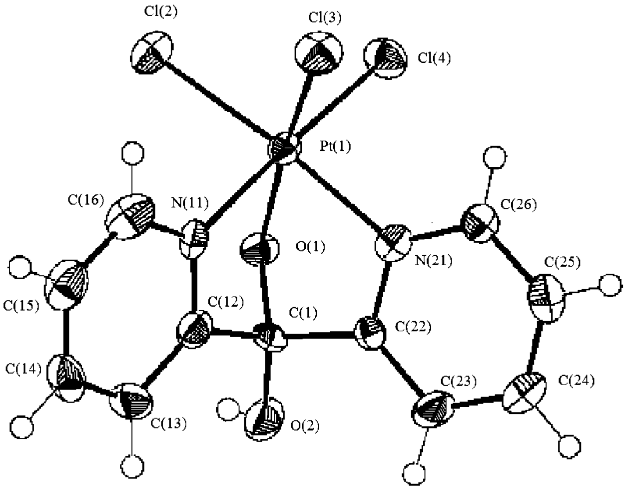

Figure 2. Ortep of compound 2. Select bond angles: N(21)−Pt−N(11) 89.9°; Cl(4)−Pt−Cl(2) 92.55°; Cl(2)−Pt−N(12) 89.07°; Cl(1)−Pt−N(22) 91.01°; Pt−O(1)−C(1) 100.99°; O(1)−C(1)−O(2) 111.89°; C(21)−C(1)−C(11) 106.49°. Selected bond lengths: C(1)−O(2) 1.376 Å; C(1)−O(1) 1.419 Å; Pt−O(1) 2.008 Å.

X-ray Analysis of Tetrachloro(di-2-pyridyl ketone)platinum(IV), [Pt(dpk)Cl$_4$].[38−42] The intensity data were collected on a Bruker SMART 1K diffractometer, using the ω scan mode. The h, k, l ranges used during structure solution and refinement were the following: $h_{\min,\max}$, −14, 14; $k_{\min,\max}$, 0, 11; $l_{\min,\max}$, 0, 14. Other X-ray data are as follows: no. of reflections measured, 11 598; no. of unique reflections, 2488; no. of reflections with $I_{\mathrm{net}} > 3.0\sigma(I_{\mathrm{net}})$, 2074; merging R-value on intensities, 0.034; program for absorption correction, SADABS; space group and cell dimensions, monoclinic, $P2_1/c$, $a = 11.92680(20)$ Å, $b = 9.97890(20)$, $c = 11.85990(20)$ Å, $\beta = 91.414(1)$°, $V = 1411.09(4)$ Å^3; empirical formula, $PtCl_4C_{11}H_8N_2O$.

Cell dimensions were obtained from 6936 reflections with 2θ angle in the range 5.00−50.00°. Other data: crystal dimensions, 0.20 × 0.15 × 0.15 mm; fw = 521.09; $Z = 4$; $F(000) = 965.65$; $D_{\mathrm{calc}} = 2.453$ Mg m^{-3}; $\mu = 10.65$ mm^{-1}; $\lambda = 0.710\,73$ Å; $2\theta(\max) = 50.0$°.

X-ray analysis of Trichloro(hydroxy-di-2-pyridylmethoxy)platinum(IV), [Pt(dpk-O-OH)Cl$_3$]·H-phenCl. The intensity data were collected on a Enraf-Noniuis CAD4 diffractometer[43] using the $\omega-2\theta$ scan mode. The h, k, l ranges used during structure solution and refinement were the following: $h_{\min,\max}$, −10, 0; $k_{\min,\max}$, −10, 11; $l_{\min,\max}$, −24, 25. Other X-ray data are as follows: no. of reflections measured, 6061; no. of unique reflections, 5669; no. of

---

(37) MidWest MicroLabs, Indianapolis, IN.

(38) Johnson, C. K. *Technical Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976 (ORTEP plotting software).

(39) Motherwell S. *Pluto Plotting Software*; University Chemical Laboratory: Cambridge, U.K., 1978.

(40) Le Page, Y. *J. Appl. Crystallogr.* **1988**, *21*, 983−984.

(41) Le Page, Y.; Gabe, E. J. *J. Appl. Crystallogr.* **1979**, *12*, 464−466.

(42) Larson, A. C. *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 291.

(43) *CAD4 Operations Manual*; Enraf-Nonius: Delft, The Netherlands, 1977.

reflections with $I_{net} > 3.0\sigma(I_{net})$, 4767; merging *R*-value on intensities, 0.031; space group and cell dimensions, monoclinic, $P\bar{1}$,[44] $a = 8.232(1)$ Å, $b = 8.714(1)$ Å, $c = 19.097(2)$ Å, $\alpha = 100.35(1)°$, $\beta = 95.19(1)°$, $\gamma = 115.12(1)°$, $V = 1198.6$ Å^3. For $Z = 2$ and fw = 719.33, the calculated density is 1.99 g/cm^3.

Empirical formula: $C_{23}H_{18}Cl_4PtN_4O_2$.

Electrochemistry. Drybox. All electrochemical experiments were conducted in a Labconco drybox with a dual-chamber dynamic drying system. While water levels were not quantitatively measured, a qualitative indication was provided by noting that exposed P_2O_5 remained unchanged as a loose powder for up to 1 week inside the drybox.

Materials entering the antechamber were subjected to, at minimum, the following procedure: 30 min of evacuation, subsequent nitrogen fill, followed by another 30 min evacuation. Items of greater surface area such as the stir plate and Kimwipes were treated similarly, followed by further antechamber evacuation for a minimum of 48 h.

Glassware and Cell Components. Before being placed in the drybox antechamber, all glassware was rinsed 5 times with DI water, rinsed with ethanol, and air-dried. It was then dried at 220 °C for >12 h before being transferred directly to the antechamber while still hot.

All components of the electrochemical cell were rinsed with DI water and ethanol and dried under vacuum for >12 h at 75 °C.

Solutions. Tetrabutylammonium hexafluorophosphate (TBAP; Sigma-Aldrich, 98%), silver nitrate (Fisher Scientific, 99%), and compound **1** were dried for 1 week in a vacuum oven at 75 °C. Appropriate masses of each solid were weighed and placed into volumetric flasks and placed back into the vacuum oven overnight before being taken into the drybox antechamber.

Molecular sieves (3 Å, Fisher), activated at 220 °C, were used to dry the solvent, acetonitrile (CH_3CN, Fisher, HPLC grade), in the following manner. Sieves were placed into each of six 500 mL Boston round bottles (Fisher), which were then placed in the hot oven (220 °C). After 12 h, two of the bottles were transferred while hot to a glovebag, which was purged with dry nitrogen, and then the bottles were filled with CH_3CN. After an additional 24 h, two more bottles (now having been at 220 °C for ≥36 h) were transferred hot to the glovebag, and the 1× dried CH_3CN was transferred to the second set of bottles. This procedure was repeated for the third set of bottles (dried for ≥60 h), and the solvent was ready for use after a final 24 h period.

Solutions of **1** were made using 0.1 M TBAP in 3× dried CH_3CN.

Electrochemical Experiments. All electrochemical experiments were conducted using a Princeton Applied Research Versastat. The working electrode used for cyclic voltammetry was a 3 mm diameter glassy carbon disk electrode (BAS), polished using 0.5 μm alumina. The counter electrode consisted of a platinum metal coil submersed in TBAP solution in a fritted compartment. The reference was a silver wire in a 0.01 M silver nitrate solution in dry acetonitrile contained in a Vycor-fritted compartment. Counter electrode frits were cleaned using 1:1 HNO_3-H_2O solution followed by rinsing with DI water and ethanol and drying at 220 °C >12 h.

Spectroscopy. UV−vis spectra were taken using a Hewlett-Packard 8452A diode array spectrophotometer. All FTIR spectra were collected on a Nicolet Magna 560 FT-IR as KBr pellets. Solvents employed for solubility studies were used as received, except for the acetonitrile and dimethyl sulfoxide (DMSO), the treatment of which is described above.

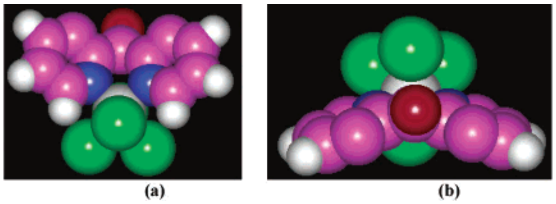

Figure 3. Spaced-filled molecular modeling (Hyperchem) of [Pt(dpk)Cl$_4$]: (a) view from bottom of molecule looking up at the dpk ligand; (b) top view of molecule looking down at the carbonyl oxygen. Molecular modeling also predicts a steric strain on the carbonyl carbon of **1**. The Hyperchem-energy minimized structure of **1** shows the py−CO−py bond angle at 106°. This is consistent with the X-ray structure for the hydrated form **2** with a py−CO−py bond angle of 106.49° but inconsistent with the X-ray structure of **1**.

Results and Discussion

X-ray Crystallography. Metal-promoted hydration of the ketone in the dpk ligand has received interest for some time as the ligand has this ability to react after initial coordination to a transition metal ion. A point of additional interest regarding this hydration stems from that fact that ketones do not normally hydrate to a significant degree in the absence of strong electron-withdrawing flanking groups. In the case of metal-chelated dpk ligands, the hydrated form of dpk, adopts a pyridyl−carbonyl carbon−pyridyl bond angle (py−CO−py) that is typically in the range of 107°. This is also the case for compound **2**. In compound **2** the bond angle for C(21)−C(1)−C(11) (py−CO−py) is 106.49°. For this reason, many research groups have erroneously proposed that the metal-promoted hydration of the ketone in the dpk ligand is solely a result of steric strain on the carbonyl carbon, a desire of the carbonyl carbon to change from sp^2 hybridization to sp^3 hybridization to better accommodate the smaller bond agle.[2,3,6,16,18,20,25] An explanation for this behavior based on molecular models is that the bond strain and steric interaction within the system of the carbonyl carbon causes a transition from an sp^2 → sp^3 orbital hybridization upon ligation of the pyridyl rings.[2,3,6,16,18,20,25] In other words, the addition of the carbonyl spacer between the two pyridyl rings causes the chelation angle to be too large. As a result, the pyridyl rings fold up and pull in. This causes the bond angle on the carbonyl carbon (py−CO−py) to be strained from a typical 120° for sp^2 hybridization to angles closer to sp^3 hybridization. This is demonstrated by the observed bond angle (106.49) in the hydrated form of our compound **2**. Molecular modeling of compound **1** further supports this conclusion. Figure 3 shows the energy-minimized structure of **1** using Hyperchem (Hypercube, Inc.). In this structure, the py−CO−py bond angle is 106° indicating a steric strain on the carbonyl carbon. However, this is inconsistent with the X-ray structure of **1,** which shows the py−CO−py bond angle at exactly 120.00°. Additionally, Bino et al.[25] reported a Pt(II) dpk compound where the dpk remained anhydrous. In that case also, the py−CO−py bond angle was consistent with an sp^2-hybridized carbon (118.9(9)°).

It is also interesting to note the Pt(1)−O(1) bond distance is 2.008 Å for compound **2**. This is consistent with the M−O bond distances (mean of 1.995 Å) reported for the cyclometalated *gem*-diols formed by other metal dpk com-

---

(44) Walker N.; Stuart D. *Acta Crystallogr.* **1983**, *A39*, 158.

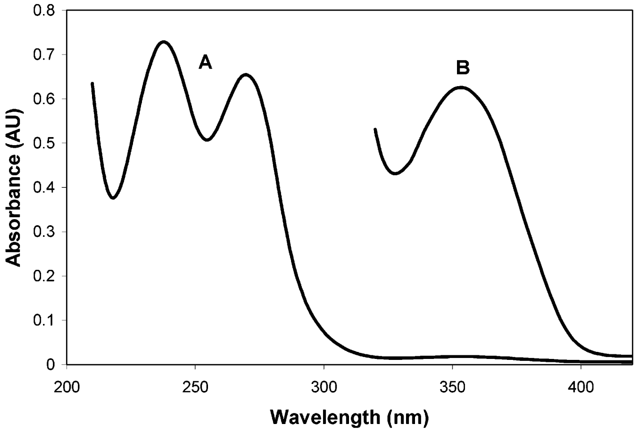

Figure 4. Ultraviolet−visible spectrum of free dpk in dry acetonitrile. The concentration of dpk is 0.0828 mM (A) and 4.17 mM (B).

Table 2. Absorption Maxima and Molar Absorptivities for Free dpk in Various Solvents

solvent	Snyder polarity index[44]	abs max, nm (ϵ, L/(mol cm))
cyclohexane	0	236 (9960), 268 (7950), 358 (150)
methyl *tert*-butyl ether (MTBE)	2.9	236 (9710), 268 (8040), 358 (144)
acetonitrile	6.2	238 (8760), 270 (7860), 354 (147)
DMSO[a]	6.5	---, 272 (8290), 354 (150)
water	9	242 (7750), 276 (9250), 342 (207)

[a] Note that the UV cutoff for DMSO is 260 nm.

plexes.[9,20,23] In each of those cases, however, the ratio of metal to ligand was 1:2. In most cases where the metal:dpk ratio is 1:1, the ketone on the dpk ligand either does not hydrate at all or it remains a true *gem*-diol. One possible exception to this was reported with a copper(II) dpk compound in which the ketone had reacted with a methanol molecule in a fashion similar to hydration.[16] In that case, the methoxy oxygen appeared to cyclometalate and coordinate with the metal center in an axial position. However, the Cu−O bond distance was notably long, at 2.497 Å, and the methyl−oxygen bond remained intact, giving that oxygen a valance of 3. Therefore, it is reasonable to assume only minor interaction between the copper and the cyclometalated oxygen occurred. Conversely, then, a relatively strong Pt−O interaction is indicated in **2** reported herein.

Spectroscopy and Solubility. Figure 4 shows a UV−visible spectrum of free dpk (not coordinated with Pt(IV)) in dry CH_3CN. Two strong bands are observed at 238 and 270 nm, and a third very weak band is observed at 356 nm. Table 2 provides absorption maxima and molar absorptivities (ϵ) for free dpk in various solvents ranging in polarity.

It is clear that the two higher energy UV bands, which likely arise from $\pi \rightarrow \pi^*$ transitions associated with the π electrons in the pyridyl rings and on the carbonyl group, undergo the expected bathochromic shift with increasing solvent polarity. The band around 238 nm exhibits a distinct hypochromic shift, but the one at around 270 nm exhibits neither hypo- nor hyperchromicity. Also as expected, the weaker near-UV band at 354 nm, probably due to the n $\rightarrow \pi^*$ transition associated with the nonbonding electrons on the pyridyl nitrogen, undergoes a hypsochromic shift with increasing solvent polarity. This assignment is further supported by the fact that the band at 354 nm is no longer seen after coordination of the dpk ligand to a metal. The 354 nm band exhibits a general hyperchromic shift, with the exclusion of the most nonpolar solvent, cyclohexane.

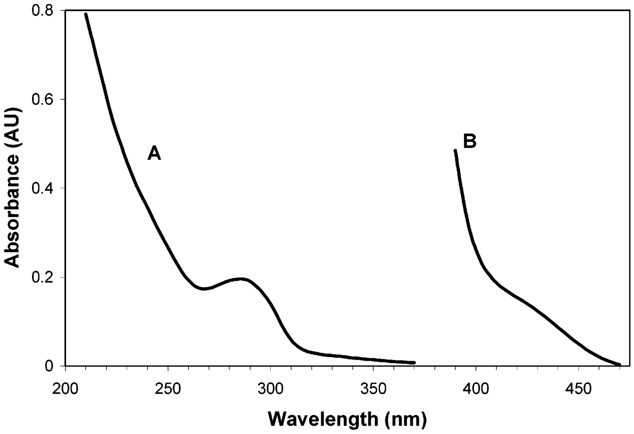

Figure 5. UV−visible absorption spectra for $Pt(dpk)Cl_4$ (**1**) in dry acetonitrile. Concentrations of the complex were 0.0193 mM (A) and 2.57 mM (B).

Table 3. Absorption Maxima and Solubility of **1** in Various Solvents

solvent	Snyder polarity index	abs max, nm (ϵ, L/(mol cm))	solubility (mM)
cyclohexane	0		0
isooctane[a]	0.4	275-295? (weak shldr)	6×10^{-4}
MTBE[a]	2.9	288	5×10^{-3}
THF[a]	4.2	288, 425 (shldr)	2.2
ethanol[a]	5.2	288 (weak shldr)	9×10^{-3}
acetonitrile	6.2	286 (9690), 425 (shldr)	3.56
DMSO	6.5	286 (11442), 425 (shldr)	>45
methanol[a]	6.6	~280 (weak shldr)	0.13
water[a]	9.0	~290 (weak shldr)	3×10^{-3}

[a] Note: calibration curves were not prepared using these solvents. The absorption maxima were determined from spectra obtained with saturated solutions of **1** in the given solvent, and solubility was estimated using the calibration curves obtained in acetonitrile and DMSO.

Bakir and McKenzie[21] observed little change in the two higher energy $\pi \rightarrow \pi^*$ transitions upon coordination of dpk with Re(I) but noted that the weaker n $\rightarrow \pi^*$ absorption disappeared on coordination with the metal and was replace by the appearance of a relatively high intensity metal-to-ligand charge transfer band at around 388 nm, presumably because the lone pairs on the pyridyl nitrogens were involved in the coordination process. Other researchers have observed similar results with pyridyl−carbonyl ligands.[46,47] In the case of $Pt(dpk)Cl_4$ (**1**), however, significant differences were observed between the UV−visible spectra of the complex and of free dpk. Figure 5 shows the UV−visible spectrum of **1**, and Table 3 presents absorption maxima and solubility data. Only one distinct band is observed below 300 nm, positioned at 288 nm, almost as a shoulder on a rising background, presumably the leading edge of a very intense absorption peak. An extremely weak absorption is observed as a shoulder at around 425 nm. This latter band is of too low intensity (ϵ < 50 L/(mol cm)) to be due to a charge

---

(45) Snyder, L. R. *J. Chromatogr. Sci.* **1978**, *16*, 223.
(46) Tangoulis, V.; Raptopoulou, P.; Terzis, A.; Paschalidou, S.; Perlepes, S. P.; Bakalbassis, E. G. *Inorg. Chem.* **1997**, *36*, 3996−4006.
(47) Paul, P.; Tyagi, B.; Bilakhiya, A. K.; Bhadbhade, M. M.; Suresh, E.; Ramachandraiah, G. *Inorg. Chem.* **1998**, *37*, 5733−5742.

Table 4. Selected IR Bands (cm^{-1}) for Free dpk and Compound **1**[a]

vibration	free dpk	compd **1**
C=O stretch	1681 (vs)	1699 (vs)
py ring stretch	1582 (vs)	1598 (vs)
py ring breathing	992 (s)	970 (vvw) 941 (vw)
CH out-of-plane stretch	660 (s)	662 (vw)

[a] Spectra were obtained as KBr pellets.

transfer event and is possibly the same d−d transition observed in $PtCl_6^{2-}$ giving rise to the yellow color of the complex. Most intriguing is that although polarity has a dramatic effect on solubility of the complex, neither of the absorption bands appears to be affected by it, and the rising background of the intense UV absorption is present with all solvents. Also of interest is the fact that, in general, solubility of **1** increases with solvent polarity, *except* when the solvent is hydrolytic and capable of hydrogen-bonding. Indeed, when placed in water, **1** is notably hydrophobic, behaving as an oily powder on the surface of the water, clinging to the glass sides of the vessel, and increasing the depth of the meniscus in a 1 cm wide test tube by a factor of about 3 compared to pure water. Only with agitation will the powder become wetted, allowing some of it to sink to the bottom of the vessel, apparently having been transformed into the hydrated form **2**.

Selected infrared bands are presented in Table 4. The absorption frequencies for the given free dpk bands are in agreement with previous workers.[36] It is interesting to note that the carbonyl stretching band shifts to a higher energy upon coordination with the Pt(IV) center. The high charge on the metal center results in a significant withdrawal of electron density from the ring π orbitals via the N,N-coordination, and the nonplanar character of the dpk in the anhydrous molecule removes the carbonyl from conjugation, causing a shift in both the carbonyl and the pyridine ring stretches to higher frequencies. This constrained conformation also results in sufficient loss in mobility within the pyridine ring. This is evidenced by the fact that the breathing vibration and out-of-plane C−H stretching are virtually completely quenched for coordinated dpk in compound **1**.

Electrochemistry. Solutions containing 1.0 and 3.0 mM of **1** were used for electrochemical studies. In all cases, the initial potential was +0.20 V vs Ag^+/Ag. Figure 6 shows a typical cyclic voltammogram obtained from a 3.0 mM solution of **1**. Three features are observed in the cathodic sweep, at −0.45, −0.94, and −1.13 V, respectively. On the return sweep, only two distinct features are observed, at −1.07 and +0.77 V. When the potential sweep was reversed at −0.60 V (just after the first reduction peak), the feature at +0.77 V remained. Also, when the potential was swept initially in the anodic direction, the +0.77 V peak was absent (see Figure 7). Clearly the reduction at −0.45 V and the oxidation at +0.77 V are linked, but the large difference in potential indicates a high degree of chemical irreversibility.

A series of studies in which the potential scan rate was varied from 50 to 1000 mV/s were conducted using solutions of **1** ranging in concentration from 1.0 to 3.0 mM in CH_3CN. The peak potential of the first reduction wave was observed to shift to a more negative value with increasing scan rate; similarly, the potential shifted to a more negative value as the concentration increased. Such behavior typically is associated with an electrochemically irreversible process. However, a plot of the peak current vs the square root of the scan rate shows a high degree of linearity ($R^2 = 0.9998$), indicating that the reduction is diffusion controlled and, as such, should be considered to be reversible with respect to electron transfer. Collectively, the electrochemical data appear to indicate that the initial reduction wave follows an EC (electrochemical followed by chemical step) mechanism.

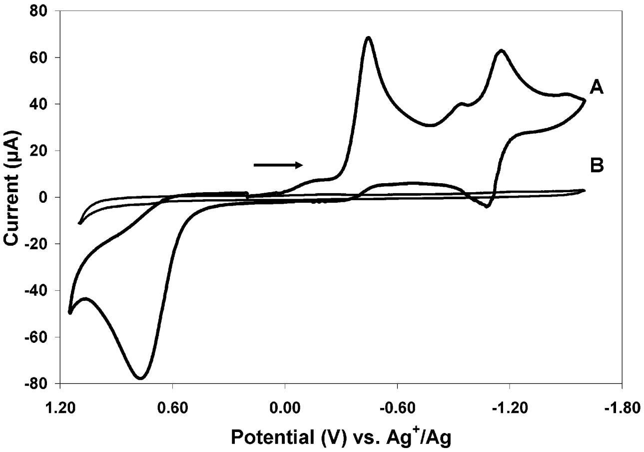

Figure 6. (A) Cyclic voltammogram obtained from a 3.0 mM solution of **1** in CH_3CN: working electrode, glassy carbon disk (3 mm diameter); scan rate, 100 mV/s; 0.20 M TBAP. (B) Blank run (0.20 M TBAP only). Arrow shows the initial direction of scan.

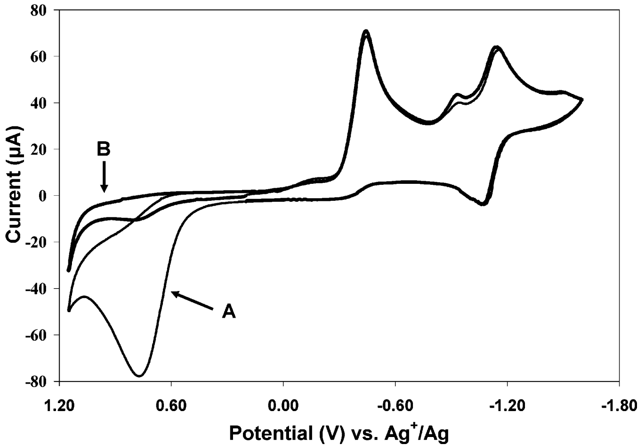

Figure 7. Same conditions as in Figure 6: (A) CV obtained from a 3.0 mM solution of **1** in CH_3CN; (B) initial potential sweep in anodic (positive) direction.

These results are substantially different from those observed by Bakir and McKenzie[21] for a Re(I) dpk complex; their work indicated that the initial reduction (presumably dpk/dpk•$^-$) occurred at a voltage of about −1 V (vs Ag^+/Ag) and that initial reduction was highly reversible. Similarly, Tong et al.[36] observed the quasi-reversible reduction of the dpk ligand at approximately −1.05 V (vs Ag^+/Ag) for a Cu(II) polynuclear complex. In contrast, Paul and coworkers[47] studied polypyridyl−carbonyl complexes of Re(III), and they postulated that the initial irreversible reduction wave they observed was metal-based and the ensuing more reversiblewaves were ligand-based. In the case of **1**, the initial reduction observed at −0.45 V is likely the reduction of the highly charged metal center from Pt(IV) to Pt(II), and the reduction observed at −0.94 V is related to reduction of the dpk ligand. This scenario would also explain the highly irreversible nature of the initial reduction of **1**, in that the chemical step in the EC mechanism could be postulated to be a rearrangement to square planar geometry with an associated loss of either the dpk ligand or two chlorides.

The final reduction/oxidation couple (observed at ca. −1.13 and −1.07 V, respectively) appears to be highly reversible both electrochemically and chemically. Little change in peak potentials were observed for this couple with changing scan rate and concentration, except in the case of the 1.0 V/s scan rate, which can be rationalize by the effect of uncompensated *IR* drop.

The small cathodic peak observed at ca. −0.94 V does not appear to have a reoxidation peak associated with it. On the basis of earlier reports,[21,36] this might be attributed to the reduction of the dpk ligand; it is possible also that it is associated with the reduction of the product of a chemical reaction following the initial reduction (at −0.45 V) or might be due to the formation of a mixed-valence cluster species. If the number of electrons for the initial reduction is presumed to be 2 (as might be expected for a Pt(IV) species), then the height of the intermediate reduction wave suggests an *n* value of less than unity. Altogether, the electrochemistry of **1** is unique and fascinating and bears further investigation; such studies are currently underway.

Conclusions

A novel Pt(IV) diimine complex was synthesized by the aqueous reaction between K_2PtCl_6 and di-2-pyridyl ketone. UV−visible and IR spectra were reasonably well defined, but the electrochemical behavior requires further study. X-ray crystallographic data show that the resulting compound can exist in either the hydrated or anhydrous form. In the hydrated form, the resulting *gem*-diol undergoes a cyclometalation/condensation reaction resulting in an anionic tridentate N−O−N coordination of the dpk ligand to the Pt(IV) center. We propose that, in water-containing solutions, compounds **1** and **2** exist in a rapid equilibrium; however, compound **2** can be stabilized if the resulting proton from the condensation reaction is scavenged in the presence of a weak base. More importantly, the X-ray structure of compound **1** contradicts the supposition that the hydration of the ketone in metal coordinated dpk compounds is driven by steric strain on the carbonyl carbon. In fact the X-ray structure of **1** demonstrates that there is no steric strain on the carbonyl carbon (120.00°). Likewise the X-ray structure of Pt(II) dpk[25] similarly shows little steric strain on the carbonyl carbon with a py−CO−py bond angle of 118.9(9)°. We propose that the driving force for hydration of metal bound dpk is due to induction resulting in a strongly electropositive carbonyl carbon. This conclusion is also supported by the infrared spectra (vide supra). In all of the structures we have seen for metal-bound dpk the pyridyl rings are folded up and out of plane from the carbonyl carbon. This would take the carbonyl out of conjugation with the π-systems of the pyridyl rings. The combined effect of the electron-withdrawing nature of the nitrogens in the pyridyl rings and their subsequent coordination to a strong lewis acid results in a very electropositive carbonyl carbon (see Figure 8). With the carbonyl taken out of conjugation with the π-system of the pyridyl rings, little of this electron deficiency can be replaced by back-bonding from the pyridyl π-system.

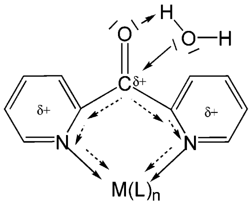

Figure 8. Schematic showing the inductive creation of a partial carbocation at the carbonyl carbon.

Acknowledgment. The authors gratefully acknowledge support from the Jeffress Memorial Trust (Sweet Briar), the J.E. Rawls Professorship for Undergraduate Research in the Sciences (Elon), the Sweet Briar Honors Summer Research Program, and the Elon Undergraduate Research Program.

Supporting Information Available: Crystallographic data for **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035102F