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Square Planar Platinum(II) Complexes: Synthesis, IR Spectroscopy, and Hydration Equilibrium of $Pt^{II}L(CN)_2$ (L = 4,4′-(*t*-Bu)$_2$-2,2′-bpy)

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The hydration behavior of a number of square planar Pt(II) bis(cyano) complexes has been examined, and the limiting stoichiometries are related to the steric requirements of the dinitrogen bidentate ligands coordinated to the metal center. In particular, the IR, UV/vis, and ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopic data for the compound Pt^{II}dtbipy$(CN)_2$ [dtbipy = 4,4′-$\{C(CH_3)_3\}_2$-2,2′-bpy] have been determined and show that, at relative humidities (rh) above ~40%, this complex sorbs five water molecules at room temperature. The sorption process consists of a rapid step in which one H_2O adds to the complex and which appears to be independent of rh, followed by a slower, rh-dependent step leading to the final stoichiometry. In contrast, the analogous 2,2′-bpy complex sorbs no water under these conditions, while the 4,4′-$(CH_3)_2$-2,2′-bpy complex sorbs three water molecules to reach a limiting stoichiometry.

Introduction

Because of their potential utility as antineoplastic chemotherapy agents,[1] the square planar cis complexes of Pt(II), related to the widely used[2] "cis-platin" [$Pt(NH_3)_2Cl_2$], have received a large amount of attention in the recent literature. Recent detailed studies have focused on the binding of Pt(II) to DNA and other biologically significant macromolecules[3] and have elucidated the factors which are involved in inter- and intrastrand binding.[4] On the other hand, the hydration properties of neutral Pt(II) complexes and the relationship between their molecular-level structure and the uptake of water have not been explored in detail and are the focus of the present study. Moreover, the tendency of Pt(II) to effect polymer formation, which is driven by the propensity of the 16-electron system Pt(II) to reach an 18-electron configuration, can be strongly influenced by chemical modification of the ligands surrounding the metal atom. A detailed study of bis(thiocyanate) complexes demonstrating this variability in the tendency for "stacking" into chain polymers has recently been published.[5] Because of the favorable spectroscopic properties of the CN group as a "reporter" ligand, cyano complexes of transition metals have been extensively discussed in the inorganic literature,[6] but no detailed systematic studies of the interaction between the anhydrous forms of these complexes and water have, to the best of our knowledge, been reported. Gillard et al.[7] have discussed the interaction of $Pt^{II}L(CN)_2$ complexes (L = 2,2′-bpy and 1,10-phen) and have cited ^{1}H NMR evidence for the formation of covalent hydrates. In the present study, the synthesis, IR spectroscopic properties, and hydration behavior of a number of square planar *cis*-dicyanoplatinum(II) complexes (of the type $Pt^{II}L(CN)_2$, where L is a bidentate di-N atom donor ligand) are reported and discussed. For reasons to be detailed below, primary attention in the present study is focused on the complex in which L = 4,4′-(*t*-Bu)$_2$-2,2′-bpy (dtbipy), which exhibits unusual reactivity toward solvent molecules, including H_2O, dmso, and *N*-methylpyrrolidone; inter alia.

A number of transition metal complexes of dtbipy, including those of Ru[8] and of Cr, Mo, and W,[9,10] have been reported in the literature. The dtbipy bis(cyano)platinum(II) complex has been the subject of a previous study by Che et al.,[11] who focused on the excimeric emission of this complex in 1,2-dichloroethane solutions. The present study was undertaken to elucidate the hydration kinetics and stoichiometry of the neat solid and to contrast this behavior with that of related $Pt^{II}L(CN)_2$ complexes, some of which may have potential antineoplastic activity in in vivo systems. In particular, because of the significant steric effects associated with the *t*-Bu side chain on an otherwise nearly planar bidentate dinitrogen donor ligand, the Pt^{II}dtbipy$(CN)_2$ complex provides a unique opportunity to distinguish between steric and electronic effects in the solvation properties of these square planar group VIII pseudohalide complexes.

Experimental Section

(a) Synthesis of the Complexes. 4-*tert*-Butylpyridine was obtained from Aldrich Chemical Co. and used as received. The 4,4′-(*t*-Bu)$_2$-2,2′-bpy (dtbipy) ligand was synthesized using the method of Badger and Sasse,[12] as modified by Hart and Newbery.[13] The pyridine was refluxed with activated Raney Ni under dry N_2 for 24 days. The resulting product mass was stirred with benzene, and the insoluble residue was filtered off. The filtrate was dried under vacuum, and the residue dissolved in pentane, followed by chromatography through an Al_2O_3 column. The eluate was vacuum dried and the residue recrystallized to yield a flaky solid (26% yield), which is readily soluble in a variety of organic solvents, including EtOH, dmso, and CH_3CN.

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Table I. UV/Vis Absorbance and CN Stretching Frequencies of Pt[L(CN)$_2$] Complexes[a]

			UV/vis, nm		IR				
L	type	color	KBr	dmso	matrix	ν, cm^{-1}			N at rh ~ 60%
2,2'-bpy		orange	321	322	KBr	2145.0	2135.2		~0
4,4'-(CH$_3$)$_2$-2,2'-bpy	hydrate		317	319	Kel-F	2154.4	2142.8		
					KBr	2150.5	2138.9		
	anhydr				Kel-F	2138.9	2127.4		~3
					KBr	2138		br, u	
5,5'-(CH$_3$)$_2$-2,2'-bpy	hydrate	orange	329		KBr	2143.3	2133.5		~3
4,4'-(COOH)$_2$-2,2'-bpy		bl purple	324, 340 (sh)		KBr	2149.1	2138.3		~1
4,4'-(*t*-Bu)$_2$-2,2'-bpy	hydrate	white	296, 285		Kel-F	2150.3	2143.4	br, u	
					KBr	2149.4	2143.9	br, u	
	anhydr				Kel-F	2144.8	2134.1		~5
					KBr	2143.3	2134.2		

[a] Kel-F = Kel-F mull spectrum; KBr = KBr spectrum; br = broad; u = unresolved; *N* = number of water molecules sorbed at equilibrium; rh = relative humidity. The ligands 2,2'-bpy, 4,4'-(CH$_3$)$_2$-2,2'-bpy, and 4,4'-(*t*-Bu)$_2$-2,2'-bpy all have an electronic absorption band at 283 nm in dmso solutions (~1 × 10^{-3} M) which is also observed for the title compound.

The Pt(II) complex was synthesized by a modification of the method of Kiernan and Ludi.[14] A 0.49 mmol amount of K$_2$Pt(CN)$_4$·3H$_2$O is dissolved in 25 mL of 1 M aqueous trifluoroacetic acid (TFAA). A 0.88-mmol amount of the dtbipy ligand is dissolved in 4 mL of EtOH, and the mixture is then added dropwise to the platinum solution, causing the formation of a white precipitate. The reaction mixture is refluxed for 16 h and cooled to 0 °C, and the slightly pink precipitate is passed through an M-grade sintered filter, washed with TFAA, and dried at room temperature under vacuum. The solid is dissolved in a minimum amount of dmso and reprecipitated by the addition of water. This white solid is centrifuged, and this procedure is repeated two more times. The resulting solid is washed successively with EtOH, acetone, and ether and dried as previously. Yield: 93%. Possibly due to the facile movement of water into and out of the solid (vide infra), elemental analysis data have proven to be unsatisfactory. Three independently recrystallized samples showed C = 41.11%, H = 4.86%, and N = 12.99%. Calcd for Pt[(dtbipy)(CN)$_2$]: C = 42.18%, H = 5.31%, N = 9.84%.

The remaining Pt(II) complexes were obtained similarly and identified by elemental analysis and IR spectroscopy. The UV/vis and pertinent IR data are summarized in Table I. Che et al.[6] have characterized the dihydrate of the L = 4,4'-(CH$_3$)$_3$-2,2'-bpy complex as yellow-green and have reported the CN stretching frequencies (Nujol mull) at 2130 and 2120 cm^{-1}.

(b) Hydration Kinetics and Stoichiometry. The platinum complexes were dried under vacuum at 80 °C to constant weight in screw cap vials, sealed while warm with Teflon lined closures, and cooled to room temperature over P$_2$O$_5$ under vacuum. The cooled samples were introduced into a Labconco glovebox maintained at constant relative humidity (monitored with a Fisher Model 11-661-9 digital humidity gauge) by the use of appropriate saturated salt solutions. The weight gain as a function of time was determined with a Mettler H51AR microbalance which was zeroed and tared prior to each sample run.

(c) Infrared Spectroscopy. Midrange IR spectra were obtained on ca. 0.5 w/w% samples in KBr, using a Mattson Cygnus 100 FTIR spectrometer. Typically 64 sample scans were co-added and ratioed against a corresponding KBr background. Spectra of rigorously anhydrous samples were obtained by transferring the KBr/sample mixture to an evacuable pellet die which had been dried at 80 °C under vacuum, redrying this assembly for 6 h, and then evacuating the sample die (while warm) and pressing a pellet under vacuum. IR spectra were also obtained on mulls in Kel-F stopcock grease, since this permits study of the CN stretching region in a nonreactive matrix while minimizing the migration of water into or out of the sample.

IR data reduction was effected using a Spectracalc curve resolution program, as described earlier,[5] assuming a Lorentzian line shape without further restrictions.

(d) ^{1}H and ^{13}C NMR Spectroscopy. Samples of the ligands and complexes were examined with a Varian 200-MHz spectrometer using dmso-d_6 as solvent. The proton data are referenced to residual dmso ($\delta(^1H)$ = 2.49 ppm) as an internal standard, while the carbon data employed the solvent ($\delta(^{13}C)$ = 39.5 ppm) for this purpose.

(e) ^{195}Pt NMR Spectroscopy. A sample of the title compound in dmf was examined at ambient temperature with a Varian VXR300s spectrometer, equipped with a 5-mm computer-switchable probehead. The spectra were obtained at 64.374 MHz. The chemical shift is referenced to K$_2$PtCl$_4$ in D$_2$O at −1624 ppm and PtenI$_2$ in dmf at −3449 ppm.[16]

(f) UV–Vis Spectroscopy. Samples of the complexes and of the corresponding free ligands were examined as dmso solutions and in KBr matrices using an Aviv Model 14DS spectrometer over the range 200 to 800 nm, with 600 data points in this interval. Spectra were recorded against a solvent or KBr blank, with throughput adjusted to give equal intensity absorption at 800 nm.

Results and Discussion

UV–Vis Spectroscopy. The dtbipy complex has a number of unusual characteristics compared to those of closely related square planar Pt(II) complexes, including color, solubility, and hydration properties, as will be discussed below. In contrast to almost all other Pt(II) complexes examined in this study, the dtbipy complex is unique in that it is essentially colorless (i.e., the microcrystalline powder is white) and does not change in appearance on hydration. The unexpected color of the title compound was a major motivation in efforts to establish the oxidation state of the metal center, as will be detailed below. Due to the hydration–dehydration equilibria (vide infra), elemental analysis results proved unreliable in establishing this parameter unambiguously, and it was thus mandatory to establish the oxidation state of Pt from independent data, as will be discussed. Che et al.[11] have described the complex examined by them as being pale green, but the synthetic product obtained in the present study shows no such characteristic. The remaining complexes appear colored to the naked eye (see Table I), and in particular, the L = 5,5'-(CH$_3$)$_2$bpy complex is noteworthy, since it changes from light yellow to deep orange on hydration. Similar polychromism in other Pt(II) complexes has been noted previously.[17] In particular, the polychromism in Pt(II) thiocyanate complexes, and its connection to the formation of Pt–Pt bonds, has been discussed earlier.[5]

Typical UV/vis spectra of the L = bpy, 4,4'-(CH$_3$)$_2$bpy, and 4,4'-(*t*-Bu)$_2$bpy Pt(II) complexes in dmso are shown in Figure 1. Both the dmso solution and KBr matrix solid UV–vis spectra of the first two complexes are characterized by a clearly resolvable absorbance in the range 300–330 nm, with another weak absorbance being noticeable as a shoulder on the KBr background at 250–270 nm. In contrast, the Pt[dtbipy(CN)$_2$] complex in dmso shows an absorbance at both ~285 and at ~263 nm, with only a weak band at ~317 nm observable at higher concentrations.

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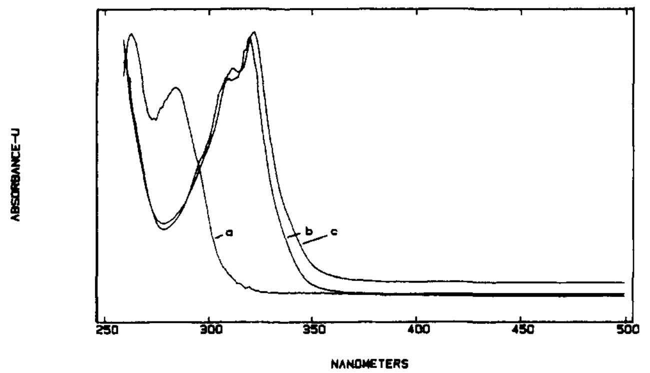

Figure 1. UV/vis absorption spectra for the Pt(L)(CN)$_2$ compounds discussed in the text: (a) L = 4,4'-(*t*-Bu)$_2$-2,2'-bpy, (b) L = 4,4'-(CH$_3$)$_2$-2,2'-bpy, (c) L = 2,2'-bpy, all in dilute dmso solution. The blank was dmso.

The intensity of the 285-nm band observed in dmso solutions of the title complex is concentration dependent. The extinction coefficient of this band is 1.12×10^4 M^{-1} cm^{-1} at infinite dilution. However, all three uncomplexed ligands [2,2'-bpy, 4,4'-(CH$_3$)$_2$-2,2'-bpy and 4,4'-(*t*-Bu)$_2$-2,2'-bpy] show an absorbance at ~285 nm, a position which is insensitive to ring substitution and presumably arises from a $\pi \rightarrow \pi^*$ transition in the ligand as suggested by Zhou and Kostic[7] and by Gidney et al.[7] The observed ϵ of $\sim 1.3 \times 10^4$ M^{-1} cm^{-1} for the dtbipy ligand in dmso is in reasonable agreement with the value of 1.5×10^4 M^{-1} cm^{-1} in CH$_3$CN reported for the 286-nm band by Belser and von Zelewsky[8] in their detailed characterization of dtbipy and its Ru(II) complexes. Che et al.[11] have also reported an intense absorbance at ~245 nm in the acetonitrile solution spectra of the dtbipy complex and comment that the nature of this transition is uncertain. The colors associated with these complexes arise from the "tail" of the absorbance curve in the visible region of the spectrum of the higher frequency (a) band. In the case of the deeply blue purple L = 4-CH$_3$-4'-COOH-2,2'-bpy and 4,4'-(COOH)$_2$-2,2'-bpy complexes, the a band maximum occurs at 324–327 nm. For the yellow-orange L = 2,2'-bpy, 4,4'-(CH$_3$)$_2$-2,2'-bpy, and 5,5'-(CH$_3$)$_2$-2,2'-bpy complexes, this band has blue shifted to ~318 nm, while, in the dtbipy complex, the band maximum is observed at ~296 nm. In the Che et al.[11] study of this complex in acetonitrile solution, a pair of absorbances are observed at 304 and 313 nm and are assigned by these authors to a $\pi \rightarrow \pi^*$ transition, with the possibility that a ligand to metal charge-transfer band lies underneath the tail of this absorbance. The UV–vis data obtained in this study are summarized in Table I.

Infrared Spectroscopy. As expected in the IR spectra of cis square planar bis(cyano) complexes, the CN stretch is observed as two bands, since both the sym and asym stretches are IR active. In the case of L = 2,2'-bipyridine (bpy), these two bands are well resolved, and the ^{13}C component of the lower frequency band is readily seen in the spectra. For those complexes which undergo hydration, IR spectra of both the anhydrous and hydrated forms were obtained in both KBr and Kel-F grease matrices. The two CN stretching frequencies are separated by 7–15 cm^{-1}, and the agreement between the results obtained in the two matrices for the hydration states is reasonably good. Of particular interest is the observation that the center of the "doublet" is red-shifted on hydration by ~14 cm^{-1} for L = 4,4'-(CH$_3$)$_2$-2,2'-bpy, and ~8 cm^{-1} for L = dtbipy, strongly suggesting that the cyano groups are involved in the hydration process, possibly by hydrogen bonding. The IR data are summarized in Table I.

Hydration Stoichiometry and Kinetics. The uptake of water, by a rigorously dried sample of the dtbipy complex, is summarized graphically in Figure 2. Replicate runs on different samples of this complex in the relatively humidity range $53 \leq$ rh $\leq 73\%$ evidence the same limiting stoichiometry (e.g. the uptake of 5 ± 0.1 water molecules) but differ in the quantitative details of the rate of hydration. This observation is not surprising, since, in addition to the relative humidity and temperature affecting the hydration rate, the particle size presumably is also significant but cannot readily be controlled between the different microcrystalline samples examined in this study. However, for a given sample, there are two distinct regimes in the water uptake curve. There appears to be a rapid addition of approximately one H$_2$O within 2–3 min at 24 °C, followed by a slower uptake of an additional four water molecules, which is complete within 100–150 min at the higher rh. At longer times, the stoichiometry appears to remain constant.

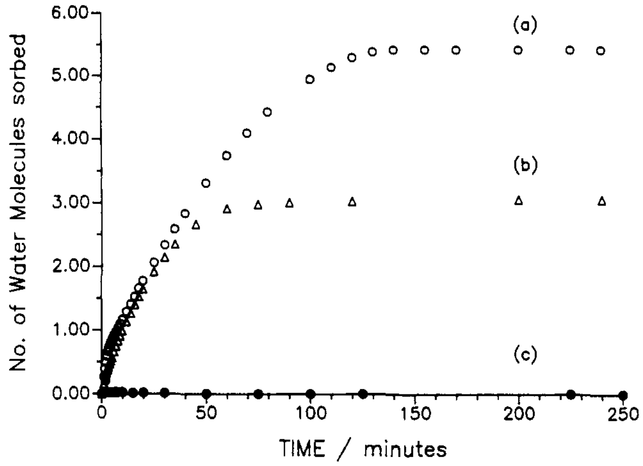

Figure 2. Water uptake by the Pt(L)(CN)$_2$ compounds at 60% relative humidity: (a) L = 4,4'-(*t*-Bu)$_2$-2,2'-bpy; (b) L = 4,4'-(CH$_3$)$_2$-2,2'-bpy; (c) L = 2,2'-bpy.

At relative humidities below rh ~ 38%, the limiting stoichiometry shows that only one H$_2$O is sorbed at ambient temperature. In the relative humidity range $40 \leq$ rh $\leq 55\%$, both the rapid and slow hydration steps can be followed experimentally.

Treatment of the "early" rate data, assuming pseudo-first-order kinetics, leads to a rate for the fast (initial) step which appears to be independent of rh. This rather surprising result is not readily accounted for by a mechanistic model, since the concentration of the vapor-phase water (as reflected in the rh) appears not to be a component of the rate-determining step. On the other hand, at rh $\geq 38\%$, the slower step in the uptake of water is clearly dependent on rh, although—as noted above—the final stoichiometry appears to be independent of the vapor-phase water concentration.

An attempt to fit these data to a first-order reaction is shown in Figure 3, which suggests that both steps are well fit by a semilogarithmic function. At rh = 48.5%, the ratio of the two rates is ca. 120:1, while, at rh = 60%, this ratio is close to 2:1.

The sorption of one H$_2$O by a fast initial step may possibly be rationalized by the coordination of one water molecule to a Pt center, converting the metal from a 16-electron to an 18-electron configuration. However, since water is known to be a relatively poor ligand with respect to Pt, this hypothesis is not very firmly grounded and does not seem to be susceptible very readily to experimental verification, since present attempts to grow diffraction size single crystals incorporating a given number of solvent molecules have proven unproductive.

As noted above, it is probable that some of the water molecules sorbed by the dtbipy complex interact directly with the cyano groups—presumably by hydrogen-bonding ligation—since the CN stretching region of the IR spectra shows consistent differences between the hydrated and anhydrous samples, as summarized in Table I.

The water sorption at about 60% relative humidity by the dtbipy complex is both qualitatively and quantitatively different from the behavior of the analogous bpy and 4,4'-(CH$_3$)$_2$bpy complexes,

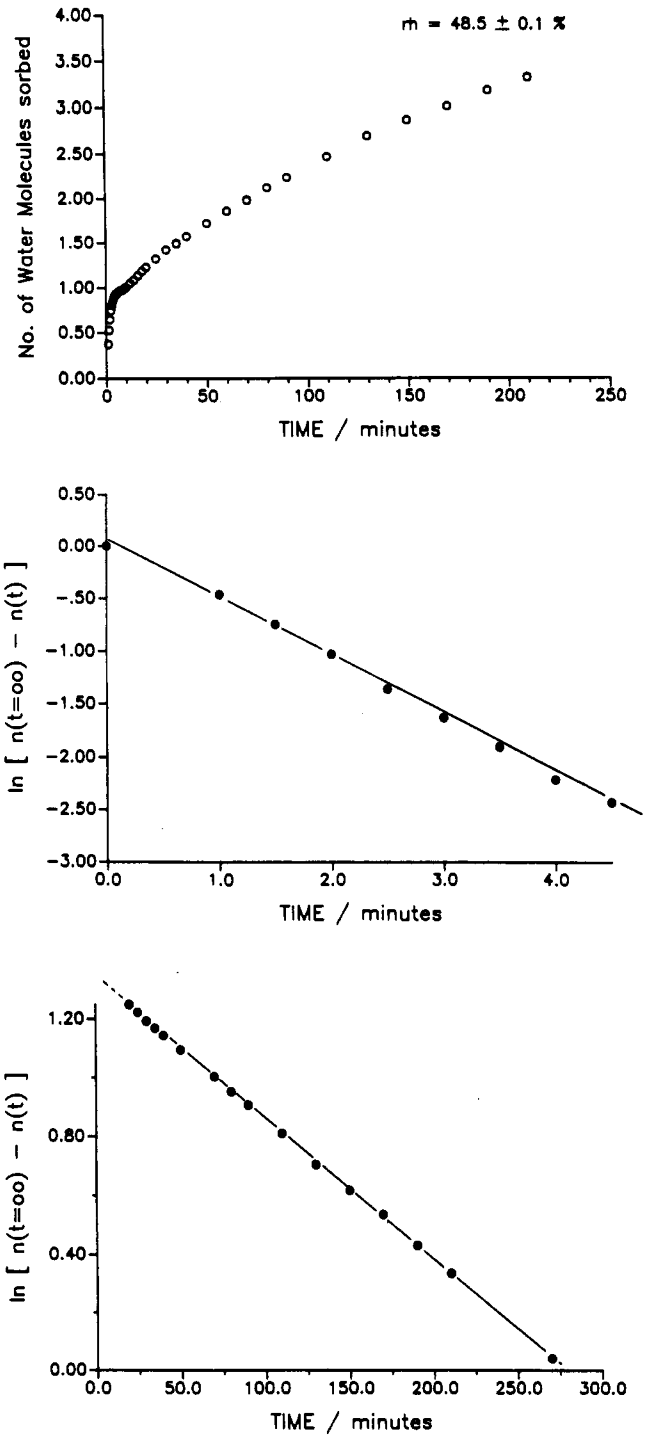

Figure 3. Water uptake by the title compound at rh = 48.5%. The top trace summarizes the raw data and clearly shows the two steps in the sorption process. The middle trace is a semilog plot for the "fast-step" data in the range $0 \leq t \leq 4.5$ min. The bottom trace is the analogous plot for the data at $t \geq 10$ min. At this rh, the ratio of the two rates is ca. 120:1.

as summarized in Figure 2. The former adds no solvent to the structure, while the latter has sorbed three water molecules at equilibrium. The kinetic data for this latter addition appear to be reasonably well described by a first-order process, with no clear evidence that the first water molecule adds at a significantly different rate than the other two, in contrast to the behavior of the dtbipy complex discussed above.

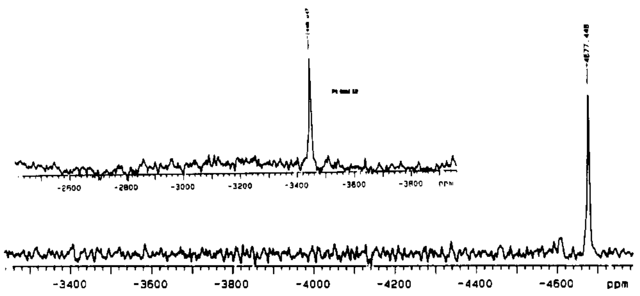

Figure 4. ^{195}Pt NMR spectra of Pt[4,4′-(t-Bu)$_2$-2,2′-bpy(CN)$_2$] and (inset) of Pt[(en)I$_2$], both in dmf at room temperature. The large downfield chemical shifts serve to confirm the (formal) charge state of the metal center as +2.

Finally, it is worth noting that the hydration of Ptdtbipy(CN)$_2$ is readily reversible. Exposure of these hydrated samples to vacuum at ca. 80 °C for 1 h is sufficient to dehydrate the sample completely. Repeated cycling of the samples through this hydration–dehydration sequence did not degrade the complex to any observable extent.

^{195}Pt NMR Spectroscopy. A representative spectrum of the title compound is given in Figure 4 and shows a single resonance at −4677 ppm (the inset shows the corresponding spectrum of PtenI$_2$). The systematics of ^{195}Pt shifts show[18] that Pt(II) evidences chemical shifts which are generally −3500 ppm (downfield) with respect to analogous Pt(IV) complexes and lie in the range of −1500 to −5000 ppm. Replacement of a halogen ligand by a pseudohalide (e.g. CN) can result in further downfield shifts of up to 3500 ppm. Clore et al.[19] have reported the chemical shift of Pt(NH$_3$)$_2$Cl$_2$ at −2161.4 ppm, so that the shift of Pt(NH$_3$)$_2$(CN)$_2$ might be expected at ca. −5660 ppm. The effect of replacing two NH$_3$ groups by the bpy ligand is not presently calibrated in the literature, largely due to solubility problems. Nonetheless, the NMR data clearly serve to identify the formal oxidation state of Pt as +2.

^{1}H and ^{13}C NMR Spectroscopy. Due to the ready solubility of the L = dtbipy Pt(II) complex in dmso, this compound provides an ideal opportunity to examine the NMR parameters of such species in solution, and the pertinent data are summarized in Table II. A comparison of the proton NMR data for the hydrated and anhydrous complex in dmso-d_6 shows a consistent (but very small) upfield shift for the hydrated complex, but the differences are not considered to be useful in discussing the electronic and steric effects in these complexes. Of more significance, however, is the observation in the ^{1}H spectrum of the hydrated complex of the appearance of a broad resonance, centered at a shift of ca. 4.45 ppm. The corresponding spectrum of the rigorously dehydrated complex shows no resonance signal in this region. On the addition of a small quantity of D$_2$O to the former solution, the broad resonance disappears and is replaced by a sharp resonance at 3.566 ppm. The chemical shift for "free" H$_2$O in dmso-d_6 is observed at 3.317 ppm. These results can be accounted for by envisioning the ~5 water molecules, which are associated with the "hydrated" complex as it is brought into solution, as either occupying coordination sites on the metal atom, or—being displaced by a dmso molecule—existing as "free" water molecules in solution. The dynamic equilibrium between these two environments gives rise to the broad NMR signal. On the addition of D$_2$O, the fraction of H$_2$O in solution is increased, giving rise to the sharp upfield resonance.

Finally, in the context of the ^{1}H NMR data summarized in Table II, it is worth noting that all of the ring protons show a

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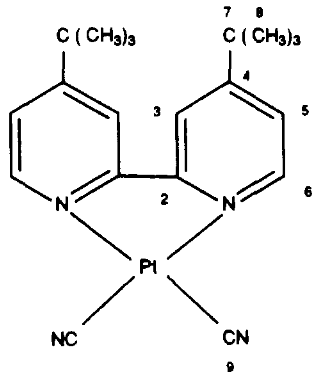
Table II. ^1H and ^{13}C NMR Data



Pt[4,4'-(*t*-Bu)$_2$-2,2'-bpy(CN)$_2$]

^1H NMR Data (δ)

compd	solvent	H(3)	H(5)	H(6)	H(8)	others	ref
Pt[4,4'-dtbipy(CN)$_2$]	dmso-d_6	8.650	7.909	8.801	1.424		*a*
	dmso-d_6	8.617	7.839	8.767	1.415		*b*
dtbipy	dmso-d_6	8.40	7.47	8.61	1.34		10
	CDCl$_3$	8.42	7.29	8.59	1.37		26
	CDCl$_3$	8.48	7.3	8.63	1.38		8
5,5'-dmbpy	CDCl$_3$	8.24		8.48		7.60 (H(4)), 2.38 (H(7))	27
4,4'-dmbpy	dmso-d_6	8.22	7.26	8.51		2.41 (H(7))	
2,2'-bpy	dmso-d_6	8.38	7.43	8.67		7.92 (H(4))	

^{13}C NMR Data in dmso (δ)

compd	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	ref
bpy		155.239	124.086	137.185	120.413	149.210			
4,4'-dtbipy		155.189	124.931	147.931	121.286	149.015	20.7768		
4,4'-dtbipy		155.472	121.142	160.444	117.098	149.174	34.6491	30.2540	
Pt[4,4'–dtbipy(CN)$_2$]^c	147.5501	123.761	166.945	120.858	146.191	35.9842	29.950		
toluene	137.70	128.50^d	129.30^e	125.60			21.30		20
	136.70	127.40^d	128.20^e	124.50			20.30		22
t-Bu-benzene	150.50	128.10^d	125.10^e				34.50	31.40	23

[a] Anhydrous form. [b] Hydrated form. [c] The broad resonance at 121 ppm is assigned to the carbon atom of the CN ligand. [d] C(3,5) resonances. [e] C(2,6) resonances.

downfield shift (average 0.29 ppm for the anhydrous complex, 0.25 ppm for the hydrated sample), in going from the free ligand to the complex. A similar observation has been reported by O'Connor and Overton[9] in their study of Mo(CO)$_4$L complexes in dmso solution, which show a corresponding (average) downfield shift of 0.21 ppm. The *t*-Bu group protons in both the Pt and Mo complexes show a similar downfield shift of 0.8 ppm.

The ^{13}C NMR data are also summarized in Table II, with the atom-numbering convention being that of the Breitmeier, Haas, and Voelter compilation.[20] Except for the expected downfield shift of the C(4) resonance in going from the 2,2'-bpy, to the 4,4'-(CH$_3$)$_2$, to the 4,4'-(*t*-Bu)$_2$ ligand, the carbon resonances are remarkably similar.[21] The 13.8 ppm downfield shift of the C(7) resonance in going from the methyl to the *tert*-butyl homologue is identical to that observed in the spectra of toluene and *tert*-butylbenzene reported by Breitmeier et al.[22] and by Lauer et al.[23] The C(8) resonance at 30.254 ppm is similar to that observed for the methyl carbon in *tert*-butylbenzene (31.40 ppm) and serves to identify the atom involved. The downfield shift of 13.9 ppm of the C(7) resonance in going from the methyl to the butyl homologue is identical to that observed in the toluene–*tert*-butylbenzene pair, as reported by Lauer et al.[23]

The broad resonance observed at a chemical shift of ca. 121 ppm is assigned to the C-atom of the CN ligands. The ^{13}C chemical shift of $Pt^{IV}(CN)_6^{2-}$ has been reported[24] at –84.7 ppm, and that of $Pt^{II}(CN)_4^{2-}$ at –125.7 ppm. Thus, again, the ^{13}C NMR data support the assignment of the metal atom oxidation state at Pt(II), as noted above.

The near identity of the ^{13}C resonances for C(2), C(3), C(5), and C(6) in the unsubstituted bpy and methyl-substituted bpy ligands, and the small upfield shift for these resonances in the *tert*-butyl-substituted ligand, suggests that the differences in the electron density at the N-atom in the pyridine ring are minimal. Since the bpy complex sorbs no water under the conditions detailed above, while the 4,4'-(CH$_3$)$_2$ complex sorbs three water molecules, and the 4,4'-(*t*-Bu)$_2$ complex sorbs five water molecules, it is clear that the steric effects of the side chain on the pyridine ring far outweigh in importance the differences in the electron densities at the N-atom. Thus, it is clear that the hydration of these essentially planar Pt(II) complexes is governed to a significant extent by factors which influence the length of the (potential) Pt–Pt bonding interaction. The formation of this metal–metal interaction, in turn, may be driven by the energetics of achieving a favorable 18-electron configuration. A brief discussion of the "18-electron rule" (and some of its problems) has recently been discussed by Dehnicke[25] in connection with the chemistry of {Ni-[P(*t*-Bu)]$_6$}. The longer the Pt–Pt bonding interaction, the more

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(20) Breitmeier, E.; Haas, G.; Voelter, W. *Atlas of ^{13}C NMR Data*; Heyden: London, 1979; spectra 2435, 1807, 1808, 575–7, and 586.

(21) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G. *Org. Magn. Reson.* **1984**, *22*, 388. Qui, Z. W.; Grant, D. W.; Pugmire, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 557.

(22) Breitmeier, et. al. Unpublished results.[20]

(23) Lauer, D.; Motell, E. L.; Traficante, D. D.; Maciel, G. E. *J. Am. Chem. Soc.* **1972**, *94*, 5335.

(24) Golub, A. M.; Koehler, H.; Skopenko, V. V. *Chemistry of Pseudohalides*; Monograph 21; Clark, R. J. H., Ed.; Elsevier: Amsterdam, 1986; p 147 (Table 3.11).

(25) Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 424.

(26) Ben Hadda, T.; Le Bozek, H. *Polyhedron* **1988**, *7*, 575.

readily a solvent molecule can enter the structure as either a molecule of hydration or as a donor ligand, transferring charge to the Pt(II) metal center. The unique nature of the Pt[4,4'-$(t\text{-Bu})_2$-2,2'-bpy$(CN)_2$] complex in this regard is reflected both in the large number of water molecules which are sorbed by the anhydrous complex and by the shift to higher frequencies observed in the UV/vis absorbance, which renders the complex colorless. On the basis of the present study, there now appears to be a reasonably good qualitative understanding of the dependence of the perceived colors and hydration properties of these Pt(II) complexes and the steric requirements of the ligands which directly influence the strength of the metal–metal interaction in the (stacked) solids. Further studies on the influence of steric and electronic effects on the chemical behavior of square planar Pt(II) pseudohalide complexes, in particular of bidentate nitrogen donor ligands which have non-alkyl (e.g. COOH and CN) side groups attached to the ring, are currently underway.

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(27) Lellouche, I. Unpublished data.