Deprotonation of Bipyridyl(ethylenediamine)platinum(II) Iodide[1]

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Abstract: In square-planar complexes of platinum(II), a bipyridyl ligand so enhances the acidity of an associated ethylenediamine ligand that it can be partially deprotonated by the relatively weakly basic ammonia molecule, N-methyl-substituted ethylenediamine ligands can be deprotonated with amide ion in liquid ammonia, and both protons can be abstracted from the same nitrogen atom. The site of deprotonation has been established by methylation of the deprotonated complexes and comparison of the physical properties of the products with those of complexes synthesized by independent methods.

Earlier studies on the deprotonation of ethylenediamine complexes of transitional metal ions[2] have failed to establish the maximum extent of deprotonation of the $-NH_2$ groups of the ligand or the exact site of proton removal. It therefore seemed attractive to examine the deprotonation of a single ethylenediamine ligand in association with a ligand not subject to deprotonation; bipyridyl(ethylenediamine)platinum(II) iodide was selected for this purpose. In the course of this work it was observed that the presence of the bipyridyl ligand enhances appreciably the acidity of the coordinated ethylenediamine. The results of these studies are reported here.

Experimental Section

Materials and Methods. With the exceptions that follow, all materials used were anhydrous reagent grade chemicals that were used without further purification. Experimental methods for carrying out reactions in liquid ammonia, purification, and handling of the resulting air-sensitive products and physical measurements made thereon were the same as those described or referred to earlier.[3] The most intense lines in the X-ray diffraction patterns of both starting materials and products are listed (*d* spacings in ångström units) with relative intensities (in parentheses) immediately following analytical data.

Potassium tetrachloroplatinate(II) was prepared by the reduction of K_2PtCl_6 with hydrazine hydrochloride.[4]

Dichloro(bipyridyl)platinum(II) was prepared initially by the somewhat tedious and time-consuming procedure of Morgan and Burstall.[5] However, the following synthesis was found to permit rapid and direct conversion of K_2PtCl_6 to $[Pt(bipy)Cl_2]$ in high yield. Thus, 2.00 g (4.1 mmoles) of K_2PtCl_6, 0.221 g (2.1 mmoles) of $N_2H_4 \cdot 2HCl$, and 0.645 g (4.14 mmoles) of bipyridyl were heated nearly to boiling in 50 ml of water until evolution of nitrogen ceased (*ca.* 20 min). The resulting bright yellow solid was filtered, washed with water, ethanol, and ether, and dried at 55°; the yield was 1.60 g or 92% based on K_2PtCl_6. *Anal.* Calcd for $[Pt(bipy)Cl_2]$: Pt, 46.2; C, 28.5; H, 1.90. Found: Pt, 46.0; C, 28.6; H, 2.08. X-Ray diffraction data were 8.04 (1.0), 5.43 (0.6), 4.55 (0.3), 3.88 (0.3), 3.34 (0.3), 2.96 (0.2), 2.76 (0.2), 2.18 (0.2), 2.09 (0.2).

Diiodo(bipyridyl)platinum(II) was prepared by heating a solution of $[Pt(bipy)(en)]I_2$ (*vide infra*) in dilute hydriodic acid nearly to boiling for 5 min and filtering the hot solution. *Anal.* Calcd for $[Pt(bipy)I_2]$: Pt, 32.2. Found: Pt, 32.4. X-Ray data were 8.04 (1.0), 6.04 (1.0), 4.69 (0.3), 3.83 (0.3), 3.36 (1.0), 3.07 (0.3), 2.58 (0.3).

Bipyridyl(ethylenediamine)platinum(II) iodide was produced from K_2PtCl_6 *via* the intermediate synthesis of $[Pt(bipy)Cl_4]$ as described elsewhere.[6] The infrared spectrum is shown in Figure 1. This complex was deuterated by recrystallization from 99.7% D_2O and drying *in vacuo* for 24 hr at 25°; the infrared spectrum of the product is included in Figure 1.

Bipyridyl(N-methylethylenediamine)platinum(II) iodide, a lemon solid, was prepared from $[Pt(bipy)Cl_2]$ by the same method as that used in the synthesis of the corresponding ethylenediamine complex. *Anal.* Calcd for $[Pt(bipy)(men)]I_2$: Pt, 28.8; C, 23.0; H, 2.65. Found: Pt, 28.5; C, 22.9; H, 2.86. X-Ray diffraction data were 8.13 (0.3), 6.87 (0.3), 5.91 (0.3), 5.16 (1.0), 4.24 (0.9), 3.94 (0.4), 3.52 (0.4), 3.16 (0.3).

Bipyridyl(N,N′-dimethylethylenediamine)platinum(II) iodide was obtained as a yellow powder by the method used for the ethylenediamine analog. *Anal.* Calcd for $[Pt(bipy)(sdmen)]I_2$: Pt, 28.2; C, 24.3; H, 2.88. Found: Pt, 28.1; C, 24.3; H, 2.87. X-Ray diffraction data were 5.12 (0.7), 4.27 (1.0), 4.00 (0.2), 3.45 (0.8), 3.14 (0.2), 3.09 (0.2), 2.62 (0.4).

Bipyridyl(N,N-dimethylethylenediamine)platinum(II) iodide was produced as orange-colored crystals by the procedure used to prepare the corresponding ethylenediamine complex. *Anal.* Calcd for $[Pt(bipy)(udmen)]I_2$: Pt, 28.2; C, 24.3; H, 2.88; I, 36.6. Found: Pt, 28.2; C, 24.2; H, 3.05; I, 36.5. X-Ray diffraction data were 6.73 (0.9), 5.43 (0.8), 4.50 (0.7), 4.17 (1.0), 3.35 (0.4), 3.25 (0.4), 3.16 (0.4).

Dichloro(ethylenediamine)platinum(II). The following synthesis was devised as a substitute for the very time-consuming procedure described earlier.[7] Ethylenediammonium chloride (0.86 g, 6.45 mmoles) was dissolved in 125 ml of water, neutralized to phenolphthalein with dilute KOH solution, and added to 2.66 g (6.40 mmoles) of K_2PtCl_4 in 10 ml of water. The color of this solution, when stirred and heated nearly to boiling for 20 min, changed from pink to yellow. This solution was cooled to 5° and filtered to provide 1.43 g (68% yield based on K_2PtCl_4) of yellow $[Pt(en)Cl_2]$. This was recrystallized from 200 ml of water and 10 ml of concentrated hydrochloric acid. *Anal.* Calcd for $[Pt(en)Cl_2]$: Pt, 59.8. Found: Pt, 59.8. X-Ray diffraction data were 7.50 (1.0), 6.76 (0.7), 6.22 (0.4), 5.72 (0.9), 3.38 (0.7), 3.21 (0.4).

Dichloro(N,N,N′,N′-tetramethylethylenediamine)platinum(II) was prepared by adding 1 g of K_2PtCl_4 and 2 ml of tetmen to 30 ml of water and adjusting to pH 7 with dilute hydrochloric acid. The solution was stirred overnight at 25° and filtered. The light yellow solid was leached with 100 ml of boiling water, filtered, washed with alcohol and ether, and dried *in vacuo* over $Mg(ClO_4)_2$ for 24 hr. *Anal.* Calcd for $[Pt(tetmen)Cl_2]$: Pt, 51.2; C, 18.9; H, 4.19. Found: Pt, 51.2; C, 19.0; H, 4.26. X-Ray diffraction data were 7.37 (1.0), 5.24 (1.0), 4.67 (0.9), 3.29 (0.7), 2.63 (0.5).

Deprotonation of $[Pt(bipy)(en)]I_2$. A 0.432-g sample of $[Pt(bipy)(en)]I_2$ was stirred with 40 ml of anhydrous liquid ammonia

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[1] Abbreviations used in this paper: en, ethylenediamine; men, N-methylethylenediamine; sdmen, N,N′-dimethylethylenediamine; udmen, N,N-dimethylethylenediamine; tetmen, N,N,N′,N′-tetramethylethylenediamine; (en-*x*H), etc., an en or substituted en ligand from which *x* protons have been removed.

[2] G. W. Watt and D. G. Upchurch, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1966, pp 253–271.

[3] G. W. Watt and J. K. Crum, *J. Am. Chem. Soc.*, **87**, 5366 (1965).

[4] N. G. Klyuchnikow and R. N. Savel'eva, *Zh. Neorgan. Khim.*, **1**, 2764 (1954).

[5] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 965 (1934).

[6] G. W. Watt and D. G. Upchurch, *Inorg. Nucl. Chem. Letters*, **2**, 363 (1966).

[7] F. Basolo, J. C. Bailar, Jr., and B. R. Tarr, *J. Am. Chem. Soc.*, 72, 2433 (1950).

at −65 for 1 hr; the color of the slightly soluble solid changed from canary yellow to orange-red. Following removal of the ammonia by filtration, the solid was again exposed to ammonia, as above. The solvent was removed by filtration and the residual homogeneous brown-violet solid product was dried *in vacuo* for 3 hr. *Anal.* Calcd for $[Pt(bipy)(en\text{-}H)]I + [Pt(bipy)(en)]I_2 \cdot 2NH_3$: Pt, 31.6; I, 30.8. Found: Pt, 31.8; I, 30.9. This product was deammoniated at *ca.* 10^{-3} mm for 48 hr at 25°. *Anal.* Calcd for $[Pt(bipy)(en\text{-}H)]I + [Pt(bipy)(en)]I_2$: Pt, 32.4; I, 31.6. Found: Pt, 32.2; I, 31.6. X-Ray diffraction data were 9.87 (1.0), 8.58 (0.4), 7.13 (0.4), 4.95 (0.7), 4.31 (0.8), 4.07 (0.8), 3.64 (0.4), 3.42 (0.6), 3.24 (0.4). Titration of 31.2 mg of this product in water to the phenolphthalein end point required 2.1 ml of 0.011 *N* nitric acid as compared with 2.4 ml calculated on the assumption of complete reprotonation. An X-ray diffraction pattern for the residue remaining after evaporation of the combined liquid ammonia filtrates provided an identification of NH_4I and some relatively weak lines suggestive of $[Pt(bipy)(en)]I_2$ but insufficient to be conclusive. This residue was found to contain 28.1% of the iodine used in the experiment as $[Pt(bipy)(en)]I_2$ as compared with 25.0% anticipated if the platinum-containing product were virtually insoluble in ammonia.

The same deprotonation was effected using liquid methylamine, as described above, except that the solid product was not solvated. *Anal.* Calcd for $[Pt(bipy)(en\text{-}H)]I + [Pt(bipy)(en)]I_2$: Pt, 32.4; I, 31.6. Found: Pt, 32.7; I, 30.5. The X-ray diffraction data for this product were in good agreement with those for the same product prepared in ammonia. Following evaporation of the methylamine filtrate, an X-ray diffraction pattern led to data in good agreement with those for an authentic specimen of CH_3NH_3I prepared from CH_3NH_2 and concentrated hydriodic acid, *i.e.*, 3.80 (0.8), 3.50 (0.5), 3.06 (0.3), 2.78 (1.0), 2.63 (0.5), 2.58 (0.5).

In contrast to the partial deprotonation reported above, the first step in the deprotonation of $[Pt(bipy)(en)]I_2$ (2.88 g, 4.33 mmoles) in 75 ml of ammonia at −35° was effected by slow addition (45 min) of the potassium amide prepared from 0.1693 g (4.34 mg-atoms) of potassium in 15 ml of ammonia. The intense purple solid and solution was stirred for 3 hr, filtered, and washed with 25-ml portions of ammonia, once at −35° and four times at −65°. The purple-black solid was dried 16 hr at 25° *in vacuo*. *Anal.* Calcd for $[Pt(bipy)(en\text{-}H)]I$: Pt, 36.3; I, 23.6; equiv wt, 537, Found: Pt, 36.6; I, 23.4; equiv wt, 540. X-Ray diffraction data were 9.40 (1.0), 5.47 (0.7), 5.09 (0.8), 3.93 (0.7), 3.63 (0.7), 3.30 (0.4). Evaporation of a solution of 0.2 g of $[Pt(bipy)(en\text{-}H)]I$ after neutralization with hydriodic acid regenerated yellow $[Pt(bipy)(en)]I_2$ which was identified by its X-ray diffraction pattern. Analysis of the residue from the liquid ammonia filtrate and washings accounted for 47.3% of the iodine used initially as $[Pt(bipy)(en)]I_2$; an X-ray diffraction pattern for this residue showed only lines attributable to KI. The infrared spectrum of $[Pt(bipy)(en\text{-}H)]I$ is shown in Figure 1.

The second step in the deprotonation of $[Pt(bipy)(en)]I_2$ (1.78 g, 2.68 mmoles) in 60 ml of ammonia resulted from addition of the KNH_2 prepared from 0.2195 g (5.61 mg-atoms) of potassium in 16 ml of ammonia at −35° over 1 hr. The reaction mixture was digested for 4 hr, cooled to −65°, and filtered, and the purple-black iodine-free solid product was washed with five 20-ml portions of ammonia at −65° and dried *in vacuo* at 25° for 16 hr. *Anal.* Calcd for $[Pt(bipy)(en\text{-}H)_2]$: Pt, 47.6; C, 35.2; H, 3.45; N, 13.7; equiv wt, 205. Found: Pt, 47.4; C, 35.3; H, 3.62; N, 13.4; equiv wt, 203. X-Ray diffraction data were 7.16 (1.0), 4.64 (0.4), 3.88 (0.5), 3.39 (0.4), 2.81 (0.3). An aqueous solution of $[Pt(bipy)(en\text{-}H)_2]$ is initially pink-violet but changes rapidly to light yellow; addition of hydriodic acid followed by evaporation regenerated $[Pt(bipy)(en)]I_2$ which was identified by its X-ray diffraction pattern. Analysis of the residue from the combined liquid ammonia filtrate and washings accounted for 96% of the iodine used as $[Pt(bipy)(en)]I_2$; an X-Ray diffraction pattern for this residue gave only the lines of KI. The infrared spectrum of $[Pt(bipy)(en\text{-}H)_2]$ is included in Figure 1.

Efforts to effect more extensive deprotonation included treatment of $[Pt(bipy)(en)]I_2$ with KNH_2 in liquid ammonia in 1:3 mole ratio at −35°, 1:3 at 25°, and 1:5 at 25°. In the first two cases, $[Pt(bipy)(en\text{-}H)_2]$ was identified as a product. In both reactions at 25°, which were carried out in Faraday tubes, black deposits formed on the walls of the tubes; this was identified as elemental platinum by means of an X-ray diffraction pattern.

Deprotonation of $[Pt(bipy)(men)]I_2$. A 0.5-g sample of $[Pt(bipy)(men)]I_2$ was treated with 40 ml of liquid ammonia at −65° for 0.5 hr and filtered; this procedure was repeated twice and the red-orange solid was dried *in vacuo* for 16 hr at 25° to provide a homogeneous brown solid. *Anal.* Calcd for $[Pt(bipy)(men\text{-}H)]I + [Pt(bipy)(men)]I_2$: Pt, 31.7; I, 30.9. Found: Pt, 31.4; I, 30.6. The solid remaining after evaporation of the combined liquid ammonia filtrates gave an X-ray diffraction pattern that showed the presence of NH_4I together with an apparently very small amount of $[Pt(bipy)(men)]I_2$.

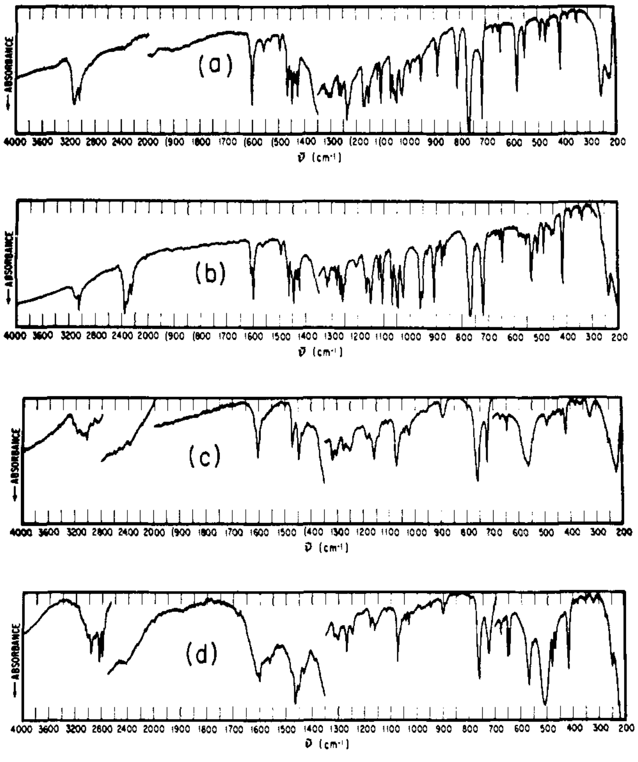

Figure 1. The infrared spectra of (a) $[Pt(bipy)(en)]I_2$, (b) deuterated $[Pt(bipy)(en)]I_2$, (c) $[Pt(bipy)(en\text{-}H)]I$, (d) $[Pt(bipy)(en\text{-}2H)]$.

This partial deprotonation was also completed by treating 1.39 g (2.05 mmoles) of $[Pt(bipy)(men)]I_2$ in 50 ml of ammonia dropwise with the KNH_2 equivalent to 0.134 g (3.43 mg-atoms) of potassium in 20 ml of ammonia. The reaction mixture was stirred for 1 hr and filtered, and the red-brown solid was washed with three 50-ml portions of ammonia at −40° and dried under reduced pressure for 18 hr at 25°. *Anal.* Calcd for $[Pt(bipy)(men\text{-}H)]I$: Pt, 35.4; I, 23.0. Found: Pt, 35.3; I, 22.5. This product failed to give a satisfactory X-ray diffraction pattern. The combined liquid ammonia filtrate and washings were found to contain 277 mg of iodine as compared with 259 mg expected if the platinum-containing product were insoluble in ammonia.

The second step in the deprotonation of this complex was accomplished by slow addition of the KNH_2 formed from 0.309 g (7.9 mg-atoms) of potassium in 16 ml of ammonia at −36° to 1.92 g (2.84 mmoles) of $[Pt(bipy)(men)]I_2$ in 40 ml of ammonia. The mixture was stirred for 2 hr and filtered. Because of the relatively high solubility of the product in ammonia, it was washed only twice with small volumes of ammonia at −45°; the yield was accordingly low but the red-black product was iodine free. *Anal.* Calcd for $[Pt(bipy)(men\text{-}2H)]$: Pt, 46.1; C, 36.9; H, 3.78; N, 13.2. Found: Pt, 46.3; C, 37.1; H, 4.42; N, 13.3. X-Ray diffraction data were 7.96 (1.0), 4.23 (0.3), 3.97 (0.2), 3.75 (0.3). Efforts to regenerate the starting material by treating $[Pt(bipy)(men\text{-}2H)]$ with hydriodic acid led to results that were inconclusive.

Deprotonation of $[Pt(bipy)(sdmen)]I_2$. The stability of this complex toward deprotonation by liquid ammonia at −65° has been reported previously.[8]

A stirred solution and suspension of 0.95 g (1.37 mmoles) of $[Pt(bipy)(sdmen)]I_2$ in 30 ml of ammonia at −36° was treated slowly with the KNH_2 equivalent to 0.0552 g of potassium in 16 ml of ammonia. After 2 hr the reaction mixture was filtered and the purple-black solid was washed with three 30-ml portions of ammonia and dried *in vacuo* for 18 hr at 25°. *Anal.* Calcd for [Pt(bipy)(sdmen-

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[8] G. W. Watt and D. G. Upchurch, *J. Am. Chem. Soc.*, **89**, 177 (1967).

H)]I: Pt, 34.5; I, 22.4. Found: Pt, 34.6; I, 21.8. X-Ray diffraction data were 4.32 (1.0), 4.03 (0.6), 3.45 (0.3), 2.62 (0.3). The combined liquid ammonia filtrate and washings contained 194 mg of iodine as compared with 174 mg anticipated if the platinum-containing product were insoluble in ammonia. Treatment of [Pt(bipy)(sdmen-H)]I with water gave immediate precipitation of a yellow solid, more of which precipitated upon addition of aqueous KI. *Anal.* Calcd for [Pt(bipy)(sdmen)]I_2: C, 24.3; H, 2.88; I, 36.6. Found: C, 23.9; H, 3.01; I, 36.3. This product was also identified by its X-ray diffraction pattern and infrared spectrum.

The removal of two protons from [Pt(bipy)(sdmen)]I_2 to provide [Pt(bipy)(sdmen-2H)] and its subsequent conversion to [Pt(bipy)(tetmen)]Cl_2 by methylation with methyl chloride has also been described elsewhere.[8] (X-Ray diffraction data for [Pt(bipy)(sdmen-2H)] were 8.07 (1.0), 5.79 (1.0), 4.41 (0.5), 4.07 (0.5), 2.89 (0.7).)

Deprotonation of [Pt(bipy)(udmen)]I_2. A 0.5-g sample of [Pt(bipy)(udmen)]I_2 was treated with 40 ml of liquid ammonia at −65° for 0.5 hr, whereupon the color of the solid changed from yellow-orange to red. After filtration, the red solid was exposed similarly to two more 40-ml portions of ammonia. The final orange-red product was dried *in vacuo* for 16 hr at 25°. *Anal.* Calcd for [Pt(bipy)(udmen-H)]I + [Pt(bipy)(udmen)]I_2: Pt, 31.0; C, 26.7; H, 3.10; I, 30.2. Found: Pt, 31.2; C, 27.5; H, 3.51; I, 30.6. The residue from evaporation of the combined ammonia filtrates was shown by X-ray diffraction data to contain NH_4I and some of the starting material.

As in foregoing cases, the first deprotonation step was completed by adding dropwise the potassium amide solution from 0.117 g (3.0 mg-atoms) of potassium in 16 ml of ammonia to 2.06 g (2.97 mmoles) of [Pt(bipy)(udmen)]I_2 in 40 ml of ammonia at −36°. After 1 hr, the mixture was filtered and the red-black solid was washed with three 40-ml portions of ammonia at −45° and dried *in vacuo* at 25° for 17 hr. *Anal.* Calcd for [Pt(bipy)(udmen-H)]I: Pt, 34.5; C, 29.7; H, 3.36; N, 9.91. Found: Pt, 36.0; C, 31.7; H, 3.95; N, 10.6. This product did not give a useful X-ray diffraction pattern. Even when treated with 0.5 *N* HNO_3, [Pt(bipy)(udmen-H)]I appeared to be stable toward reprotonation.

To determine whether two protons could be abstracted from the same ligand nitrogen atom, [Pt(bipy)(udmen)]I_2 was treated with 2 molar equiv of KNH_2 in ammonia at −35°. Analysis of the product indicated that deprotonation had proceeded beyond removal of one proton but was incomplete. Accordingly, the reaction was repeated using a twofold excess of KNH_2. Thus, 2.29 g (3.31 mmoles) of [Pt(bipy)(udmen)]I_2 in 50 ml of ammonia was treated dropwise with the KNH_2 formed from 0.517 g (13.2 mg-atoms) of potassium over 0.5 hr. After 2 hr, the brown-black solid was washed with three 40-ml portions of ammonia and dried for 20 hr *in vacuo* at 25°. *Anal.* Calcd for [Pt(bipy)(udmen-2H)]: Pt, 44.6; C, 38.4; H, 4.12; N, 12.8; equiv wt, 219. Found: Pt, 45.0; C, 35.8; H, 4.74; N, 12.8; equiv wt, 238. This product did not give a satisfactory X-ray diffraction pattern.

Methylation of Deprotonated Complexes. The methylation of [Pt(bipy)(en-2H)] with methyl iodide[9] and of [Pt(bipy)(udmen-2H)][8] have been described previously and it has been shown[10] that, under appropriate conditions, methylation can be effected using methyl chloride or bromide. One additional methylation has been demonstrated and is reported here.

About 15 ml of redistilled CH_3I was added to *ca.* 0.3 g of [Pt(bipy)(en-H)]I in a tube containing a magnetic stirring bar. The tube was sealed and its contents stirred at 25° for 2 weeks. Excess CH_3I was removed under reduced pressure and the dark yellow residue was recrystallized from water. *Anal.* Calcd for [Pt(bipy)(men)]$I_2 \cdot 0.5H_2O$: Pt, 28.3; C, 22.7; H, 2.78; N, 8.14. Found: Pt, 28.2; C, 22.7; H, 2.98; N, 8.46. Both the X-ray diffraction pattern and infrared spectrum of this product were substantially identical with those of an authentic specimen prepared by an independent method, as described above. During the recrystallization, a small quantity of dark brown water-insoluble solid was separated; an infrared spectrum showed that this contained [Pt(bipy)I_2] but analytical data showed that is was impure.

Discussion

It is now well established[2] that the ethylenediamine ligands in complexes such as [Pt(en)$_2$]I_2 can be deprotonated by amide ion in liquid ammonia or stronger bases in other media. The work reported here shows that substitution of a bipyridyl ligand for one of the ethylenediamine ligands influences significantly the reactivity of the latter.

The presence of the π-bonding and nondeprotonatable bipyridyl ligand so enhances the acidity of the remaining ethylenediamine ligand that it can be partially deprotonated by the relatively weakly basic ammonia molecule. This leads to the establishment of equilibria of the type

$$[\mathrm{Pt(bipy)(en)}]\mathrm{I_2} + \mathrm{NH_3} \rightleftharpoons [\mathrm{Pt(bipy)(en\text{-}H)}]\mathrm{I} + \mathrm{NH_4I} \qquad (1)$$

For the case shown in (1), the ammonia-insoluble product consists of a 1:1 mixture of starting material and the singly deprotonated species; ammonium iodide was identified as the ammonia-soluble product. As shown above, the same type of equilibrium is established in liquid methylamine but, as expected in view of the greater base strength of CH_3NH_2 as compared with NH_3, deprotonation was somewhat more extensive. Partial deprotonation by ammonia occurs similarly with N-methylethylenediamine and N,N-dimethylethylenediamine but not wth N,N′-dimethylethylenediamine. Thus it appears that (1) occurs only if there is a primary amino group in the ligand.

By use of amide ion in ammonia, (1) was carried to completion

$$[\mathrm{Pt(bipy)(en)}]\mathrm{I_2} + \mathrm{NH_2^-} \longrightarrow [\mathrm{Pt(bipy)(en\text{-}H)}]\mathrm{I} + \mathrm{NH_3} + \mathrm{I^-} \qquad (2)$$

and the second step in the deprotonation process was effected

$$[\mathrm{Pt(bipy)(en\text{-}H)}]\mathrm{I} + \mathrm{NH_2^-} \longrightarrow [\mathrm{Pt(bipy)(en\text{-}2H)}] + \mathrm{NH_3} + \mathrm{I^-} \qquad (3)$$

but only through the use of excess amide ion. The latter probably results from the increased charge density about the nitrogen atom in the singly deprotonated species; by inductive effects this could decrease the polarizing ability of the Pt^{2+} ion and thus diminish the acidity of the remaining amino group.

Although it was not possible previously to prove the removal of the second hydrogen from a ligand nitrogen in an ethylenediamine ligand, this was accomplished as described above in two ways. First, N,N′-dimethylethylenediamine was deprotonated with amide ion in ammonia and both deprotonated species were isolated. Second, N,N-dimethylethylenediamine was shown also to participate in a two-step deprotonation, and again both deprotonated species were isolated. There is no evidence that ethylenediamine (or substituted ethylenediamine) ligands will participate in such reactions in the absence of the associated bipyridyl ligand.

Any explanation of the demonstrated influence of the bipyridyl ligand upon the properties of the ethylenediamine ligand must take into account the greater basicity of the latter[11] and the known stability of the bipyridyl–platinum(II) bond.[12] The enhanced acidity of the ethylenediamine ligands in [Pt(bipy)(en)]$^{2+}$ as compared with [Pt(en)$_2$]$^{2+}$ seems most likely to result from the

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(9) G. W. Watt and D. G. Upchurch, *J. Am. Chem. Soc.*, **87**, 4212 (1965).

(10) G. W. Watt and D. G. Upchurch, *J. Inorg. Nucl. Chem.*, **29**, 1174 (1967).

(11) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).

(12) P. D. Gillard and G. Wilkinson, *ibid.*, 2835 (1964).

formation of strong π bonds between Pt^{2+} and the bipyridyl ligand. Applicable hydridization schemes have been suggested[13-16] and others can be devised but without sound basis for preference. In any case the effect of coordination of a Lewis base about the Pt^{2+} must diminish the effective positive charge[17] so that in $[Pt(en)]_2^{2+}$ the metal ion does not polarize the nitrogen atoms sufficiently to permit proton dissociation in ammonia. The formation of π bonds in $[Pt(bipy)(en)]^{2+}$ allows the bipyridyl ligand to act as an electron sink, the effective charge on the metal ion is thereby increased, and the net effect is therefore the same as an increase in oxidation state, but to a lesser extent. Thus, the more positive platinum ion should form stronger bonds to the ethylenediamine ligand, and support for this view is found in the infrared spectral evidence discussed below.

Results announced previously[8,9] and described here show that these deprotonated complexes are readily methylated under quite mild conditions, *e.g.*

$$[Pt(bipy)(sdmen\text{-}2H)] + 2CH_3I \longrightarrow [Pt(bipy)(tetmen)]I_2 \quad (4)$$

In all cases, the identity of the methylation products was established by comparison of analytical, X-ray diffraction, and infrared spectral data with those for the corresponding complexes synthesized by independent methods. Reaction 4 is of particular interest because it has not been found possible to produce the product by any direct synthesis.[8] On the assumption that proton migration does not occur in the deprotonated species, these results serve to establish the site of deprotonation. Thus, the generation of [Pt(bipy)(en-2H)] and its subsequent methylation to provide $[Pt(bipy)(sdmen)]I_2$ show that the two protons are removed from different ligand nitrogen atoms.

Because of the complexity of the infrared spectra and the lack of theoretical calculations, complete assignments could not be made. The most pertinent spectra are shown in Figure 1, but a complete tabulation of band positions[18] is not included here. Accordingly, only spectral features of special interest and involving reasonably certain assignments for Pt–en modes are considered here.

In agreement with previous work,[19] the symmetric and antisymmetric ν(Pt–N) occur at 554 and 583 cm^{-1}, respectively, for $[Pt(bipy)(en)]I_2$ as compared with 537 and 579 cm^{-1} for $[Pt(en)_2]I_2$. As suggested above, the implied increase in Pt–N bond strength and resultant weakening of the N–H bond is consistent with the enhanced acidity observed upon incorporation of the π-bonding bipyridyl ligand. On the basis of earlier work,[3] the change in ν(Pt–N) upon deprotonation should be a shift to higher energies, thus reflecting an increase in Pt–N bond strength. In the present cases, however, just the opposite was observed. Thus, the bands at 553 and 584 cm^{-1} for $[Pt(bipy)(en)]I_2$ occur as one strong band at 563 cm^{-1} with shoulders at 547 and 577 cm^{-1} in [Pt(bipy)(en-H)]I. Removal of a second proton to form [Pt(bipy)(en-2H)] results in a further lowering to 510 and 569 cm^{-1}. Similarly, the bands at 550 and 577 cm^{-1} for $[Pt(bipy)(sdmen)]I_2$ are lowered to 520 and 553 cm^{-1} in [Pt(bipy)(sdmen-2H)]. Although it might otherwise be attractive to attribute these changes to intermolecular hydrogen bonding, such is not possible in [Pt(bipy)(sdmen-2H)].

The ν(N–H) vibrations for these complexes are not well resolved owing to the relatively poor resolving power of the instrument in this region and possible hydrogen bonding to halide when present. The strong band at 3120 cm^{-1} in $[Pt(bipy)(en)]I_2$ is assigned as ν(N–H); it disappears upon deuteration. The spectrum of [Pt(bipy)(en-H)]I is ill-defined in this region, and assignments cannot be made with certainty. The spectrum of [Pt(bipy)(en-2H)] includes three sharp bands at 2795, 2840, and 2940, and 2963 cm^{-1}. Comparison of this spectrum with that for [Pt(bipy)(sdmen-2H)] shows the two to be quite similar except for the absence of the 2963-cm^{-1} band in the spectrum of the methylated complex. This suggests that the 2963-cm^{-1} band is attributable to ν(N–H); if so, the energy is abnormally low for this vibration.

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