concentrated lithium perchlorate solution, ethanol, and ether and drying by suction.

Anal. Calcd for $[Co(en)_2(DMF)_2](ClO_4)_3$: C, 19.26; H, 4.85; Cl, 17.05; N, 13.48. Found: C, 19.02; H, 4.93; Cl, 17.18; N, 13.27.

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Nuclear Magnetic Resonance Studies of N–H Proton Dissociation and Inversion of Platinum(II) Complexes of Substituted Ethylenediamines

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Abstract: The effects of high KOH concentrations on nmr chemical shifts of ligand protons have been used to determine the fractional extent of titration and pK_a's of weakly acidic N–H protons of several Pt(II) complexes. For five methyl-substituted bipyridyl-ethylenediamine complexes, pK_a's range from $0.07K_w$ to $0.20K_w$ at $\mu = 1.3$. For $Pt(NH_3)_2(N,N'\text{-dmen})^{2+}$ and $Pt(NH_3)_2(EDDA)$, $pK_a \cong 0.01K_w$. For asymmetric complexes, rate constants for OH^--catalyzed inversion (k_{in}') have also been determined by analysis of nmr line shapes as a function of pH. Coupled with the pK_a determinations, these data permit calculation of k_3 ($= 10^5$–10^6 sec^{-1} at 30° for four complexes), the rate constant for inversion of deprotonated complex. More limited temperature-dependence data suggest that $\Delta H°_{N-H}$ for the ionization of N–H for three complexes $\cong \Delta H°_{H_2O}$, which requires that ΔH_{in}^*, the activation energy derived from the temperature dependence of k_{in}', $\cong \Delta H_3^*$, the activation energy for inversion of deprotonated complex.

The increased acidity of N–H protons resulting from coordination of nitrogen by a metal ion has been recognized for a long time. Although for small highly charged cations, including the proton, the increase in acidity is sufficient to permit pK_a determination by titration in aqueous solution, for N–H protons of Pt(II) and Co(III) complexes of NH_3, amines, and amino acids, K_a for the dissociation represented by (1) is gen-

$$\text{N-H} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{N:}^- + H_3O^+ \qquad (1)$$

erally $<10^{-12}$ so that such determinations are not feasible.[1] Interest in the determination of pK_a's of these weakly acidic protons can often be traced to their importance to the interpretation of kinetic data for basic hydrolysis of metal complexes in terms of the S_N1CB mechanism proposed originally by Garrick.[2,3] However, our interest in the problem originated in our attempts to interpret rate data for the inversion of $Pt(NH_3)_2(N,N'\text{-dmen})^{2+}$ [4] and $Pt(NH_3)_2(EDDA)$.[5] Since inversion requires prior proton abstraction, the rate of inversion of the deprotonated nitrogen species can be obtained from the observed over-all rate of inversion of the complex, derived from analysis of nmr line shapes, only if the extent of dissociation is known.

Protonation equilibria in aqueous solutions have been investigated extensively by nmr spectroscopy.[6,7] In general, pK_a's of weak acids can be determined from the inflection point in a plot of chemical shift *vs.* pH. On the basis of k_1's (eq 1) determined from the rate of water-catalyzed N–H exchange of these and similar complexes (10^{-4}–10^{-6} sec^{-1})[4,5,8] and an estimate of k_{-1} for the recombination of N:$^-$ and H_3O^+ as 10^{10} l. mole^{-1} sec^{-1},[9] we estimated that K_a would lie in the range 10^{-14}–10^{-16}. Therefore, it appeared to be feasible to determine pK_a's from the effect of 0.1–10 *M* KOH in chemical shifts of ligand protons. In this paper, we report the results of such investigations for the two complexes noted above and for several substituted ethylenediamine–bipyridyl complexes of Pt(II). The latter were selected for a detailed study because they do not have potentially titratable NH_3 protons so that deprotonation sites are unambiguous. In addition, recent studies of deprotonation in liquid ammonia by Watt and coworkers[10] indicated that bipyridyl complexes are more acidic than corresponding ammine complexes and hence more accessible to study by the nmr technique.

In view of the difficulties and uncertainties encountered in earlier studies of EDDA[5] and N,N'-dmen[4] complexes, which have two asymmetric centers and exist in both *meso* and *dl* forms, we also investigated or rein-

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[1] For a more complete discussion of this subject and a table of pK_a's and corresponding references, see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 33.

[2] F. J. Garrick, *Nature*, **139**, 507 (1937).

[3] F. Basolo and R. G. Pearson, ref 1, pp 183, 416.

[4] P. Haake and P. C. Turley, *J. Am. Chem. Soc.*, **90**, 2293 (1968).

[5] L. E. Erickson, H. L. Fritz, R. J. May, and D. A. Wright, *ibid.*, **91**, 2513 (1969).

[6] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, pp 517–520, and references cited therein; see also N. E. Rigler, S. P. Bag, D. E. Leyden, J. L. Sudmeier, and C. N. Reilley, *Anal. Chem.*, 37, 872 (1965).

[7] E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, 27, 641 (1957).

[8] L. E. Erickson, A. J. Dappen, and J. C. Uhlenhopp, *J. Am. Chem. Soc.*, **91**, 2510 (1969).

[9] E. F. Caldin, "Fast Reactions in Solution," John Wiley & Sons, Inc., New York, N. Y., 1964, p 75.

[10] G. W. Watt and D. G. Upchurch, *J. Am. Chem. Soc.*, 90, 914 (1968).

vestigated the kinetics of proton exchange and inversion at the Pt–NH(CH_3) site of several of the complexes.

Experimental Section

Bipyridylethylenediamineplatinum(II) Nitrate. [Pt(bipy)(en)](NO_3)$_2$ and corresponding complexes of N-substituted ethylenediamines were prepared by stirring 5–10 mmoles of free amine with 5 mmoles of dichlorobipyridylplatinum(II), prepared by the procedure of Morgan and Burstall,[11] in 20–30 ml of water at 70–80° for about 1 hr or until solution was complete. After filtration, when necessary to remove unreacted Pt(bipy)Cl_2, an equal volume of saturated KNO_3 was added and the solution was kept at 0° for several hours to precipitate the nitrate salt. The pale yellow solid was separated by filtration, washed once with cold 0.5 *N* HNO_3, and dried in a dessicator. Yields ranged from 70 to 90%. Confirmation of the assigned formulas was provided by the nmr spectra.

Diamine complexes were prepared as described earlier.[4,5]

Samples for K' **determinations** were prepared by adding stock solutions of 1.25 *M* KNO_3, 1.25 *M* KOH, and 0.5 *M* complex[12] in appropriate ratios from syringe-controlled micropipets to obtain 1.0 ml total volume and 0, 0.25, 0.50, 0.75, and 1.00 *M* KOH, 0.10 *M* complex, and $\mu = 1.3$.

Samples for kinetic measurements were prepared similarly by mixing 0.40 *M* stock solutions of the ligand[12] and 0.20 *M* borate or phosphate buffers containing 0.8 *M* KCl so as to obtain solutions which were 0.20 *M* in complex and $\mu = 1.0$. pH measurements were made with a Leeds and Northrup line-operated pH meter, equipped with a combination microelectrode.

Proton nmr spectra were recorded with a Varian A-60 or HA-100 nmr spectrometer. Temperatures of samples recorded at elevated temperatures were determined from a prior standardization of the dial of the temperature controller with an ethylene glycol standard. An internal standard, 0.5% TMACl or *t*-butyl alcohol, was used in all samples for chemical shift measurements, but the strong water signal was used as the lock signal for the HA-100 spectrometer.

Results

General Observations. Spectra of solutions of several substituted ethylenediamine and EDDA complexes (0.1 to 1.0 *M*) in 0.01 to 5 *M* KOH were obtained. Resonance signals of ligand protons invariably moved upfield with increasing KOH concentration. Plots of the observed shift *vs.* log (KOH) closely resembled typical low pH nmr titration curves of amines, etc., except that pK_a's were too high to obtain the shifts of the deprotonated forms directly or even to reach the inflection at the half-titration point. Typical shifts, relative to the low pH form, for protons bonded to carbons adjacent to N–H sites in 5 *M* KOH ranged from 0.042 ppm for ammine complexes to 0.250 ppm for some dipyridyl complexes. This compares with 0.45 and 0.70 ppm for the difference between methyl shifts of protonated and neutral HN(CH_3)$_2$ and N(CH_3)$_3$, respectively, which should give a good indication of the shift expected for complete deprotonation.[7] In view of the significantly greater acidity of the bipyridyl complexes revealed by these data, they were selected for a detailed study in the pH 12 to 1.0 *M* KOH range at constant ionic strength of 1.3.

Spectra of Bipyridyl Complexes. Chemical shifts and spin coupling constants of ligand protons of five bipyridyl complexes are summarized in Table I. The chemical shifts given are for the fully protonated form at pH 12–13. At this pH, the protonated form predominates, but inversion at asymmetric nitrogens is rapid so, for example, only one methyl signal is observed for N,N′-dmen, and only two methyl signals (2:1 ratio) are observed for N,N,N′-tmen (Figure 1), although separate peaks are observed at low pH. For each species, at this or slightly higher pH, the sometimes very complex low pH en–CH_2 pattern has coalesced to a single (often fairly broad) peak, indicating similar chemical shifts of all four en–CH_2 protons. Platinum side bands of the en–CH_2 peak are symmetric in spacing, but unequal in line width in all the methyl-substituted complexes reflecting unequal coupling between ^{195}Pt and the different kinds of CH_2 protons. Spin-coupling constants given in Table I are thus average values for the rapidly equilibrating different conformations— and, in some cases, different isomers—present in solution.

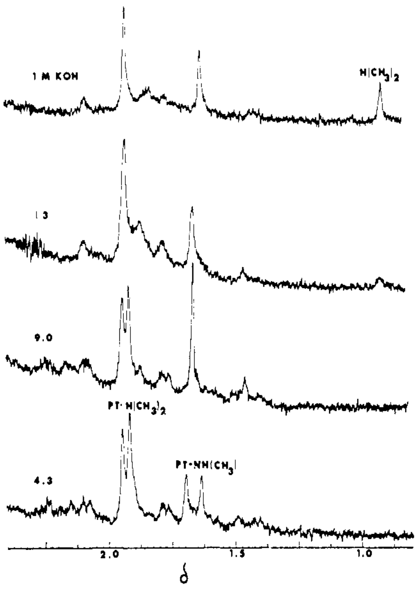

Figure 1. Effect of pH on the 100-MHz nmr spectrum of 0.2 *M* [Pt(bipy)(N,N,N′-tmen)](NO_3)$_2$. The scale is calibrated in terms of ppm downfield from internal 0.5% *t*-butyl alcohol.

Table I. Nmr Parameters[a] for Pt(bipy)L^{2+} Complexes in Water at pH ≅12 and Ionic Strength 1.3

L	δ_{CH_3}	δ_{CH_2}	J_{Pt-CH_3}	J_{Pt-CH_2}
en		1.647		40.5
N-meen	1.688	1.798	38.3	37.2
N,N-dmen	1.890	1.728	29.5	35.0
N,N′-dmen	1.725	1.913	39.6	34.0
N,N,N′-tmen	1.678 (CH_3) 1.935 (CH_3)$_2$	1.875	40.3 (CH_3) 31.0 (CH_3)$_2$	30.8

[a] Chemical shifts are in ppm downfield from internal 0.5% *t*-butyl alcohol ($\tau = 8.77$); spin coupling constants, Hz.

Mathematical Formulation for pK_a Determinations. The basic assumption involved in the nmr technique for pK_a determinations is that unique chemical shifts, δ_i, can be assigned to protonated (N–H) and deprotonated (N:$^-$) species so that the fractional extent of deprotonation can be calculated from the observed weighted-average shift, δ_{obsd}, and the shifts of protonated and deprotonated forms, δ_{N-H} and $\delta_{N:^-}$. The equilibrium constant, K, for the deprotonation reaction

$$\text{N-H} + \text{OH}^- \rightleftharpoons \text{N:}^- + \text{H}_2\text{O} \qquad (2)$$

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[11] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 968 (1934).

[12] As the nitrate salt, except for Pt(bipy)(N,N′-dmen)$^{2+}$, which because of exceptionally low solubility was first converted to the chloride form by passing through a Dowex 1 X8 anion-exchange resin in the chloride form.

can be expressed in terms of K_a and K_w as

$$K = [\mathrm{N}:^-]/[\mathrm{N{-}H}][\mathrm{OH}^-] = K_aK_w = K'K_\gamma \qquad (3)$$

where brackets indicate activities and K' and K_γ are corresponding concentration and activity coefficient ratios. K', the experimentally determined mass action equilibrium quotient, can be expressed in terms of chemical shifts by

$$K' = \delta/(\delta' - \delta)(\mathrm{OH}^-) \qquad (4)$$

where $\delta = \delta_{\text{obsd}} - \delta_{\text{N-H}}$ and $\delta' = \delta_{\text{N:}^-} - \delta_{\text{N-H}}$. Rearrangement of (4) yields

$$1/\delta = 1/\delta' + (1/\delta'K')(1/(\mathrm{OH}^-)) \qquad (5)$$

pK_a's of Bipyridyl Complexes. Equation 5 indicates that $K' = K_a/K_wK_\gamma$ can be obtained as the ratio of intercept to slope of a $1/\delta$ *vs.* $1/(\mathrm{OH}^-)$ plot at constant ionic strength. Although such plots were linear for all five bipyridyl complexes and the slopes based on five concentrations could be determined with good accuracy (±5–10%), the intercepts, which are the reciprocals of the total deprotonation shifts, were very uncertain since the extent of titration is only 10–20% for even the most acidic complexes. Therefore, K's were calculated from total deprotonation shifts (δ') estimated on the basis of arguments outlined below. Using N-methylethylenediamine, designated HH'A, as a model, two deprotonated species HA^- and $\mathrm{H'A}^-$ (where H and H' represent protons on primary and secondary amine groups, respectively) need to be considered. Estimated deprotonation shifts in ppm for the three different types of ligand protons for HA^- and $\mathrm{H'A}^-$ are indicated below.

HH'A =	NH_2—	CH_2—	CH_2—	$NH'CH_3$
$\mathrm{H'A}^-$		0.50	0.20	0.10
HA^-		0.25	0.67	0.67

These estimates are based on data for free amines[7] and amino acids.[13] The observation that further methyl substitution increases protonation shifts of CH_2 protons of glycine and of methyl protons of N-methylamines and glycine accounts for the differences in estimated deprotonation shifts for HA^- and $\mathrm{H'A}^-$. For example, applying these values to N,N,N'-tmen yields 0.67, 0.5(0.67 + 0.25) = 0.46, and 0.10 for the estimated deprotonation shifts of $N(CH_3)$, en–CH_2 (average), and $N(CH_3)_2$, respectively. For the N-meen complex, it was assumed that there is no preference for primary over secondary nitrogen deprotonation; for the N,N'-dmen complex, it was assumed that *dl* and *meso* isomers would be affected similarly by deprotonation.

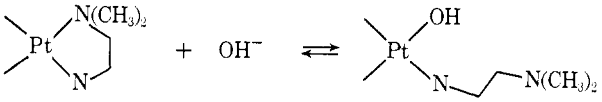
Values of δ' estimated in this way and the resultant K' for each complex are given in Table II. The slope of a δ *vs.* (OH^-) plot = δ(1 *M* KOH), which is also essentially linear over this narrow (OH^-) range, is included in Table II to indicate the magnitude of the shifts involved. Estimated uncertainties in δ' (10–15%) and slopes of $1/\delta$ *vs.* $1/(\mathrm{OH}^-)$ plots (5–10%) require at least a 20% uncertainties in the values given for K'.

Ring Opening by OH^-. For complexes containing a coordinated $N(CH_3)_2$ moiety, an additional complication arises. This is illustrated in Figure 1 for the N,N,N'-tmen complex. As the KOH concentration is increased, a new peak appears 0.98 ppm downfield from *t*-BuOH. Its intensity increases with KOH concentration. It does not have ^{195}Pt side bands. As the new peak increases, the relative size of the peak assigned to Pt–$N(CH_3)_2$ decreases, suggesting the following competition equilibrium.

Table II. KOH Concentration Dependence of Chemical Shifts and Equilibrium Quotients for Deprotonation of Pt(bipy)L^{2+} Complexes by OH^- in Water at 30° and Ionic Strength 1.3

L	δ(1 *M* KOH), ppm	δ', ppm[a]	K' [b]	K_6[b]
en	0.023	0.35	0.07	
N-meen	0.028 (CH_3)	0.38	0.08	
	0.033 (CH_2)	0.40	0.09	
N,N-dmen	0.063 (CH_2)	0.35	0.18	0.39
	0.012 (CH_3)			
N,N-dmen	0.027 (CH_3)	0.38	0.07	
	0.040 (CH_2)	0.45	0.10	
N,N,N'-tmen	0.045 (CH_3)	0.68	0.07	0.33
	0.028 (CH_2)	0.45	0.07	
	0.010 $(CH_3)_2$			

[a] See text for a discussion of the estimation of these values. [b] ±20%.



(6)

Equilibrium quotients for (6), K_6, estimated from relative areas of peaks assigned to chelated and free $N(CH_3)_2$, are also included in Table II.

Limits on the rate of the ring-opening process can be set by the observations (a) that separate peaks separated by 94 Hz at 100 MHz are observed for the two types of $N(CH_3)_2$ protons and (b) that equilibrium is established in less than 1 min when the complex is dissolved in 1.0 *M* KOH.

K's of Ammine Complexes. For the two ammine complexes which inspired this investigation, the effect of increased KOH concentration is too small to permit reliable K' determination from deprotonation shifts measured in the 0.01–1.0 *M* KOH range. However, relative K's of bipyridyl and ammine complexes were estimated by comparing their shifts with a similar bipyridyl complex at higher KOH concentrations where both types are deprotonated significantly.

Table III lists deprotonation shifts in 3 *M* KOH for en–CH_2 protons of three similar complexes. Values were obtained for each complex from the smooth curve drawn through at least five points on a δ *vs.* KOH concentration plot. They were used to calculate K' for the two diammine complexes on the assumption that the

Table III. Effect of High KOH Concentrations on en–CH_2 Chemical Shifts and Resultant K' Values for Some Ammine Complexes of Pt(II)

Complex	δ(3 *M* KOH), ppm[a]	K'
Pt(dipy)(N,N'-dmen)$^{2+}$	0.17	0.09 ± 0.02[b]
$Pt(NH_3)_2$(N,N'-dmen)$^{2+}$	0.033	0.010 ± 0.003
$Pt(NH_3)_2$(EDDA)	0.020	0.007 ± 0.003

[a] Relative to low pH species. [b] Determined at μ = 1.3.

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(13) L. E. Erickson, R. P. Clow, J. K. Howie, and J. C. McDonald, *J. Am. Chem. Soc.*, **90**, 6371 (1968).

ratio of K's for two complexes, 1 and 2, at constant (OH^-) is given by

$$K_2'/K_1' = \frac{\delta_2(\delta_1' - \delta_1)}{\delta_1(\delta_2' - \delta_2)} \tag{7}$$

Pt(bipy)(N,N′-dmen)$^{2+}$ was used as the reference complex and it was further assumed that $\delta' = 0.45$ ppm for en–CH_2 protons of all three complexes. Plots of δ *vs.* KOH concentration showed a small, but distinct upward curvature for all complexes studied. Since such curves must level off and approach a limiting value asymptotically as the extent of deprotonation approached 100%, this upward curvature probably reflects increased contribution from doubly deprotonated species and/or significant deviation from ideality at higher KOH concentrations. Thus, the values at 3 *M* KOH, where the upward curvature was not as significant, were used in the calculations. However, since K' for the reference substance was determined at ionic strength 1.3, all values given in Table III apply at ionic strength 1.3.

Temperature Dependence of K'. The effect of temperature on K' of three complexes was also investigated. In order to optimize the opportunity to observe significant effects, the complexes were dissolved in 2–3 *M* KOH so that the extent of deprotonation at 30° was appreciable. Since chemical shifts of CH_2 or CH_3 protons of the fully protonated ligand also depend slightly on temperature (2–3 cps/100° at 100 MHz), the temperature dependence of a pH 12–13 sample was also measured. All shifts were measured with respect to 0.5% internal *t*-butyl alcohol or TMACl. At each temperature the deprotonation shift, δ, and K' were calculated from the observed shifts. Results are given for Pt(dipy)(N,N′-dmen)$^{2+}$ in Table IV. The qualitative conclusion is that the extent of deprotonation increases with increased temperature. The difference in K's based on CH_2 and CH_3 shifts is similar to that found at $\mu = 1.3$. It no doubt reflects the inadequacy of the model used to estimate δ'. Using the average K' for each temperature, $\Delta H' = 2.5 \pm 0.5$ kcal was calculated for reaction 2 from a linear plot of log K' *vs.* $1/T$.

Table IV. Temperature Dependence of Deprotonation Shifts[a] and K' for Pt(dipy)(N,N′-dmen)$^{2+}$ in 1.88 *M* KOH

t, °C	δ-(CH_3)	δ-(CH_2)	K'(CH_3)	K'(CH_2)	K'(av)
30	4.2	5.4	0.067	0.073	0.070 ± 0.01
70	6.1	8.9	0.101	0.133	0.117 ± 0.02
90	7.0	10.5	0.120	0.167	0.145 ± 0.02

[a] Defined as ($\delta_{obsd} - \delta_{N-H}$) at the same temperature.

For Pt(NH_3)$_2$(N,N′-dmen)$^{2+}$ and Pt(NH_3)$_2$(EDDA), the temperature dependence of deprotonation shifts was less than 10% over a 60° temperature range. This requires that $\Delta H'$ for these two complexes is less than ±1.0 kcal mol^{-1}.

Deprotonation Effects on J_{Pt-H}. With one exception, the effect of deprotonation on ^{195}Pt–proton spin coupling constants for Pt–N–C–H fragments is negligible, *i.e.*, less than 1 Hz, even for the highest KOH concentrations investigated. The single exception is J_{Pt-H} for acetate protons of Pt(NH_3)$_2$(EDDA) which decreases approximately linearly with KOH concentration from 31 to 26 Hz between pH 12 and 10 *M* KOH. Over this KOH concentration range, J_{Pt-H} for en–CH_2 protons of the same complex does not change, while the en–CH_2 deprotonation shift for the complex in 10 *M* KOH (0.09 ppm) indicates substantial deprotonation.[14]

Proton Exchange and Inversion Rates. N–H proton exchange rates of all three bipyridyl–diammine complexes which contain an NH(CH_3) fragment were determined by analysis of line shapes of the methyl doublet (J = 6.0 Hz for all three compounds) as a function of pH near coalescence.[8] Second-order rate constants, k_{OH^-}, calculated from the observed first-order rate constants and the measured pH,[15] for the exchange process are given in Table V.

For the N,N,N′-tmen and N,N′-dmen complexes, the rate of inversion of the complex was obtained from the further collapse of methyl singlets at still higher pH. These changes and the low pH doublet collapse are illustrated for Pt(bipy)(N,N,N′-tmen)$^{2+}$ in Figure 1. At pH 4, the spectrum consists of a spin-coupled doublet (J = 6.0 Hz) for $NHCH_3$ at 1.678 ppm and a pair of singlets at 1.922 and 1.948 ppm for the two nonequivalent N(CH_3)$_2$ methyl groups. The 6.0-Hz doublet coalesces at pH 7.0 ± 0.1 as the rate of N–H exchange reaches a critical value. At pH 9.9 ± 0.1, the two N(CH_3)$_2$ signals coalesce as the rate of inversion reaches its critical value. Comparison of experimental line shapes near coalescence with computer generated line shapes based on $\Delta\nu = 2.7$ Hz for two-site exchange led to the second-order rate constant $k_{in}' = k_{in}/(OH^-) = 3.6 \times 10^4$ l. mole^{-1} sec^{-1}, where k_{in} is the first-order rate constant for inversion in either direction, equal to $^1/_2\,\tau$.[16]

Similar, but greatly expanded, traces near coalescence are shown in Figure 2 for Pt(bipy)(N,N′-dmen)$^{2+}$ for which the process

$$dl \underset{k_{-in}}{\overset{k_{in}}{\rightleftarrows}} meso$$

produces coalescence of the two unequal intensity peaks near pH 9. The second-order rate constants for inversion, k_{in}' and k_{-in}', were calculated from $1/\tau = k_{in} + k_{-in}$, $k_{in}/k_{-in} = 0.29/0.71$, and the pH of several traces near pH 9. For each trace, τ was estimated by comparison between experimental and calculated spectra based on $\Delta\nu = 2.5$ Hz, $p_{dl} = 0.71$, $p_{meso} = 0.29$, and $1/T_2 = 3.1$ sec^{-1}.

Values for k_{OH^-} and k_{in}' for Pt(bipy)(N,N′-dmen)$^{2+}$ reported by Haake and Turley are also included in Table V for comparison. Since their work was done at 60 MHz they observed only that the methyl peaks of *dl* and *meso* isomers had coalesced at any pH great enough to collapse the N–H doublet splitting. From this they tentatively concluded that inversion and exchange rates are approximately equal. We also failed to encounter the solubility problems they reported for the chloride salt, but the nitrate salt is too insoluble to obtain good spectra.

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[14] By extrapolation, the deprotonated species should have J_{Pt-H} close to 0. This no doubt reflects a drastic change in the preferred conformation of the acetate fragment. See ref 5, Figure 6, and accompanying discussion.

[15] Based on pK_w = 13.83 at 30°.

[16] J. W. Emsley, *et al.*, ref 6, p 486.

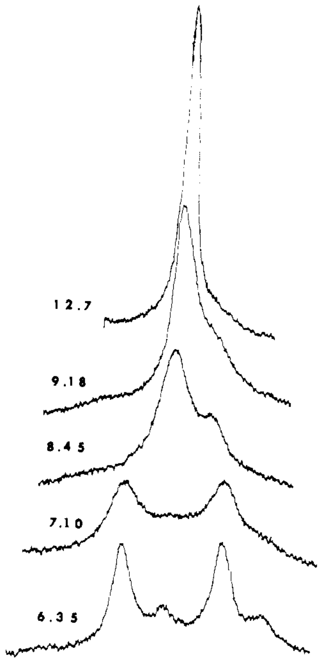

Figure 2. Effect of pH on the central CH_3 pattern of 0.2 *M* Pt(bipy)(N,N′-dmen)Cl_2. Note the separate doublets for *dl* (larger) and *meso* (smaller) isomers at pH 6.35.

Discussion

Acidity, Exchange, and Inversion. Table VI summarizes kinetic and equilibrium data for proton exchange and dissociation and for inversion of several platinum(II) complexes. The following five closely related parameters are given: k_{OH^-} and k_{H_2O}, the rate constants for OH^-- and H_2O-catalyzed proton exchange, $K' = K_a/K_wK_\gamma$, and k_{in}' and k_3, the rate constants for inversion of protonated and deprotonated complexes, respectively. Two significant conclusions can be drawn from the data. First, there is a great variation in k_{OH^-} for several complexes having very similar K' values.[17] Second, rates of inversion of deprotonated nitrogen complexes, like K' values, are remarkably insensitive to substitution. These two conclusions warrant further analysis.

Table V. Rate Constants for OH^--Catalyzed N–H Exchange and Inversion of Pt(bipy)L^{2+} at 30° and Ionic Strength 1.0

L	pH at coalescence of CH_3 doublet[a]	$10^{-7} \cdot k_{OH^-}$, l. mole^{-1} sec^{-1}	$10^{-4}k_{in}'$, l. mole^{-1} sec^{-1}
N-meen	8.4	0.27	
N,N′-dmen	7.9	1.02	9 (k_{in}')
			21 (k_{-in}')
		0.9[b]	265 ($k_{in}' + k_{-in}'$)[b]
N,N,N′-tmen	7.0	8.7	3.6

[a] Resulting from N–H spin coupling (J = 6.0 Hz). [b] P. Haake and P. C. Turley, ref 4; recalculated for pK_w = 13.83, assuming 30° for sample temperature.

The failure of a simple correlation between k_{OH^-} and K' is most evident in the data given for the three bipyridyl complexes which differ only in extent of methyl substitution of the en moiety. Although K' is virtually constant for the series, k_{OH^-} varies by a factor of 30. Furthermore the effect of methyl substitution on k_{OH^-} differs drastically for negatively and positively charged complexes. Whereas methyl substitution decreases the rate of proton exchange for $PtGlyCl_2^-$ by a factor of 10, similar substitution increases the rate of proton exchange by a factor of 10 for the bipyridyl–en complexes. The much smaller difference in k_{H_2O} for $PtGlyCl_2^-$ and $PtSarCl_2^-$ suggests that K_a for these two complexes, like the bipyridyl complexes, may be much more similar than relative proton exchange rates indicate.[8] Thus, considerable caution is called for in estimating relative acidities from relative proton exchange rates. Nevertheless, diammine complexes, which are weaker acids than corresponding bipyridyl complexes, also have slower exchange rates and $Pt(NH_3)_3(Sar)^+$, with the slowest exchange rate given, is probably also the weakest acid.

The second observation, that $k_3 = k_{in}'/K'$ is almost invariant for four complexes, is of interest in itself and suggests an alternative approach to determining relative acidities of similar complexes. If the complexes have appropriate asymmetry to permit an nmr or polarimetric determination of the second-order rate constant for inversion, k_{in}', the order should parallel the order of K's. For example, if k_3 is taken to be 10^6 for $Pt(NH_3)_3(Sar)^+$, $K' = 25/10^6 = 2.5 \times 10^{-5}$. This approach could perhaps be employed profitable to estimate K' for the dien complexes[18] listed in Table VI. Although the comparatively fast exchange rates of the secondary nitrogen proton in these complexes should permit significant titration in 1 *M* KOH, direct determination of K from the effect of 0.01–1.0 *M* KOH on chemical shifts would very likely be complicated by rapid displacement of X^- by OH^-. However, inversion rates should be sufficiently fast to produce coalescence of CH_2 nmr signals at much lower pH's where hydrolysis rates are much slower.

Some Other Correlations for Bipyridyl Complexes. The large variation in k_{OH^-} in spite of almost constant K' values for the five bipyridyl complexes has already been noted. Tables VII and VIII list values for other properties of the complexes or of the substituted en ligands which might be expected to be closely related to K'. These include acid dissociation constants of free ligands, ^{195}Pt spin coupling constants of en–CH_2 protons, and stability constants and nmr contact shifts of en–CH_2 protons of paramagnetic 1:1 Ni(II) complexes.

The most striking thing about values for K' of the complexes and K_1 and K_2 of the protonated ethylenediammines (Table VII) is the very small variation in each of the three parameters with methyl substitution. However, N,N-dmen is the strongest acid of the ligands for which data are available and Pt(bipy)(N,N-dmen)$^{2+}$ is the strongest acid of the corresponding complexes.

One might reasonably expect some correlation between J_{Pt-H} for en protons and the acidity of N–H protons of the coordinated ligand. An increase in J_{Pt-H} in a series should reflect an increase in the Pt–N bond

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[17] As noted in ref 5, this can be described in terms of failure of a simple, two-parameter Brønsted relation to correlate k_{OH^-} and K' (or K_a) for R–H. This accounts for most of the substantial variation in the k_{OH^-}/k_{in}' ratio for a series of complexes.

[18] J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).

Table VI. Equilibrium and Rate Data for Platinum(II) Complexes at 30 ± 5°

Complex	k_{OH^-}, l. mole^{-1} sec^{-1}	k_{H_2O}, sec^{-1}	K', l. mole^{-1}	k_{in}', l. mole^{-1} sec^{-1}	k_3, sec^{-1}	Ref[a]
$PtGlyCl_2^-$	1×10^7	6×10^{-5}				8
$PtSarCl_2^-$	1×10^6	4×10^{-5}				8
$Pt(NH_3)_3Sar^+$	2×10^3			25		5
$Pt(NH_3)_2(EDDA)$	2×10^5		0.007	2×10^3	3×10^5	5
$Pt(NH_3)_2$(N,N′-dmen)$^{2+}$	4×10^4		0.010	2×10^3	2×10^5	4
Pt(bipy)(en)$^{2+}$			0.07			
Pt(bipy)(N-meen)$^{2+}$	3×10^6		0.08			
Pt(bipy)(N,N′-dmen)$^{2+}$	1×10^7		0.09	9×10^4	1×10^6	
				21×10^4	2×10^6	
Pt(bipy)(N,N-dmen)$^{2+}$			0.18			
Pt(bipy)(N,N,N′-tmen)$^{2+}$	9×10^7		0.07	4×10^4	6×10^5	
$Pt(en)_2^{2+}$	2×10^5					18
$Pt(dien)Cl^+$	2×10^5					18
$Pt(dien)Br^+$	$2(6) \times 10^6$					18
$Pt(dien)I^+$	$2(200) \times 10^6$					18
$Pt(dien)SCN^+$	$3(600) \times 10^6$					18

[a] If other than this work.

Table VII. Comparison of K' Values for Pt(bipy)L^{2+} Complexes with pK_a's of L

L	pK'[a]	pK_1[b]	pK_2[b]
en	1.15	10.18	7.47
N-meen	1.07	10.4	7.56
N,N′-dmen	1.04	10.29	7.47
N,N-dmen	0.75	10.0	6.79
N,N,N′-tmen	1.15		

[a] ±0.1. [b] Values at 25° as reported by F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 5243 (1952).

Table VIII. Comparison of Pt–H Spin Coupling Constants and K' of Pt(bipy)L^{2+} with Properties of Corresponding Ni^{II}L^{2+} Complexes

L	pK'	$J_{Pt-enCH_2}$	Log K_f[a]	Contact shift in paramagnetic NiL^{2+} complex[b]
en	1.15	40.5	7.60	93.3
N-meen	1.07	37.2	7.36	93.2
N,N′-dmen	1.04	34.0	7.11	92.2
N,N-dmen	0.75	35.0	6.77	80.4
N,N,N′-tmen	1.15	30.8		80.2
N,N,N′,N′-tetramen				69.5

[a] Formation constants for formation of 1:1 Ni^{2+} complexes in 0.5 *M* KNO_3 at 25°. [b] In ppm downfield from free ligand for en–CH_2 protons: F. F. L. Ho, personal communication.

strength which would be expected to increase the N–H proton acidity. However, although increased methyl substitution produces a monatonic decrease in J_{Pt-H} for en–CH_2 protons, there is no corresponding trend for pK'. This again illustrates that pK_a's of acids in aqueous solutions are often determined by compromise between competing interactions so that simple correlations involving compounds of similar acidities are often more fortuitous than fundamental.[19]

Although there is no simple correlation between pK's and J_{Pt-H} for en–CH_2 protons, there is a good correlation between J_{Pt-H} and the more direct indicators of metal–nitrogen bond stability that are given in Table VIII. Both formation constants and contacts shifts of en–CH_2 protons of corresponding paramagnetic 1:1 complexes of Ni(II) decrease with extent of methyl substitution. Other observations confirm this decrease in the stability of the platinum–nitrogen bond with increased methyl substitution. J_{Pt-H} for CH_3 protons is about 40 Hz for the Pt-$NHCH_3$ configuration but is reduced to about 30 Hz for the Pt-$N(CH_3)_2$ configuration. Furthermore, only dimethyl-substituted nitrogens are displaced by OH^- in 1 *M* KOH. In preparing the complexes by stirring solid Pt(bipy)Cl_2 with an aqueous solution of the amine ligand, it was observed that the rate at which solid dissolved decreased significantly with increased methyl substitution. In fact, attempts to prepare Pt(bipy)(N,N,N′,N′-tetramen)$^{2+}$ by the same technique were unsuccessful, since Pt(bipy)Cl_2 failed to dissolve at all in an aqueous solution of the ligand.

$\Delta H'$, $\Delta H°_{N-H}$, and ΔH_3*. From $\Delta H'$, the measured $\Delta H°$ for reaction 2, it is possible to calculate two other quantities of interest, $\Delta H°_{N-H}$, the enthalpy of dissociation of the N–H proton, and ΔH_3^*, the enthalpy of activation for the inversion of the deprotonated complex. Assuming that K_γ is independent of temperature, the former is given by $\Delta H' + \Delta H_{H_2O}$. The latter can be calculated from the temperature dependence of k_{in}'. Since $k_3 = k_{in}'/K'$, $\Delta H_3^* = \Delta H_{in}^* - \Delta H'$. Available data for the three complexes for which $\Delta H'$ values were determined are summarized in Table IX.

Table IX. ΔH Values[a] for Deprotonation and Activation of Platinum(II) Complexes at 30°

Complex	$\Delta H'$	$\Delta H°_{N-H}$	ΔH_{in}^*	ΔH_3
Pt(bipy)(N,N′-dmen)$^{2+}$	2.5	16		
$Pt(NH_3)_2$(N,N′-dmen)$^{2+}$	±1	13.3		
$Pt(NH_3)_2(EDDA)$	±1	13.3	15.4[5]	15.4

[a] All values are in kcal mole^{-1}; estimated uncertainty, 1–2 kcal mole^{-1}.

The $\Delta H°_{N-H}$ values of all three complexes are comparable to $\Delta H°_{H_2O}$, as might be expected on the basis of the similar acid strengths of N–H and H_2O. However, the more acidic Pt(bipy)(N,N′-dimen)$^{2+}$ has a somewhat larger $\Delta H°_{N-H}$. This requires that it also has a

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(19) See R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter V, for a detailed discussion and several examples.

larger positive $\Delta S°_{N-H}$ by about 4 eu. Such a difference is not unreasonable in view of the substantial difference between two NH_3 molecules and bipyridyl, the ligands occupying the other coordination sites.[19]

The fact that $\Delta H'$ is so small requires that $\Delta H_3^* \cong \Delta H_{in}^*$ for these Pt(II) complexes. This leads to values for both $k_3(30°)$ and ΔH_3^* that are very similar to those for typical aliphatic amines.[5] The similarity in ΔH_3^* is not surprising, since the structure at the asymmetric center is similar for all complexes, *i.e.*, a tertiary nitrogen bonded to Pt, CH_2 of an en fragment, and CH_3 or $CH_2CO_2^-$. Unfortunately, there are serious limitations to accurate determinations of both ΔH_{in}^* and $\Delta H'$ for many complexes that one might like to study. For the former, both pH and k_{in} vary with temperatures, so that k_{in}' must be evaluated from a detailed analysis of the effect of pH on line shapes at each temperature.[5] Alternatively, rates and activation energies for inversion can be obtained from the rates of racemization of resolved complexes, as reported by Sargeson and coworkers for several Co(III) complexes.[20,20a] For the latter, the extent of deprotonation must be sufficient at room temperature to permit significant deprotonation so that changes in the extent of deprotonation with temperature can be accurately determined. Under these conditions, many complexes are decomposed at high temperatures.

Isolation of Deprotonated Species from Aqueous KOH. On the basis of the K' values reported in this paper, it appears that it should be possible to isolate deprotonated species from strongly basic aqueous solutions. The chance observation that red needle-shaped crystals formed in strongly basic solutions (~2 *M* KOH) of $[Pt(bipy)en]Cl_2$ provided a clue that led to the isolation of a deep red compound whose analysis corresponds fairly closely to the formula $[Pt(bipy)(en\text{-}H)]\,[Pt(bipy)(en)]Cl_3$, where en-H designates singly deprotonated en. Such species have been isolated as iodide salts from liquid ammonia by Watt and coworkers.[10] However, the possibility that the compound is actually a hydrate or the mixed chloride hydroxide precipitate cannot be excluded on the basis of the data presently available. We are planning further experiments to clear up this point and to attempt to isolate other deprotonated complexes from aqueous medium. Included among these are several yellow bipyridyl amino acid (AA) nitrates, $[Pt(bipy)(AA)]NO_3$, which appear to be converted almost completely to insoluble red deprotonated species (or hydroxides) by the addition of stoichiometric amounts of aqueous 0.2 *M* KOH.

Critique of the Nmr Technique. This work illustrates well both advantages and limitations of nmr studies of deprotonation of weakly acidic ligand protons of metal complexes. In addition to extending the determinable range of acid strengths about 4 pK_a units beyond potentiometric methods, the nmr technique indicates which proton is being titrated. The chief limitation, especially for studies of very weakly acidic complexes, is the great tendency of OH^- to destroy the complex. Thus, only complexes which are resistant to rapid attack by OH^- can be conveniently studied. This limits one to relatively inert species like certain Pt(II), Co(III), and Pt(IV) complexes. As demonstrated by $[Pt(bipy)(N,N\text{-}dmen)](NO_3)_2$, even some of these may react quite readily with OH^-. For example, $Co(NH_3)_4(Sar)^{2+}$ decomposes rapidly in 1 *M* KOH so that we have so far not been able to determine its K'. The determination of K' and k_3 for this and the other Co(III) complexes[20] would be particularly interesting for evaluating the effect of metal ion charge on k_3 and activation energies for inversion. The technique should also be a particularly valuable supplement to ir techniques in studying deprotonation in nonaqueous solvents.[10]

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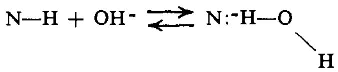
[20] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, 90, 6028 (1968), and earlier references cited therein.

[20a] NOTE ADDED IN PROOF. In a recent publication, Buckingham, Marzilli, and Sargeson (*ibid.*,) **91**, 5227 (1969)) reported exchange and inversion rate data for $Pt(Meen)(en)^{2+}$ and *trans*-$Pt(Meen)(en)Cl_2^{2+}$. Some comparison of results is in order. The rate data and retention ratio they obtained for $Pt(Meen)(en)^{2+}$ ($k_{OH^-} = 2 \times 10^5\ M^{-1}\ sec^{-1}$ and $k_{in}' = 7.9 \times 10^{-2}\ M^{-1}\ sec^{-1}$) are consistent with data for other platinum(II) complexes as summarized in Table IV. Furthermore, since K' has been shown to be quite insensitive to methyl substitution in bipyridyl complexes, K' for $Pt(Meen)(en)^{2+}$ is probably close to that of $Pt(N,N'\text{-}dmen)(NH_3)_2^{2+}$ (10^{-2}) so that $k_3 \cong 10^5\ sec^{-1}$. Our direct measurements of $\Delta H'$ and ΔH_{in}^* for $Pt(NH_3)_2(EDDA)$ provide a value for $\Delta H_3^* = 15$ kcal, a value which is within the range they report for the more acidic Pt(IV) system, but which exceeds the value they estimated for the Pt(II) system by 5–7 kcal. A more thorough study of the temperature dependence of k_{in}' and K' for these complexes will be required to determine whether there is a significant difference in the energy barrier to inversion between deprotonated Pt(II) and Pt(IV) complexes. The similarity in the retention ratio for diamine and bipyridyl complexes adds further evidence to their rejection of an earlier suggestion that the lone pair of the deprotonated complex is stabilized by hydrogen bonding to an adjacent NH_3 molecule. However, the relatively small value of k_3 for all these metal complexes, compared to inversion rates for amines in the gas phase, suggests that the deprotonated intermediate is stabilized with respect to inversion by hydrogen bonding to a solvent molecule. Thus the intermediate shown by Buckingham, *et al.* (p 5231), should probably be drawn with a water proton attached to the lone pair and the equilibrium represented by eq 2 in this paper should be written



$$N{-}H + OH^- \rightleftharpoons N{:}^-H{-}O{-}H$$