Proton Magnetic Resonance Spectra of Platinum(II) Complexes. III. Proton Exchange and Inversion at Nitrogen in N,N′-Dimethylethylenediamineplatinum(II) Complexes[1]

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Abstract: The rates of base-catalyzed proton exchange at nitrogen have been measured in two N,N′-dimethylethylenediamineplatinum(II) complexes. The bipyridyl complex, $[(\mathrm{bipy})(\mathrm{dmen})\mathrm{Pt}]^{2+}$, undergoes proton exchange about 300 times faster than the diammine complex, $[(\mathrm{NH_3})_2(\mathrm{dmen})\mathrm{Pt}]^{2+}$. A limiting rate of inversion at nitrogen was measured in the diammine complex by observing *meso* ⇄ *dl* forms.

In parts I and II of this series of papers[1b] the rates of inversion at sulfur when bonded to platinum(II) were studied in a variety of sulfide complexes. Inversion at nitrogen has been made measurable in dibenzylmethylamine by slowing the inversion through protonation of a large fraction of the amine.[3] Recently a cobalt complex has been resolved into optical isomers, and the rates of racemization and deuterium exchange were measured.[4] We have been able to observe rates of proton exchange and inversion at nitrogen in N,N′-dimethylethylenediamineplatinum(II) complexes. The rate of proton exchange was measured by the presence and loss of H–N–C–H couplings. Inversion at nitrogen was observed by interconversion of *dl* and *meso* forms due to geometrical isomerism in the chelate ring.

Experimental Section

The nmr spectra were recorded with a Varian A-60 spectrophotometer. Spectra were calibrated by the side-band technique[5] using Hewlett-Packard 200AB or 200CD wide-range oscillators and a Hewlett-Packard 5233L frequency counter. Sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) was used as the internal standard.

pH Determination. The pH of solutions was determined potentiometrically using a Radiometer titrator.

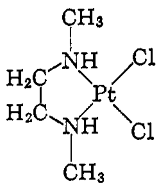
Dichloro-N,N′-dimethylethylenediamineplatinum(II) (1). To K_2PtCl_4 (2.08 g) in 25 ml of H_2O was added 4 ml of a 5% solution of N,N′-dimethylethylenediamine. On heating, a green precipitate formed and was filtered. The filtrate yielded, on cooling, fine yellow needles.

Anal. Calcd for $PtC_4H_{14}N_2Cl_2$: Pt, 55.1. Found: Pt, 55.6.

The dication, diammine-N,N′-dimethylethylenediamineplatinum(II) (2), was generated by heating at ~95° a mixture of 1 and NH_4OH in a 1:5 molar ratio. After the solid, 2, had dissolved and the solution had lost its color, the liquid was evaporated to give the dichloride salt as a white, hygroscopic glass which could not be crystallized presumably because it was a *dl-meso* mixture. The dication 3 was generated by a similar method from dichloro-2,2′-bipyridylplatinum(II)[6] and N,N′-dimethylethylenediamine. Both these ions gave nmr spectra consistent with structures 2 and 3.

Results

Planar N,N′-dimethylethylenediamine complexes can exist in isomeric *dl* and *meso* forms. This is illustrated for complex 2 as 4 (*dl*) and 5 (*meso*). Interconversion of *dl* and *meso* forms can occur by inversion at a nitrogen atom, but loss of an N–H proton must precede inversion.[3]



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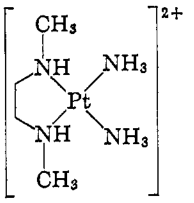

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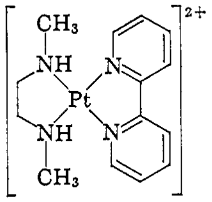

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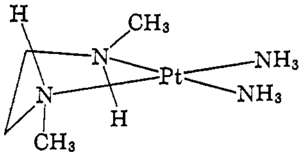

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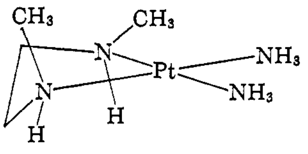

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Pmr spectra of 2 in H_2O are given in Figure 1. At pH 6.8 the spectrum (Figure 1a) indicates the presence of a slowly interconverting mixture of 4 and 5. There are two doublets with corresponding ^{195}Pt satellites (^{195}Pt = 33.8% of naturally occurring platinum) due to the methyl groups of 4 and 5. The doublets are approximately equal in intensity, indicating an equilibrium constant near 1.0 for 4 ⇄ 5. One signal (peaks first and third from the right in the intense quartet, Figure 1a) is centered at −157.3 cps with $J(\mathrm{HNCH_3})$ = 5.9 cps and $J(\mathrm{PtNCH_3})$ = 39.9 cps. The other methyl signal (peaks second and fourth from the right in the intense quartet, Figure 1a) is centered at −159.5 cps with $J(\mathrm{HNCH_3})$ = 5.9 cps and $J(\mathrm{PtNCH_3})$ = 39.2 cps. The methylene absorption is poorly resolved, as would be expected from two different AA′BB′ systems with additional splitting due to ^{195}Pt and the protons on nitrogen.

The isomers 4 and 5 are written in conformationally preferred forms,[7] but it seems unlikely that there should be any significant barrier to conformational changes.[8]

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[1] (a) Supported by Grant GM-9294 from the U. S. Public Health Service and by a grant from the Faculty Research Committee of University of California at Los Angeles. (b) Parts I and II: P. C. Turley and P. Haake, *J. Am. Chem. Soc.*, **89**, 4611, 4617 (1967).

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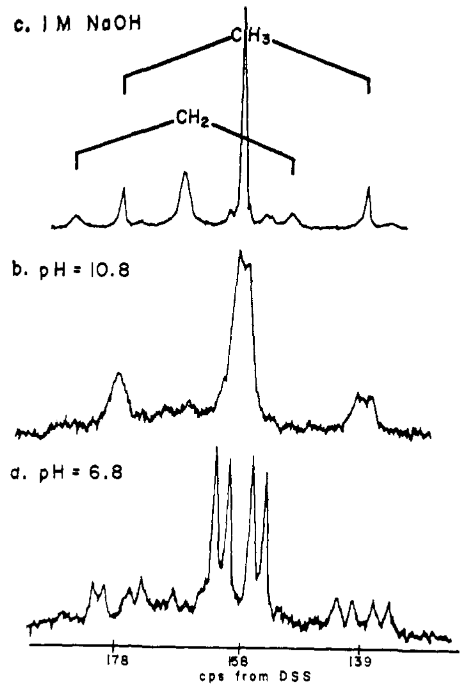

Figure 1. Pmr spectra of complex 2 in H_2O.

The observed spectra and their pH dependence (see below) are consistent with the methyl signals representing a time average of all conformational positions.

At pH 10.5 proton exchange is sufficiently rapid to coalesce each methyl doublet to a singlet. A similar rate of *dl* $\rightleftharpoons$ *meso* isomerization is also suggested since the two methyl resonances coalesce at only slightly higher pH. The spectrum at pH 10.8 is shown in Figure 1b. The 1:4:1 resonances of the methylene protons become distinct at pH's above 13, as shown in Figure 1c. Using our observations on coalescence of doublets due to HNCH splittings and on coalescence of signals due to *dl* and *meso* isomers, we can calculate first-order rate constants for exchange at pH 10.5 and for *dl* $\rightleftharpoons$ *meso* at pH ~11 (eq 1 and 2).[3,5,9]

$$k_{ex} = \frac{\pi}{\sqrt{2}}J(\mathrm{HNCH_3}) = 13.3\ \mathrm{sec^{-1}\ at\ pH\ 10.8} \tag{1}$$

$$k_i = \frac{\pi}{\sqrt{2}}\Delta\nu_{\mathrm{CH_3}} = 4.6\ \mathrm{sec^{-1}\ at\ pH\ 11} \tag{2}$$

The pH dependence indicates base catalysis. Assuming first-order dependence on HO^- (eq 3),[10] the second-order rate constant for exchange will be given by eq 4. With an isomerization rate slower than the

$$\mathrm{HO^-} + \mathrm{>NH^+} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \mathrm{H_2O} + \mathrm{>N:} \tag{3}$$

$$k_2 = k_{ex}/[\mathrm{HO^-}] = 4.2 \times 10^4\ M^{-1}\ \mathrm{sec^{-1}} \tag{4}$$

exchange rate, knowledge of the pK_a of 3 might make it possible to evaluate the rate constant for inversion at nitrogen from k_i.[3] However, potentiometric titration of 2 and 3 with NaOH only gave pH readings indicative of dilution of the added base, so we can only say that $K_a < 10^{-13}$ for 2 and 3. However, we can calculate limiting values for the rate constant for inversion at nitrogen (eq 5–7) and for k_1 (eq 3 and 8).

$$\mathrm{>N:} \underset{k_3}{\overset{k_3}{\rightleftharpoons}} \mathrm{:N<} \tag{5}$$

$$v_{\mathrm{inversion}} = k_i[\mathrm{NH^+}] = k_3[\mathrm{N:}] \tag{6}$$

$$k_3 = k_i\frac{[\mathrm{NH^+}]}{[\mathrm{N:}]} > 4.6 \times 10^2\ \mathrm{sec^{-1}} \tag{7}$$

$$k_1 = \frac{k_2[\mathrm{NH^+}][\mathrm{OH^-}]}{[\mathrm{N:}]} > 4.2 \times 10^3\ \mathrm{sec^{-1}} \tag{8}$$

Proton exchange was also investigated in 2,2′-bipyridyl-N,N′-dimethylethylenediamineplatinum(II) chloride (**3**). At pH 4.0 the two sets of methyl resonances in the pmr spectrum are about 1.7 cps apart. The sites are not equally populated: the downfield resonance is about twice the intensity of the upfield set. The more intense methyl group falls at −179.4 cps with $J(\mathrm{HNCH_3}) = 6.0$ cps and $J(\mathrm{PtNCH_3}) = 40.5$ cps. The other methyl resonances occur at −177.7 with $J(\mathrm{HNCH_3}) = 5.6$ cps; $J(\mathrm{PtNCH_3})$ could not be determined due to insufficient solubility of the complex. The methylene absorption is poorly resolved. When the solution of the complex attains pH 8.0, proton exchange is sufficiently rapid to collapse each methyl doublet to a singlet. The base-catalyzed exchange rate can be calculated in the same way as for **2** (eq 9 and 10).

$$k_{ex} = \frac{\pi}{\sqrt{2}}J(\mathrm{HNCH_3}) = 12.9\ \mathrm{sec^{-1}} \tag{9}$$

$$k_2 = k_{ex}/[\mathrm{^-OH}] = 1.3 \times 10^7\ M^{-1}\ \mathrm{sec^{-1}} \tag{10}$$

At pH $\geqslant 8$ separate *dl* and *meso* methyl resonances are not observed, indicating inversion at nitrogen, although the initially small separation of methyl resonances makes this a tentative conclusion. The rate constants for inversion are given by eq 11 and 12.

$$k_i = \frac{\pi}{2}\Delta\nu_{\mathrm{CH_3}} \sim 4\ \mathrm{sec^{-1}\ at\ pH\ 8} \tag{11}$$

$$k_3 = k_i\frac{[\mathrm{NH^+}]}{[\mathrm{:N}]} > 4 \times 10^5\ \mathrm{sec^{-1}} \tag{12}$$

Discussion

In the pmr spectra of both **2** and **3** at low pH the downfield methyl resonance is larger than the upfield one. One would expect the *trans* complex ions to be more stable.[7] However, the chemical shift differences are small and there is no clear evidence on which to base assignments.

Within experimental error, removal of a proton is the rate-limiting process for inversion at nitrogen. This observation contrasts with recent work on a cobalt(II)[4] complex for which proton exchange is about 10^3 times faster than inversion at nitrogen. Our work on these planar complexes supports the explanation[4] that inversion is slow in the octahedral Co(II) complex due to hydrogen bonding to an apical ammonia ligand.

A possible explanation for the fast inversion and proton exchange in platinum(II) complexes can be based on the faster exchange and probably faster inversion in the bipyridyl complex **3** compared to the diammine complex **2**. Bipyridyl also increases the

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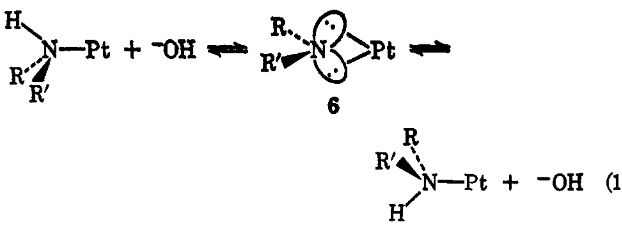
[9] Symbols are: k_{ex} = first-order rate constant for exchange; k_i = first-order rate constant for *dl* $\rightleftharpoons$ *meso* isomerization; $\mathrm{NH^+}$ = protonated complex;[10] N: = deprotonated complex.[10]

[10] We write $\mathrm{>NH^+}$ and >N: for simplicity; in both species there will probably be an intermediate charge situation.

rate of displacement of chloride in Pt(II) complexes,[11] and it therefore can be said to have a considerably greater *trans* effect than ammonia and other simple amine ligands. Other exchange rates[12] on Pt(II) complexes also show a strong *trans* effect, so the same ligands which stabilize the transition state for displacement at Pt(II) also stabilize the transition state for proton exchange. We have previously found a *trans* effect in inversion at sulfur bonded to Pt(II) where the suggested mechanism involves an internal displacement of one sulfur pair of electrons by the other.[2] The most likely mechanism for displacement at platinum(II)[13,14] involves stabilization of a transition state with geometry near that of a trigonal bipyramid. These considerations suggest that the mechanism of proton exchange and inversion at nitrogen in Pt(II)-N<H complexes involves a process (eq 13) similar to the one we have suggested for inversion at sulfur in Pt(II)-sulfide complexes.[1b] The intermediate **6** is drawn to indicate possible stabilization through double coordination of nitrogen to platinum; **6**, then, is a distorted pentacoordinate intermediate. This mechanism would predict that inversion should proceed half as fast as exchange. This would be the maximum rate for inversion since an exchange mechanism (other than eq 13) involving a nitrogen pair not bonded to platinum could only give slower inversion due to protonation of $\geqslant$N: before inversion. Our results (eq 1 and 2) are within experimental error of agreement with eq 13. Therefore this may be an inversion at nitrogen which does not proceed through a planar state with trigonal hybridization at nitrogen, as has been found in other studies of inversion at nitrogen [3,15-17] and as may apply in Co(II) complexes.[4] Alternatively, the *trans* effect in inversion might be explained by π bonding to platinum when the nitrogen is in the trigonal planar configuration.



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The Reactions of L-Carnosine with Metal Ions. Copper(II)[1,2]

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Abstract: The temperature-jump method has been used to determine the complexation rate constants for the reactions of L-carnosine (HL) with copper(II) at 25° and ionic strength 0.1 *M*. It had been previously postulated that L-carnosine is a bidentate ligand in the lower pH range forming a complex containing a seven-membered chelate ring. The complexation reactions observed are $Cu^{2+} + H_2L^+ \rightleftharpoons CuHL^{2+} + H^+$ and $Cu^{2+} + HL \rightleftarrows CuHL^{2+}$. The rate constants for the former reaction are $k_1 = 8.9 \times 10^2 M^{-1} sec^{-1}$ and $k_{-1} = 5.0 \times 10^4 M^{-1} sec^{-1}$; for the latter they are $k_2 = 3.5 \times 10^6 M^{-1} sec^{-1}$ and $k_{-2} = 35 sec^{-1}$. These rate constants are consistent with a sterically controlled substitution (SCS) mechanism. The complex $CuHL^{2+}$ can release a proton, producing CuL^+; this latter complex can also release a proton to form CuA. The rate constants for $CuHL^{2+} \rightleftharpoons CuL^+ + H^+$ are 230 sec^{-1} for the forward reaction and $1.0 \times 10^7 M^{-1} sec^{-1}$ for the reverse process. For the reaction $CuL^+ \rightleftharpoons CuA + H^+$, the values are 360 sec^{-1} for the forward reaction and $5.0 \times 10^7 M^{-1} sec^{-1}$ for the reverse process. Both reverse reactions are several orders of magnitude slower than the diffusion-controlled limit. This is attributed to intramolecular changes which are concurrent with proton attack.

Relaxation techniques have been used extensively in the study of complexation reactions of labile transition metal ions. A general two-step mechanism has proven consistent with the available experimental data.[4] This mechanism begins with the formation of a diffusion-limited ion pair between the aquated metal ion and the reactant ligand. Second, and rate-determining, is the substitution of the reactant ligand into the inner coordination sphere of the metal ion. For reactions obeying

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