determined from the decrease in the total area of the CH signal. This area is proportional to [2(H_2complex) + (HDcomplex)]. Assuming that the over-all rate of H_2 complex $\rightarrow$ HDcomplex is twice the rate of HD-complex $\rightarrow$ D_2complex, it can be shown that $k_{ex} = k_1/2$. Thus, $k_1 = 2k_{ex}$ is somewhat *greater than* k_r. Since deprotonation in D_2O invariably leads to racemization, k_1 so calculated corresponds to k_1 in the above scheme. The only condition under which k_r could be *as great as* k_1 would be if $k_{in} \gg k_{in}'$, so that inversion would *invariably* accompany removal of the first proton. If H–L–Pt–L$^-$ ever captures a deuteron, exchange occurs without inversion. The fact that $k_1/k_r = 0.7$, rather than 0.5, suggests that inversion of H–L–Pt–L$^-$ probably occurs more than half of the time before a proton is recaptured. This requires some preference for H–L–Pt–D$^-$ over H–L–Pt–L$^-$, which does not seem unreasonable in view of the higher symmetry of H–L–Pt–D$^-$ with its bulky, negatively charged $CH_2CH_2CO_2^-$ groups on opposite sides of the coordination plane. Unfortunately, the complexity of the system precludes a more complete analysis, which could lead to relative values of k_{in} and to the equilibrium constant for the reaction

$$2\text{D–Pt–L} \rightleftarrows \text{D–Pt–D} + \text{L–Pt–L}$$

Attempts to study this equilibrium by observing the relative areas under peaks of diastereoisomers in the proton nmr spectrum[9] were also unsuccessful, since both species had essentially identical spectra, even at 100 MHz.[11]

Measurably fast C–H proton exchange was also observed in several other complexes at high pH, but difficulties associated with maintaining constant pH made it impossible to obtain data of comparable accuracy. Nevertheless, the rate of exchange is comparable to that of **3** and to other α-carbon protons of chelated amino acids[6–9] for **1** and **2** as well as for Pt(L-Glu)Cl_2^{2-}, Pt(L-Asp)$_2^{2-}$, and Pt(L-Asp)Cl_2^{2-}.

Acknowledgment. This investigation was supported by Public Health Service Research Grant No. CA-06852 from the National Cancer Institute.

Proton Magnetic Resonance Studies of Amino Acid Complexes of Platinum(II). III. Isomerism, Proton Exchange, and Inversion at Asymmetric Coordinated Nitrogens[1]

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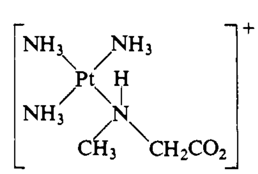
Abstract: Rates of N–H proton exchange of **1** and **2** were determined (a) by analysis of line-shape changes of H_2O solutions at high pH and (b) by analysis of slow spectral changes of D_2O solutions at mid pH. The exchange reactions are OH^- catalyzed. However, intramolecular catalysis by acetate fragments is also important in the mid-pH range. Rates of inversion were determined by line-shape analysis of the acetate methylene AB quartet at high pH. Inversion rates were found to be less than N–H proton exchange rates by a factor of 70. The rate of inversion of the deprotonated nitrogen of $Pt(NH_3)_2$(EDDA) was determined to be 10^5–10^6 sec^{-1} at 39° on the basis of an nmr-determined N–H acid dissociation constant, $K_a \cong 0.01K_w$. Activation energies for inversion of **1** and **2** are 14–16 kcal. Conformational implications of nmr parameters, including J_{Pt-H}, are also considered.

In an accompanying paper[4] we have discussed the nmr determination of N–H exchange rates of Pt(Gly)Cl_2^- and Pt(Sar)Cl_2^-. This paper reports similar studies of two other amino acid complexes, **1** and **2**. For these complexes, asymmetry at the coordinated nitrogen also permitted evaluation of rates of inversion and, therefore, a comparison of the rates of N–H exchange and inversion as reported by Buckingham, Sargeson, and coworkers for Co(III) complexes[5] and by Haake and Turley for Pt(II) complexes of N,N′-dimethylethylenediamine.[6,7]



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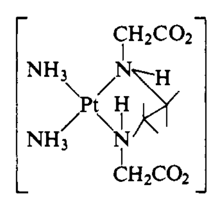

2

Compounds **1** and **2** differ from the glycine and sarcosine complexes in another important respect. Both have free acetate fragments which might be expected to participate in intramolecular catalysis of N–H proton exchange.

Since the EDDA complex has two asymmetric centers, both *meso* and *d,l* forms are possible. The two isomers would be expected to have somewhat different spectra, so as to permit evaluation of the isomer ratio. Signif-

(1) A portion of this work was reported at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.
(2) National Science Foundation Undergraduate Research Participant, summer, 1967.
(3) National Science Foundation Undergraduate Research Participant, summer, 1968.
(4) L. E. Erickson, A. J. Dappen, and J. C. Uhlenhopp, *J. Am. Chem. Soc.*, **91**, 2510 (1969).
(5) References 1–4 of ref 4.
(6) P. Haake and P. C. Turley, *J. Am. Chem. Soc.*, **90**, 2293 (1968).
(7) It should be noted that a similar study of $KPt(Sar)Cl_2$ was unsuccessful because of rapid hydrolysis of the ligand in the critical pH range.

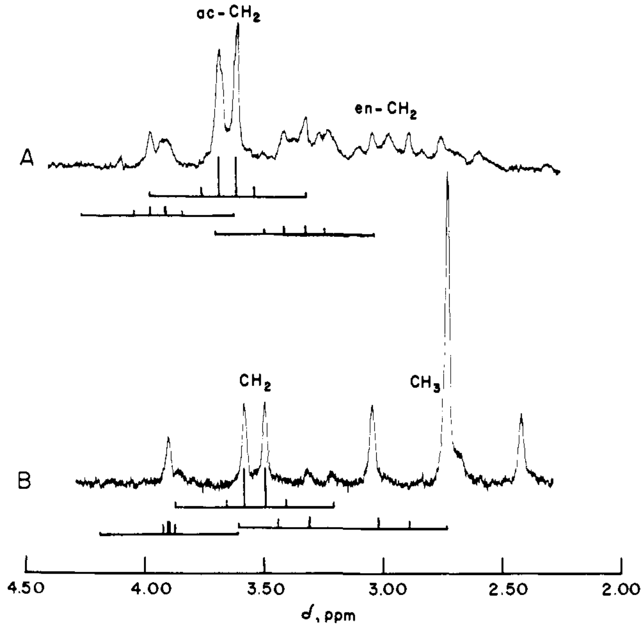

Figure 1. Proton nmr spectra of D_2O solutions at pD 7–9 showing assignment of methylene AB quartets to major species and to upfield and downfield side bands: (A) $Pt(NH_3)_2(EDDA)$; (B) $Pt(NH_3)_3(Sar)^+$. Dotted lines indicate calculated effective chemical shifts for each quartet.

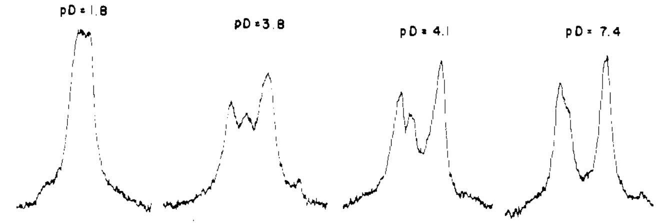

Figure 2. Central part of acetate methylene spectrum of **2** in D_2O as a function of pD.

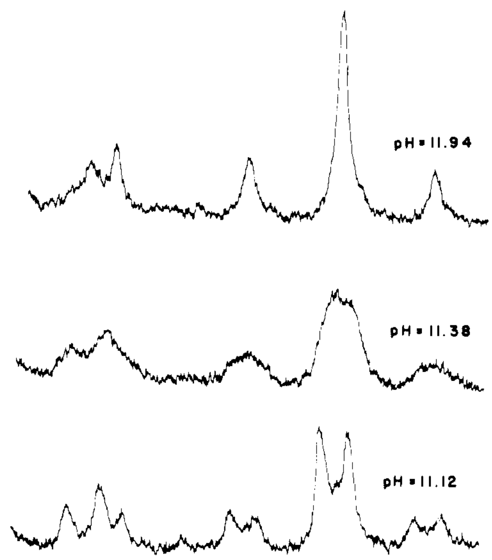

Figure 3. Variation in spectrum of H_2O solutions of **1** with pH due to changes in rate of N–H proton exchange.

icant deviation of this ratio from unity would be expected if the acetate fragments exhibit a strong conformational preference. The conformational implications of ^{195}Pt–^1H spin coupling constants for both **1** and **2** have also been considered.

Experimental Section

Preparation of Complexes. Sarcosinatotriammineplatinum(II) chloride (**1**) was prepared by heating $KPt(Sar)Cl_2$ with excess concentrated aqueous ammonia (~10 ml of NH_3/mmol of complex) and evaporating to dryness. Samples for kinetic runs were prepared from a stock solution of this solid by evaporating an amount containing 0.5 mmol to dryness and subsequently dissolving the solid in 1.0 ml of solvent, containing an appropriate buffer or other reagent.

$Pt(NH_3)_2(EDDA)$ was prepared from $H_2Pt(EDDA)Cl_2$ by treatment with excess aqueous NH_3,[8] followed by titration with KOH and evaporation to dryness. No attempt was made to isolate $H_2Pt(NH_3)_2(EDDA)Cl_2$, which would have required subsequent titration with KOH to yield a KCl-containing solution identical with that obtained from $H_2Pt(EDDA)Cl_2$ without prior isolation. The spectrum was identical with that of the product of the reaction of excess ammonia with tetradentate Pt(EDDA).

Kinetic Studies. The procedures employed in solution preparation and kinetic studies were the same as those already described.[4]

Results

Analysis of Spectra of $Pt(NH_3)_2(EDDA)$ and $Pt(NH_3)_3(Sar)^+$. Spectra of D_2O solutions of **1** and **2** at pD 7 are shown in Figure 1. The spectrum of each compound consists of a single AB quartet, flanked by ^{195}Pt side bands, for the acetate (ac) methylene protons and a second absorption region at higher field for the ethylendiamine (en) or methyl protons and their ^{195}Pt side bands. For $Pt(NH_3)_2(EDDA)$ there is no evidence of a second species, implying either (a) that the *meso* or the *d,l* configuration dominates or (b) that the two species have almost identical proton spectra.[9] The two compounds contrast sharply in the appearance of Pt side bands. For **1**, the downfield side band is more spread

(8) C. F. Liu, *Inorg. Chem.*, 3, 680 (1964).

Table I. Proton Nmr Data[a] for $Pt(NH_3)_3(Sar)^+$ and $Pt(NH_3)_2(EDDA)$ at pH 7

Configuration	Parameter	$Pt(NH_3)_3(Sar)^+$	$Pt(NH_3)_2(EDDA)$
$NH_XCH_AH_BCO_2^-$	J_{AB}	16.7	16.4
	J_{AX}	8.0	4.2
	J_{BX}	4.9	6.9
$NHCH_3$	J_{H-CH_3}	6.1	
$PtNHCH_AH_BCO_2^-$	J_{Pt-H_A}	25	30
	J_{Pt-H_B}	55	32
$PtNCH_3$	J_{Pt-CH_3}	37.2	
$PtNCH_2$	$J_{Pt-en-CH_2}$		32.5[b]
$NH_XCH_AH_BCO_2^-$	δ_A	3.57	3.65
	δ_B	3.49	3.44
$NHCH_3$	δ_{CH_3}	2.76	
$NHCH_2$	δ_{en-CH2}		2.90

[a] Spin coupling constants, *J*, are in Hz; chemical shift, δ, in parts per million downfield from internal NaTMS. [b] Average value from side band splitting at high pH.

(9) A third possibility, that the interconversion of the two forms is rapid on the nmr time scale, at pH 7, is ruled out by the subsequently described kinetic results.

Table II. Rate Constants for N–H Exchange and Inversion of **1** and **2** at 39° and Ionic Strength 1.0[a]

Compd, process	Medium[b]	pH meter reading(s)	Method of analysis	k, sec^{-1}	k', $=k/(OH^-)$, l. mol^{-1} sec^{-1}
1, exchange	KHP, D_2O	5.65	Slow spectral changes	1.4×10^{-4}	2.5×10^4
1, exchange	Phosphate, D_2O	6.25	Slow spectral changes	1.6×10^{-4}	6.8×10^3
1, exchange	Phosphate, D_2O	7.00	Slow spectral changes	3.3×10^{-4}	2.5×10^3
1, exchange	Phosphate, H_2O	10.96–11.56	Line shape: CH_3 doublet	9–40	3.5×10^3
1, inversion	NaOH, H_2O	0.49–0.98 M NaOH	Line shape: CH_2 AB quartet	28–44	50
2, exchange	KHP, D_2O	3.9	Slow spectral changes	9×10^{-4}	9×10^6
2, exchange	Borate, H_2O	9.29–9.51	Line shape: CH_2 part of ABX	15–23	2.8×10^5
2, inversion	Phosphate, H_2O	11.40–12.08	Line shape: CH_2 AB quartet	5.5–35	3.9×10^3

[a] Except for inversion rate of **1**, for which the ionic strength ranged from 1.0 to 2.0. [b] Total buffer concentration was 0.05 M, except for borate (0.025 M); complex concentration was 0.50 M and KCl was the inert electrolyte.

out than the parent quartet. This implies substantial differences in Pt–H spin coupling to the CH_2 protons. By contrast the side bands of **2** are almost mirror images of the parent quartet, implying almost equal coupling between Pt and the two methylene protons. Analysis of the AB parent quartet and the ABX side band patterns yielded the spin coupling constants (J_{AB}, J_{Pt-HA}, J_{Pt-HB}) and chemical shifts (δ_A and δ_B) given in Table I.

Although the pH 7 spectrum of $Pt(NH_3)_2(EDDA)$ in D_2O can be accounted for in terms of a single species (*d,l* or *meso*), the presence of both configurations is suggested by the slight splitting of the downfield component of the two strong central AB lines. The splitting increases at low pH where the acetate carboxyl groups are partially protonated. The effect of complete protonation is to shift the methylene quartet downfield about 0.5 ppm and to decrease the chemical shift difference between methylene protons to the point where only a single peak is observed. However, as shown in Figure 2, at pH 3.2, where only about one-half of the CO_2^- groups are protonated, the strong central components of two overlapping AB quartets are clearly visible. Since proton exchange rates are too slow at low pH to permit a shift in the *d,l–meso* equilibrium ratio upon protonation, this observation requires that the two configurations are present in approximately equal amounts for $Pt(NH_3)_2(EDDA)$.[10]

In H_2O solutions at pH <8, spectra of **1** and **2** are further complicated by spin coupling to N–H. As illustrated in Figure 3 for **1** (pH 11.2 trace), the two strong central lines of the CH_2 AB pattern are thereby split into the four lines (two overlapping) expected for the central components of the AB portion of an ABX pattern (where X = N–H). Under these conditions, the upfield CH_2 or CH_3 signals are also further split by NH. A complete summary of spectral parameters is given in Table I.

N–H Exchange Rates of $Pt(NH_3)_2(EDDA)$ and $Pt(NH_3)_3(Sar)^+$. The effect of pH changes on the appearance of the spectrum of H_2O solutions of $Pt(NH_3)_3(Sar)^+$ is shown in Figure 3. Near pH 11.4, the methyl doublet and its side bands collapse to single lines. Simultaneously the CH_2 pattern collapses to the AB quartet and Pt side bands characteristic of D_2O solutions. Similar changes in ac methylene absorption are observed near pH 9.4 for H_2O solutions of $Pt(NH_3)_2$-(EDDA).

(10) This experiment required rejection of tentative conclusion a, which was given in the earlier report of this work.[1]

Rate constants for N–H exchange of $Pt(NH_3)_3Sar^+$ were determined from the line shape of the CH_3 doublet for several traces near coalescence.[4] It is of interest that the minimum in the CH_3 doublet (6.1 Hz) disappears at slightly higher pH that the more closely spaced pair (4.7 Hz) and at slightly lower pH than the more widely spaced pair (6.8 Hz) in the CH_2 pattern. This observation was employed to determine rate constants for N–H exchange of $Pt(NH_3)_2(EDDA)$ where only the corresponding four ac CH_2 lines showed changes that could be used for quantitative evaluation of rates. The separation between pairs of peaks that coalesced (3.0 and 5.5 Hz) was considered to be the doublet splitting for calculating line shapes from which τ near coalescence was determined. T_2 values for calculation of spectra were determined from line widths of low pH traces and were generally taken to be about 0.5 sec.

Values for k_{ex} and for $k_{ex}/(OH^-) = k_{ex}'$, obtained by this approach, are included in Table II. $Pt(NH_3)_3(Sar)^+$ data were obtained for 0.05 M phosphate buffer solutions; $Pt(NH_3)(EDDA)$ data, for 0.025 M borate buffer solutions. Preliminary runs in unbuffered systems indicate that the presence of the buffer has no significant effect on the observed rates in the pH range studied.

Intramolecular Catalysis of N–H Exchange of 1 and 2. After determining proton exchange rates for **1** and **2** from line-shape changes at high pH in H_2O, some runs were made at pH 4–7 in D_2O, assuming that the rate would be decreased sufficiently to follow the slow spectral changes resulting from N–H replacement by N–D, as reported for $Pt(Gly)Cl_2^-$, etc.[4] However, for both **1** and **2**, low-pH exchange rates in D_2O were considerably greater than expected on the basis of the second-order rate constants for OH^- catalysis determined at high pH. If the rate law is

$$\text{rate} = k_{ex}(\text{N–H}) = [k_{ac} + k_{OD^-}(OD^-)](\text{N–H}) \quad (1)$$

a plot of k_{ex} *vs.* (OD^-) should be linear with slope k_{OD^-} and intercept k_{ac}, the first-order rate constant for the intramolecular process, presumably catalysis by acetate fragments. Treatment of the data for **1** in this way yields $k_{ac} = 1.3 \times 10^{-4}$ sec^{-1} and $k_{OD^-} = 1.6 \times 10^3$ l. mol^{-1} sec^{-1}, as compared to 3.6×10^3 l. mol^{-1} sec^{-1} for k_{OH^-} at high pH. For **2**, only one experiment at low pH was completed (pH 3.9). Assuming negligible contribution from OD^- catalysis at this pH, $k_{ac} = 9 \times 10^{-4}$ sec^{-1}.

Inversion Rates of $Pt(NH_3)_3(Sar)^+$ and $Pt(NH_3)_2$-(EDDA). At high pH in both D_2O and H_2O, the

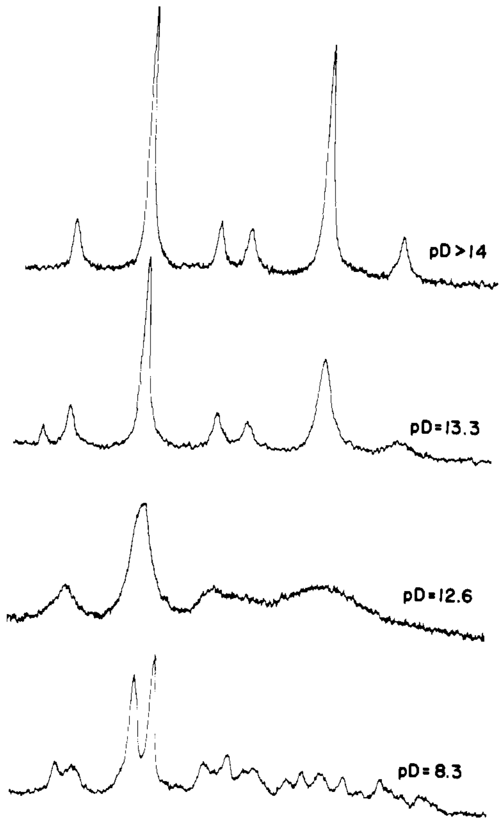

Figure 4. Variation in spectrum of D_2O solutions of **2** with pH due to changes in rate of inversion at coordinated nitrogen.

methylene AB quartets of **1** and **2** collapse further to single lines, flanked by Pt side bands. Changes in line shape near coalescence, illustrated for **2** in Figure 4, confirm the earlier cited spectral assignments. For **2**, side-band and parent ac methylene quartets all coalesce at approximately the same pH. By contrast, for the ethylene portion of the spectrum, the downfield side-band collapse precedes the collapse of the parent AA′BB′ pattern, while the upfield side band collapse follows it. Similarly, for **1**, the compressed downfield side band (Figure 1) collapses before the parent AB quartet while the more spread out upfield side band collapses after the parent quartet.

Inversion rates were determined from line shapes at pH values near coalescence of the AB quartet. The equations of Alexander[11] as employed by Biffin, *et al.*,[12] were used for calculation of line shapes for comparison with observed spectra. A rate constant for the inversion process, *i.e.*, for the process designated by eq 2, was

$$\text{N–H} \underset{k_{in}}{\overset{k_{in}}{\rightleftharpoons}} \text{H–N} \qquad (2)$$

calculated from τ for each trace ($k_{in} = 1/2\tau$) near coalescence, where τ values were assigned by matching observed and computer-generated spectra.

The second-order rate constants $k_{in}' = k_{in}/(OD^-)$ or $k_{in}/(OH^-)$ given in Tables II and III were determined

(11) S. Alexander, *J. Chem. Phys.*, 37, 967, 974 (1962).
(12) M. C. Biffin, L. Crombie, T. M. Connor, and J. A. Elvidge, *J. Chem. Soc., B*, 841 (1967).

Table III. Temperature Dependence of Inversion Rates of **1** and **2** in D_2O

Compd	t, °C	pH (meter) range or (OD^-), M	k_{in}, sec^{-1}	k_{in}', l. mol^{-1} sec^{-1}
1	39	0.56	21	38
1	45	0.56	36	65
1	48	0.56	41	73
1	51	0.56	48	85
1	53	0.56	54	97
2	24	12.51–12.78	16–27	1.1×10^3
2	39	11.40–12.08	5.5–35	3.9×10^3
2	50	10.96–11.37	18–27	11×10^3

Table IV. Activation Parameters for Inversion of **1** and **2**

Compd	E_a, kcal	ΔH^*, kcal/mol	ΔS^*, eu
1	14 ± 2	13.4	-8 ± 7
2	16 ± 2	15.4	$+8 \pm 7$

as the slopes of plots of k_{in} *vs.* (OD^-). At least four different pH values were used for each plot. Data are reported for H_2O solutions of **1** and D_2O solutions of **2**. However, a single value determined for a D_2O solution of **1** (Table III) and earlier work[4] suggest that very similar results would have been obtained in either solvent.

Activation Energies. Arrhenius activation energies for the inversion process were determined from the temperature dependence of k_{in}'. Since the pH meter reading and K_w also vary with temperature, changing the temperature of a single sample produces a very rapid change in both spectrum and measured pH with a resultant very large uncertainty in k_{in}' at each temperature. Therefore, for **2**, traces were recorded for separate samples over a narrow pH range near coalescence at each of three temperatures, and k_{in}' for each temperature was calculated as the slope of the k_{in} *vs.* (OD^-) plot. For **1**, where the (OD^-) was 0.56 M, and therefore almost independent of temperature, the change in line shape of the AB quartet was used to evaluate the rate at several temperatures using a single sample which was below coalescence at the lowest temperature investigated. The data obtained in this way are summarized in Table III and the resultant activation parameters are given in Table IV.

Discussion

Comparison of Inversion and Exchange Rates. In contrast to the Pt(II) compounds studied by Haake and Turley, for **1** and **2** the rates of N–H exchange substantially exceed the rates of inversion. The ratio of k_{OH^-} to k_{in}' at a given pH is about 70 for both compounds. A summary of available literature data for Co(III) and Pt(II) complexes is given in Table V. The 10^5-fold variation in $k_{OH^-}/k_{in}' = r$ for the seven complexes can be attributed to either (a) unusually large k_{OH^-} for the complexes for which r is large, (b) unusually large k_{in}' for complexes for which r is small, or (c) some combination of a and b. The following analysis suggests that factor a is responsible for the variation for at least some of the complexes.

Table V. Rate Constants for N–H Exchange and Inversion of Metal-Coordinated Nitrogen Donors

Complex	k_{OH^-}, l. mol^{-1} sec^{-1}	k_{in}', l. mol^{-1} sec^{-1}	r	k_3	Ref
$Pt(NH_3)_3(Sar)^+$	3.5×10^3	50	70		This work
$Pt(NH_3)_2(EDDA)$	2.8×10^5	3.9×10^3	70	6×10^5	This work
$Pt(NH_3)_2(N,N'\text{-dmen})^{2+}$	4×10^4	4.6×10^3	10	5×10^5	[b]
$Pt(bipy)(N,N'\text{-dmen})^{2+}$	1.3×10^7	4×10^6	3[a]		[b]
$Co(NH_3)_4(N\text{-meen})^{3+}$	1×10^7	1×10^2	10^5		[d]
$Co(NH_3)_4(Sar)^{2+}$	6×10^7	2×10^4	3000		[c]
$Co(NO_2)_2(N\text{-meen})_2{}^+$	1×10^4	1×10^0	10^4		[e]

[a] Probably significantly less reliable than other values given. Revised value will be included in ref 14. [b] Reference 6. [c] B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966). [d] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967). [e] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 3428 (1967).

If we assume that the mechanism of inversion is as

$$\text{N–H} + \text{OH}^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{N:}^- + \text{H}_2\text{O} \qquad (3)$$

$$\text{N:}^- \xrightarrow{k_3} \text{:N}^- \qquad (4)$$

given in eq 3 and 4, where N:$^-$ represents the deprotonated nitrogen, the rate law for inversion can be written as in eq 5, where k_3 is the first-order rate constant for

$$\text{rate} = k_{in}(\text{N–H}) = k_3(\text{N:}^-) \qquad (5)$$

inversion of the deprotonated nitrogen. From (5), it follows that

$$k_{in}/(\text{OH}^-) = k_{in}' = k_3K_a/K_w \qquad (6)$$

If we further assume that k_{OH^-} values can be related to N–H K_a values for the series by a simple Brønsted relation,[13] *i.e.*

$$k_{OH^-} = G(K_a)^\beta \qquad (7)$$

where G and β are constants, it follows that

$$r = k_{OH^-}/k_{in}' = K_wG(K_a)^{\beta-1}/k_3 \qquad (8)$$

Equation 8 requires that r depends on both k_3 and K_a, as well as on the constants G and β. For example, if k_3 is constant for a series, r should decrease as K_a increases, since β is typically <1; *i.e.*, the ratio should be smallest for the most acidic complexes.

Values of K_a/K_w for **2** and $Pt(NH_3)_2(N,N'\text{-dmen})^{2+}$ (0.007 and 0.01, respectively) have recently been obtained from the effect of high OH$^-$ concentrations on chemical shift of ligand protons.[14] These have been used to calculate the k_3 values from eq 6, which are given in Table V. Since K_a and k_3 are essentially equal for this pair, the factor of 10 difference in r must be attributed to a failure of the simple Brønsted relation to hold precisely. This is certainly not unreasonable, but it does seem surprising that OH$^-$ is relatively more effective in removing the proton from **2**, which has protruding negatively charged acetate fragments, than from $Pt(NH_3)_2(N,N'\text{-dmen})^{2+}$, which has a net positive charge and no acetate fragments. The recent isolation of potassium salts of Co(III) complexes of chelated amino acids from liquid ammonia–potassium amide[15] suggests that $Co(NH_3)_4(Sar)^{2+}$ should also be fairly acidic in water. For example, if $K_a = 0.01K_w$, $k_3 = 10^5$–10^6, comparable to

(13) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 160.
(14) To be described in detail in a subsequent publication.
(15) G. W. Watt and J. F. Knifton, *Inorg. Chem.*, 7, 1159 (1968).

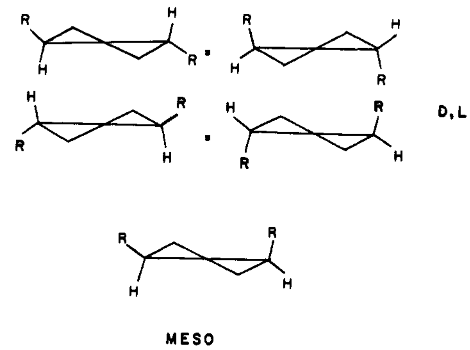

Figure 5. The two possible configurations (*d,l* and *meso*) of $Pt(NH_3)_2(EDDA)$. R designates $CH_2CO_2^-$.

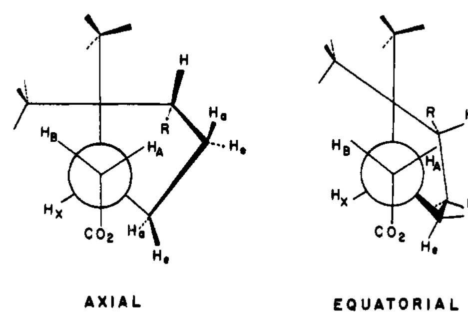

Figure 6. Conformational representation of $Pt(NH_3)_2(EDDA)$ looking down one of the ac–carbon–nitrogen bonds. Axial and equatorial refer to the conformation of $CH_2CO_2^-$ fragment with reference to the en ring.

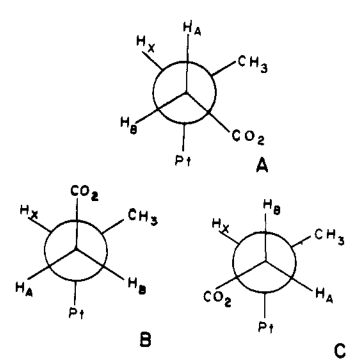

Figure 7. Rotamers of $Pt(NH_3)_3(Sar)^+$.

the values obtained for the two Pt(II) complexes. Further consideration of differences in r for the seven complexes will be possible when K_a values for more of them have been determined.[14]

The values determined for k_3 for these Pt(II) complexes are very similar to rate constants for inversion of several other tertiary amines, including piperazines[16] and acyclic amines,[17] among others.[18] Haake and Turley proposed a pseudo coordination number 5 transition state for the inversion of Pt(II) complexes.[6] However, the similarity between rate constants and activation energies for inversion of Pt(II) complexes and organic amines suggests that the inversion process is similar in the two kinds of compounds and that there is no experimental basis for the proposed transition state.

Conformational Implications of Spectra. *meso* and *d,l* configurations of **2** have been shown to be equally probable and to have essentially identical spectra. Both conclusions can be accounted for in terms of the conformational preference of the acetate fragments. As shown in Figure 5, the *d,l* configuration should predominate if acetate groups strongly prefer either the axial or the equatorial conformation, since both acetate fragments can be so located in the *d,l* configuration. On the other hand, if the acetate groups exhibit no preference for axial or equatorial conformations, both *d,l* and *meso* isomers should be equally probable. Therefore, the observation that *meso* and *d,l* configurations are equally probable implies no preference for axial over equatorial conformation and accounts for the close similarity in spectra of the two configurations at mid pH.[19] Similar arguments have recently been used to account for the fact that a single species, presumably the one with methyl groups *trans*, is observed in the nmr spectrum of $Co(NH_3)_4$(N-methyl-L-alanine)$^{2+}$.[20]

Information about the preferred rotational conformation of the acetate fragments of **2** can also be inferred from the spectra. Figure 6 shows a projection of the structure onto a plane perpendicular to one of the ac carbon–nitrogen bonds. Since a given acetate fragment can be either axial or equatorial, six rotamers need to be considered, three rotamers (as shown in Figure 7) for **1** for each conformation. The approximate dihedral angle dependence of vicinal platinum–proton coupling constants of Pt–N–C–H fragments has been established with $J_{trans} \cong 60$ and $J_{gauche} \cong 10$ Hz.[21] These values and $J_{trans} = 11$ and $J_{gauche} = 3$ Hz for vicinal proton–proton coupling constants[22] indicate about a 1 : 2:1 distribution among the three rotamers for each conformation, that is, such a distribution yields $J_{Pt-H_A} = J_{Pt-H_B} = 35$ Hz and J_{AX} and $J_{BX} = 7.0$ and 5.0 Hz. The values found for J_{Pt-H} are 30 and 32 Hz; for J_{HH}, 7.2 and 4.4 Hz.

Similar arguments require that **1** has a strong preference for rotamer C (Figure 7). In rotamer C, the methylene proton designated H_B is *trans* to Pt and *gauche* to H_X, corresponding to the observation that the methylene proton which is coupled more strongly to Pt is coupled less strongly to H_X. It should be emphasized that knowledge of proton coupling constants alone would not have indicated which methylene proton is coupled more strongly to N–H. Therefore, it would not have been possible to determine whether B or C is the preferred conformation.

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