Coordinated Asymmetric Nitrogen Donor Centers. The $[\mathrm{Pt^{II}(Meen)(en)}]^{2+}$ and $[\mathrm{Pt^{IV}(Meen)(en)Cl_2}]^{2+}$ Ions

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Abstract: The ions $[\mathrm{Pt^{II}(Meen)(en)}]^{2+}$ and $[\mathrm{Pt^{IV}(Meen)(en)Cl_2}]^{2+}$ have been obtained in optically active forms, and their rates of proton exchange and racemization at nitrogen have been measured. For both species, the rate expression for racemization is $R = k_R[\mathrm{Pt}][\mathrm{OH^-}]$; at 34° $k_R = 7.9 \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$ and $6.5 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ for Pt(II) and Pt(IV), respectively. The rate expression for H exchange for Pt(II) in acetate–D_2O buffers at 34° is $R = (k_{D_2O} + k_{OAc^-}[\mathrm{OAc^-}] + k_{OD^-}[\mathrm{OD^-}])[\mathrm{Pt}]$ with $k_{D_2O} = 1.5 \times 10^{-5}\ \mathrm{sec}^{-1}$, $k_{OAc^-} = 1.6 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$, and $k_{OD^-} = 1.9 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$. In D_2O–DCl solution, the rate dependence of Pt(IV)–H exchange has the form $R = (k_{D_2O} + k_{OD^-}[\mathrm{OD^-}])[\mathrm{Pt}]$ with $k_{D_2O} \simeq 2 \times 10^{-4}\ \mathrm{sec}^{-1}$ and $k_{OD^-} = 2 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$. The retention ratio, $k_{OD^-}/k_R \simeq 10^2$, is small for square-planar Pt(II), but the larger value for Pt(IV), $\sim 10^4$, is similar to those found for octahedral Co(III) complexes. Although the $\mathrm{p}K_a$ for the Pt(II) complex cannot be measured >14, the Pt(IV) complex is more acidic, $\mathrm{p}K_a = 10.6$ at 30°, and this result allows the inversion rate at nitrogen to be estimated as $\sim 400\ \mathrm{sec}^{-1}$. The results are interpreted mechanistically by invoking a common deprotonated intermediate.

The ability of many transition metal ions to reduce the acidity of coordinated primary and secondary amines over that for the corresponding ammonium ion is now well established. This effect is reflected in the unusually slow rates for proton exchange with amine complexes of Co(III), Rh(III), Ir(III), Cr(III), Pd(II), Pt(II), Ru(III), and Os(III).[1] The reason for this behavior is not well understood, but the effect allows coordinated secondary amines to be resolved into their optical antimers[2–9] and also allows the proton exchange and racemization at the asymmetric centers to be measured.[2–6] The evidence suggests that the base-catalyzed proton exchange leads to a deprotonated intermediate,[4–6] and for the cobalt complexes at least, a substantial difference between the rates of exchange and racemization has been observed such that $k_{ex}/k_{rac} \sim 10^3$–10^5.[2,3,5,6] This has been interpreted as the deprotonated complex ion largely reacting with solvent with retention of the original configuration which probably requires that the lifetime of the intermediate is short relative to its inversion rate.[2,3,5,6]

Several questions have arisen in the course of these investigations. For example, do electronegative groups in the 1 and 6 coordination positions reduce the retention ratio? What effect does a change in metal ion have? What is the inversion rate for the deprotonated form and what is the barrier to inversion? The cobalt(III) complexes were not sufficiently acidic to allow the determination of their dissociation constants and thence ΔH for deprotonation, but the Pt(IV) amine complexes in general do allow these measurements. This article is concerned with the resolution, proton exchange, and racemization of $[\mathrm{Pt(Meen)(en)Cl_2}]$ and *trans*-$[\mathrm{Pt(Meen)(en)Cl_2}]\mathrm{Cl_2}$ in relation to the questions raised above.

Experimental Section

Analytical reagents were used throughout. Optical rotations were measured in 1-dm quartz cells using a Perkin-Elmer P22 polarimeter. Proton magnetic resonance spectra were obtained with Perkin-Elmer R10 or Varian HA100 spectrometers using sodium trimethylsilylpropanesulfonate or *t*-butyl alcohol as internal references. Uv spectra were measured with a Cary 14 spectrophotometer. A Cambridge Bench Type pH meter (±0.005 pH unit) was used to measure the pH of the reaction solutions and for the $\mathrm{p}K_a$ determination.

(±)-$[\mathrm{Pt(Meen)(en)}]\mathrm{Cl_2 \cdot 0.5H_2O}$. A mixture of $\mathrm{Pt(en)Cl_2}$ (5.5 g) and N-methylethylenediamine (1.3 g) in water (250 ml) was heated at 80° until it became a clear pale yellow and the solution was neutral. This volume was reduced (to ~10 ml) and the solution treated with ethanol (200 ml). The resultant white crystals were collected and washed well with ethanol and acetone. Further treatment of the filtrate with ethanol and ether gave a second crop; total yield, 6.15 g. The conductivity of a $10^{-3}\ M$ aqueous solution (230 ohm^{-1}) is consistent with a uni-bivalent electrolyte. *Anal.* Calcd for $[\mathrm{PtC_5N_4H_{18}}]\mathrm{Cl_2 \cdot 0.5H_2O}$: C, 14.67; H, 4.68; N, 13.69; Pt, 47.69. Found: C, 14.6; H, 4.7; N, 13.6; Pt, 46.7.

(±)-$[\mathrm{Pt(Meen)(en)}]\mathrm{I_2}$. Sodium iodide (6 g) in water (20 ml) was added to $[\mathrm{Pt(Meen)(en)}]\mathrm{Cl_2}$ (4.5 g) in water (12 ml) and the solution cooled. The white crystals were collected, washed with methanol, and air-dried (yield, 5.0 g). Evaporation of the filtrate to 10 ml and addition of a little ethanol crystallized the remainder of the complex. *Anal.* Calcd for $[\mathrm{PtC_5N_4H_{18}}]\mathrm{I_2}$: C, 10.29; H, 3.09; N, 9.61; Pt, 33.49. Found: C, 10.4; H, 3.2; N, 9.7; Pt, 33.5.

$(-)_{350}$-$[\mathrm{Pt(Meen)(en)}]((+)\text{-BCS})_2 \cdot \mathrm{H_2O}$. The complex $[\mathrm{Pt(Meen)(en)}]\mathrm{Cl_2 \cdot 0.5H_2O}$ (6.0 g) was dissolved in 150 ml of boiling water with Ag-(+)-BCS (12.45 g). The AgCl was removed and washed with successive lots of boiling water (total ~50 ml). The filtrate and washings were combined and the solution was evaporated to near dryness under vacuum. The residue was dissolved in 200 ml of boiling methanol by adding water dropwise. Three drops of acetic acid was added and the solution filtered to remove a small amount of less soluble material. While still hot, an equal volume of ethanol was added and the solution allowed to cool at room temperature. After an hour, the white flaky crystals that formed were collected and washed with ethanol and acetone (A, 5.1 g). The ethanol washings were added to the filtrate and the solution was allowed to stand for a further hour. The next fraction was removed (B, 1.6 g) and washed similarly. The filtrate was cooled in ice (2 hr) and a third fraction was collected (C, 2.15 g). The filtrate was then evaporated to dryness and redissolved in an equal volume of methanol and ethanol as before (100 ml of each solvent). One

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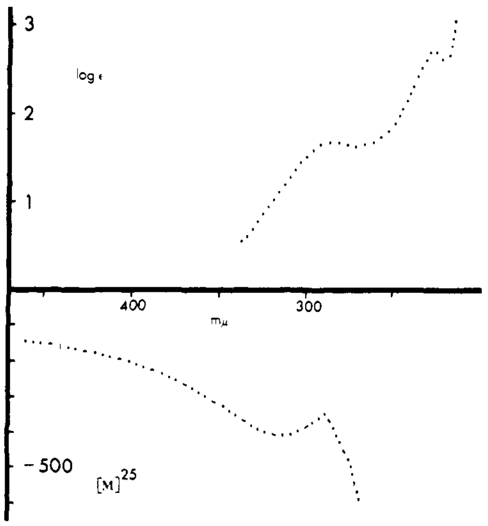

Figure 1. Absorption spectrum and rotatory dispersion curve for $(-)_{350}$-[Pt^{II}(Meen)(en)]Cl$_2$ (0.1 *M* HCl).

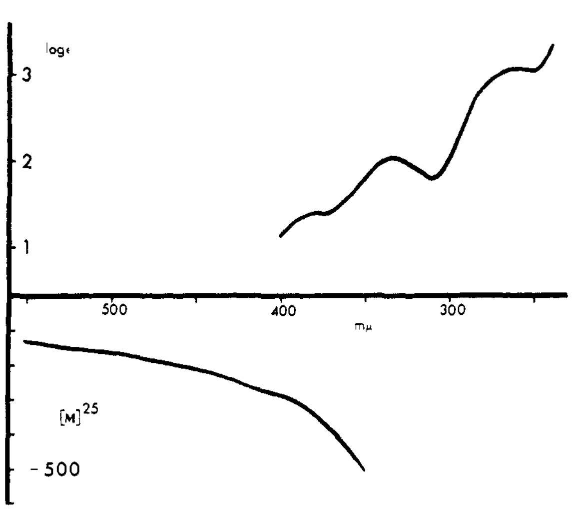

Figure 2. Absorption spectrum and rotatory dispersion curve for $(-)_{350}$-[Pt^{IV}(Meen)(en)Cl$_2$]Cl$_2$ (3.0 *M* HCl).

fraction was collected after cooling to room temperature (D, 1.6 g) and another after cooling in ice (E, 0.7 g).

Each diastereoisomer fraction was checked for optical purity by dissolving the diastereoisomer (0.02 g) in HClO$_4$ (10^{-3} *M*) and measuring the rotation at 350 mμ (which was due mainly to the (+)-BCS$^-$ ion). A drop of NaOH (5 *M*) was then added and the rotational change due to the racemization of the $(-)_{350}$-[Pt(Meen)(en)]$^{2+}$ ion was obtained. Fractions of similar activity were combined and recrystallized from hot methanol and ethanol containing a trace of acetic acid as described above. The fractions containing both diastereoisomers were recrystallized first, and the least soluble fraction containing more of the least soluble diastereoisomer was then added to a similar fraction from the first separation. This process was continued until further recrystallization gave no change in activity. The final fraction (0.2% solution) obtained after seven recrystallizations changed from +0.841 to +0.907° when treated as outlined above. *Anal.* Calcd for [PtC$_5$H$_{18}$N$_4$][C$_{20}$H$_{30}$O$_9$S$_2$Br$_2$]: C, 31.03; H, 5.00; N, 5.79; Pt, 20.17. Found: C, 31.0; H, 5.1; N, 5.8; Pt, 20.2. The optically pure more soluble diastereoisomer was not sought because of the poor discrimination between the diastereoisomers.

$(-)_{350}$-[Pt(Meen)(en)]I$_2$. The diastereoisomer was converted to the iodide salt in a mortar with a little water and excess NaI containing acetic acid (1 drop of 17 *N*). The iodide was recrystallized by dissolving it in a minimum of warm water containing a drop of acetic acid and adding NaI. A 0.1% solution gave α_{350} −0.055°, whence $[\alpha]_{350}$ −55°. Addition of base to this solution reduced the rotation to zero at all wavelengths. *Anal.* Calcd for $(-)_{350}$-[PtC$_5$N$_4$H$_{18}$]I$_2$: C, 10.29; H, 3.09; N, 9.61; Pt, 33.49. Found: C, 10.3; H, 3.2; N, 9.4. Pt, 33.2.

(±)-*trans*-[Pt(Meen)(en)Cl$_2$]Cl$_2$·H$_2$O. Chlorine was bubbled into an aqueous solution of (±)-[Pt(Meen)(en)]Cl$_2$ (1.0 g in 2 ml) until a faint orange color appeared, and the solution was then flushed with air. Pale yellow crystals separated from the cooled solution. Ethanol (4 ml) was added and the solution cooled in ice (0.75 g), whereupon a second crop of crystals was obtained (1.1 g). The complex was recrystallized from warm water by adding ethanol. *Anal.* Calcd for [PtC$_5$N$_4$H$_{18}$Cl$_2$]Cl$_2$·H$_2$O: C, 12.27; H, 4.18; N, 11.45; Pt, 39.9. Found: C, 12.1; H, 4.2; N, 11.5; Pt, 40.9.

$(-)_{350}$-*trans*-[Pt(Meen)(en)Cl$_2$]Cl$_2$·H$_2$O. A solution of $(-)_{350}$-[Pt(Meen)(en)]I$_2$ in HCl (5 ml of 0.01 *N*) was shaken with AgCl and filtered. The insoluble silver salts were washed with 10 ml of 0.01 *N* HCl, and Cl$_2$ was bubbled into the filtrate until a faint yellow tint appeared. The solution was flushed by bubbling in air and evaporated to dryness under vacuum. The residue was then extracted with ethanol and washed liberally with ethanol (150 ml) and acetone (50 ml). The white crystals were dried under vacuum. For a 0.1% solution (10^{-3} *M* HClO$_4$), α_{350} −0.097°, whence $[\alpha]^{25}_{350}$ −97°. *Anal.* Calcd for [PtC$_5$N$_4$H$_{18}$Cl$_2$]Cl$_2$·H$_2$O: C, 12.27; H, 4.12; N, 11.45. Found: C, 12.1; H, 4.1; N, 11.3.

Kinetic Studies. The methods employed in this investigation for following the rates of racemization of $(-)_{350}$-[Pt(Meen)(en)]I$_2$ and $(-)_{350}$-*trans*-[Pt(Meen)(en)Cl$_2$]Cl$_2$ have been detailed in a previous paper.[3] The Pt(II) compound had a rate similar to that for the [Co(NH$_3$)$_4$(Meen)]$^{3+}$ ion,[3] and both acetate and collidine buffer systems were employed, whereas the Pt(IV) complex racemized more rapidly and only acetate buffers were used. The addition of compound did not change the pH of the buffers. Light was excluded from the experiments as far as possible and the ionic strength was maintained constant with KCl.

Hydrogen exchange studies in acetate buffer and in DCl were carried out by observing the change of the pmr spectra with time at the probe temperature, 34°, and the ionic strength was maintained at μ = 1 with the complex. Acetate buffers in D$_2$O were made from stock solutions of 0.2 *M* DOAc and 0.2 *M* NaOAc. The pH of the solutions was measured and the expression pD = pH + 0.4 was used to evaluate [D$^+$].[10] DCl solutions were made by diluting a standardized concentrated DCl solution.

Acid Dissociation Constant of *trans*-[Pt^{IV}(Meen)(en)Cl$_2$]Cl$_2$ at 30°. A solution of complex (6.81 × 10^{-4} *M*) was diluted 1:1 in a rapid reaction apparatus[11] with either 0.01 *N* butylamine buffer (μ = 0.01) or at pH >11.5 with dilute KOH (μ = 0.01).[12] The absorption at 310 mμ was measured spectrophotometrically and the optical densities of the complex and the deprotonated complex were 0.038 and 0.763, respectively, in a 1-cm cell. The densities of the solutions at the various acidities were: 9.67 (0.115), 10.00 (0.189), 10.18 (0.245), 10.40 (0.330), 10.64 (0.415), 10.88 (0.492), 11.03 (0.562), 11.21 (0.615), 11.46 (0.666), 11.64 (0.694).

Results

The complex [Pt(Meen)(en)]Cl$_2$ was prepared by treating N-methylethylenediamine and [Pt(en)Cl$_2$] in boiling aqueous solution and was resolved through the π-bromocamphorsulfonate salt. Both the racemate and optical isomer of the Pt(IV) complex were obtained from the appropriate Pt(II) chloride salt using Cl$_2$ as the oxidizing agent. The rotatory dispersion and uv spectra of these compounds are given in Figures 1 and 2.

The pmr spectra of the complex ions (Figures 3 and 4) are complicated and the methyl signal is not well separated from the methylene signals in both compounds. Also the protons are coupled to ^{195}Pt (33.7% abundance, $S = {}^1/_2$) which gives rise to the side bands. The assignments, chemical shifts, and Pt-N-C-H coupling constants of the two species are given in Table I. The Pt-N-C-H coupling constants are diminished from ~40 to ~20 cps in the change from Pt(II) to Pt(IV). It has been reported that the analogous Pt(IV) complex *trans*-[Pt(en)$_2$Cl$_2$]$^{2+}$ exchanges its protons readily[1] in 0.1 *N* D$^+$. It was found here that [Pt(Meen)(en)Cl$_2$]Cl$_2$ gave the same pmr spectrum in 3 *M* HCl and 2.8 *M* DCl, but the

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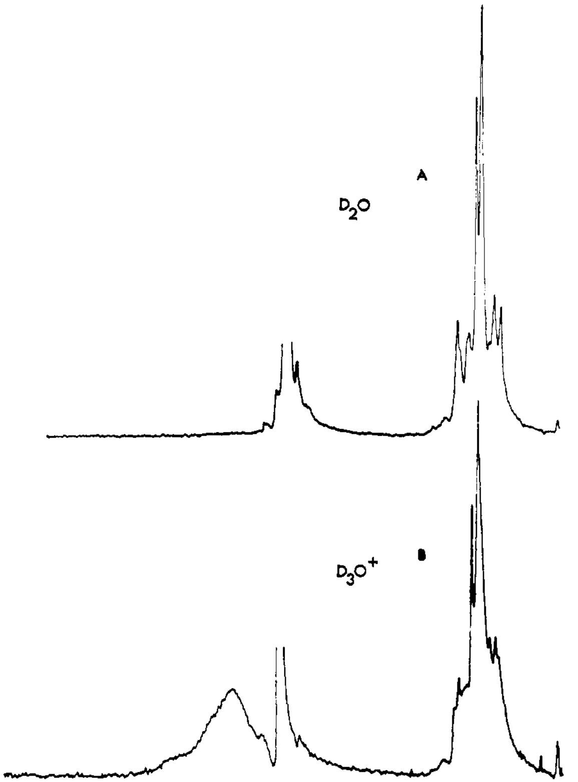


Figure 3. The 100-Mc spectrum of $[Pt^{II}(Meen)(en)]Cl_2$ (0.1 *M* DCl).

rate of N-proton exchange was measured in the latter solvent at lower acid concentrations, 1.0–0.1 *M* D^+.

Table I. Assignments (ppm) for Signals in 100-Mc Spectra

	$[Pt^{IV}(Meen)(en)Cl_2]Cl_2$ ND	$[Pt^{IV}(Meen)(en)Cl_2]Cl_2$ NH	$[Pt^{II}(Meen)(en)]Cl_2$ ND	$[Pt^{II}(Meen)(en)]Cl_2$ NH
$-CH_3$	2.9	2.9	2.75	2.75
J_{PtNCH_3}	22[a]	. . .[b]	37[a]	36[a]
$-CH_2CH_2-$	3.1	3.0	2.7	2.68
$J_{PtNCH_2CH_2-}$	25[a]	. . .[b]	34[a]	. . .[b]
N-H		7.3		5.2

[a] In cps. [b] Unresolved.

Both complexes contain seven N protons, all nonequivalent and all of which exchange in D_2O. The methyl doublet arising from the coupling of the methyl protons on the N atom collapsed to a singlet as the N proton exchanged, but the analysis of the data was complicated by the superimposition of the other C–H signals. It is clear from the spectra shown in Figures 3 and 4 that in these platinum complexes the methyl doublet and the ethylene signals of the chelate ring overlap. Nevertheless, the downfield half of the methyl doublet in $[Pt(Meen)(en)]^{2+}$ occurs in the trough between the ethylene signal and the ^{195}Pt side band. During the exchange the height of this trough above the base line varies little in comparison to the complete disappearance of the visible half of the methyl doublet (Figure 5). Plots of log[peak height)$_t$ – (peak height)$_\infty$] against time for the collapse of the doublet were linear for at least three half-lives and the rate constants obtained (± 15%) are given in Table II.

The dependence of k_{obsd} on pD gave an indication also of a dependence on OAc^- concentration. This was confirmed by studying the rate at 0.2 and 0.1 *M* acetate buffer concentration at constant pD. The value of K_a for acetic acid in D_2O and under these conditions was unknown, but the rate constants at zero buffer anion concentration were obtained by extrapolating the observed values at pD 4.40, 5.07, and 6.07. A plot of these values against $[D^+]$ then gave the acid-dependent rate constant k_{D_2O} = 1.5 × 10^{-5} sec^{-1}, and ultimately the second-order rate constants involving OD^- and OAc^- (Table II). From these values pK_{DOAc} was calculated as 4.4, and the k_{obsd} *vs.* k_{calcd} values for each pD studied are compared in Table II. The rate law for the exchange path then has the form

$$k_{obsd} = (k_{D_2O} + k_{OD^-}[OD^-] + k_{OAc^-}[OAc^-])$$

The rate constant for 0.01 and 0.117 *N* DCl was 1.4 × 10^{-5} sec^{-1} which confirms the presence of the acid-in-

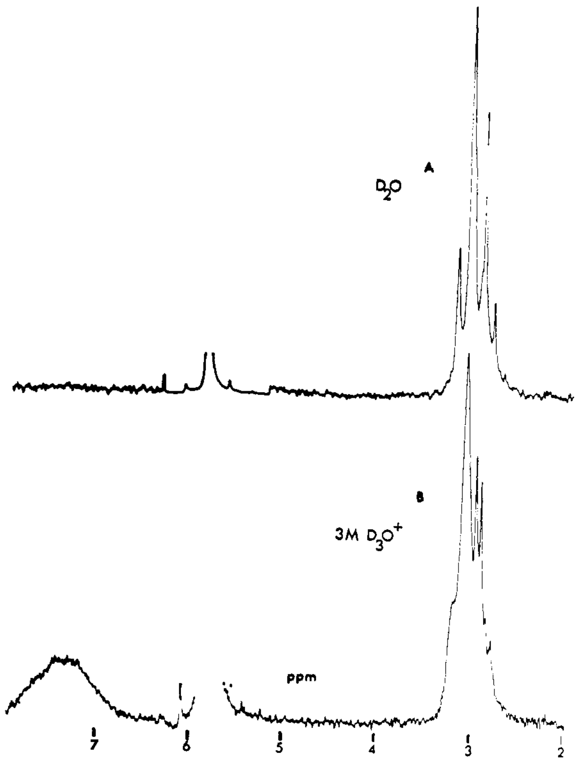


Figure 4. The 100-Mc spectrum of $[Pt^{IV}(Meen)(en)Cl_2]Cl_2$ (3.0 *M* DCl).

Table II. Rate Constants for H Exchange of the $[Pt^{II}(Meen)(en)]^{2+}$ Ion at 34° and μ = 1 *M*

pD	$k_{OD^-}\cdot[OD^-] \times 10^4$, sec^{-1}	$k_{OAc^-}\cdot[OAc^-] \times 10^4$, sec^{-1} [a]	$k_{calcd} \times 10^4$, sec^{-1} [a]	$k_{obsd} \times 10^4$, sec^{-1}
	A. 0.2 *M* Buffer			
3.60	0.03	0.55	0.7	0.7
4.36	0.16	1.54	1.9	2.0
4.40	0.17	1.68	2.0	2.1
5.07	0.85	2.45	3.5	3.2
5.45	2.05	2.65	4.9	4.7
6.07	8.50	2.76	11.4	11.6
	B. 0.1 *M* Buffer			
4.40	0.17	0.84	1.2	1.3
5.07	0.85	1.23	2.2	2.3
6.07	8.50	1.38	10.0	10.3

[a] $k_{calcd} = k_{D_2O} + k_{OD^-}[OD^-] + k_{OAc^-}[OAc^-]$; $k_{D_2O} = 1.5 \times 10^{-5}$ sec^{-1}; $k_{OAc^-} = 1.6 \times 10^{-3}$ $M^{-1} sec^{-1}$; $k_{OD^-} = 1.9 \times 10^5$ $M^{-1} sec^{-1}$.

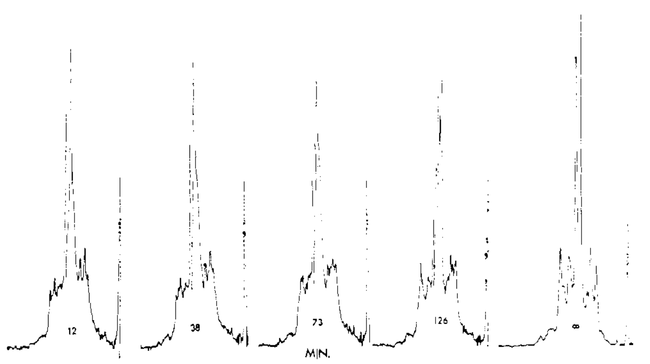


Figure 5. Change in pmr spectrum with time for [Pt^{II}(Meen)(en)]Cl$_2$ in 0.1 M buffer, pD 4.40.

dependent path and agrees with the extrapolated value mentioned previously.

For the *trans*-[Pt(Meen)(en)Cl$_2$]$^{2+}$ ion, the ethylene pmr signal conflicts with the methyl signal to such an extent that it is not possible to plot the data as for the Pt(II) complex. However, the exchange rate was followed by observing the change in the ethylene signal around 3 ppm (Figure 6). Plots of log [(peak height)$_t$ − (peak height)$_\infty$] against time were linear for more than two half-lives and the rate law established by this means was of the form $k_{obsd} = k_{D_2O} + k_{OD^-}[OD^-]$. The rate constants obtained are given in Table III. We infer that this applies to exchange for the $-NH_2$ groups, and it seems highly probable that the same rate law holds for exchange at the methyl nitrogen center.

Table III. Rate Constants for H Exchange in [Pt^{IV}(Meen)(en)Cl$_2$]Cl$_2$[a]

DCl, N	$k_{obsd} \times 10^4$, sec^{-1}	k_{D_2O}, sec^{-1}	$k_{OD^-} \times 10^{-10}$ M^{-1} sec^{-1} [b]
0.933	3.2[c] (1.0)[d]		2.0[c]
0.466	4.1[c] (1.5)[d]	2.4×10^{-4} [c]	2.1[c]
0.233	5.4[c] (2.2)[d]		1.8[c]
0.116	8.4[c] (3.3)[d]		1.8[c]

[a] At 34.3°, $\mu = 3.5$ M. [b] $k_{OD^-} = (k_{obsd} - k_{D_2O})[D^+]/3.8 \times 10^{-15}$. [c] Obtained by potting ethylene signal; exchange at $-NH_2$. [d] Estimated using shape of methyl signal; exchange at $-NHCH_3$.

Because of the difficulty in treating the doublet and singlet methyl signals to give rate constants, we have chosen to make a relative comparison of the rates under different pH conditions by selecting the signal shape where the doublet and singlet are near the same level. This is clearly not the half-life, and we estimate that it is close to $t_{0.2}$. Certainly the rate constants estimated in this manner are not in error by more than a factor of 2. Some of the signals used for this purpose are depicted in Figure 6. This procedure gave the same rate law as that obtained from the ethylene signal, and the rate constants so obtained were used ultimately to calculate the retention ratio for the Pt(IV) complex. These estimated rate constants are given in parentheses in Table III.

The racemization rates for both complex ions were followed in buffered solutions at constant ionic strength, $\mu = 1$. Plots of log α^0 against time were linear for at least three half-lives. Some rates were followed to zero rotation for both ions, and under these circumstances no rotation remained from 700 to 350 mμ. The rate constants at several temperatures and pH values are given in Tables IV and V, and both sets of results fit a rate law of the form

$$R = k[\mathrm{Pt}][\mathrm{OH}^-]$$

This result was not surprising since the rates were measured in the pH region where the term first order in [OH$^-$] predominated. The absence of the buffer dependence receives some support from the rates in acetate and collidine buffers. Extrapolation of the second-order rate constants to the same temperature gave the same result.

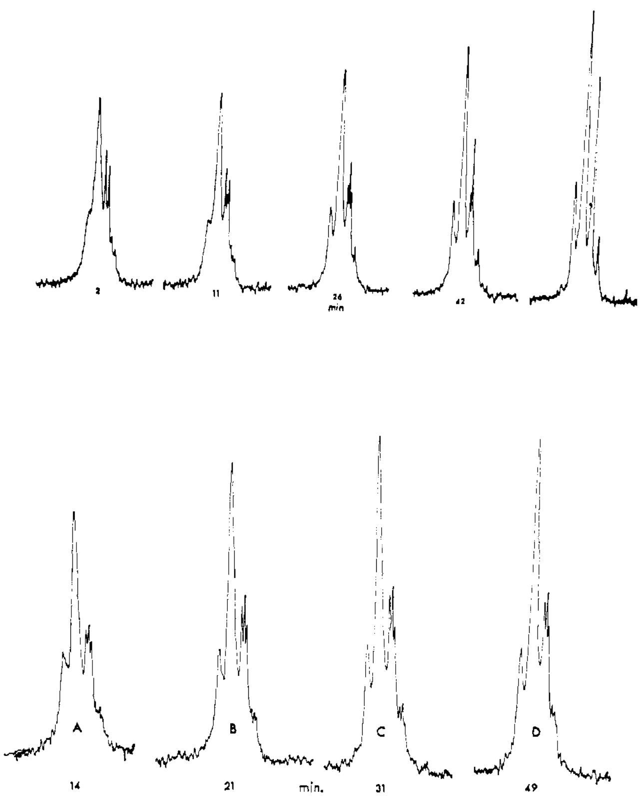


Figure 6. (Top) Equivalent spectra of [Pt^{IV}(Meen)(en)Cl$_2$]Cl$_2$ after time indicated in (A) 0.117, (B) 0.233, (C) 0.466, and (D) 0.933 N DCl. (Bottom) Change in pmr spectrum with time for [Pt^{IV}(Meen)(en)Cl$_2$]Cl$_2$ in 0.233 N DCl.

Table IV. Rate Constants for Racemization of (−)$_{350}$-[Pt(Meen)(en)]Cl$_2$

Temp, °C	pH	$k_{obsd} \times 10^3$, sec^{-1}	k_R,[c] M^{-1} sec^{-1}
30.0	7.69[a]	0.39	
30.0	8.16[a]	1.16	
30.0	8.80[a]	4.95	
34.3	6.91[b,c]	0.13	7.9×10^2
40.0	6.92[b]	0.34	
43.0	6.92[b]	0.55	

[a] 0.05 M collidine buffer, $\mu = 1.05$ M. [b] 0.2 M acetate buffer, $\mu = 1.2$ M. [c] $k_R = k_{obsd}[H^+]/1.95 \times 10^{-14}$.

From the second-order rate constants for racemization and exchange (Tables II–V) a retention ratio of ~10^2 for the Pt(II) and ~10^4 for the Pt(IV) complex was calculated. For the Pt(II) ion the ratio is obtained from the exchange rate constant in D$_2$O *vs.* the racemization constant in H$_2$O at $\mu = 1.0$. A direct determination of this value under the same experimental conditions was obtaihed from the following experiments. (−)$_{350}$[Pt(Meen)(en)]Cl$_2$ (0.02 g) was dissolved in 0.1 M

Table V. Rate Constants for Racemization of $(-)_{350}$-$[Pt(Meen)(en)Cl_2]Cl_2$

Temp, °C	pH	$k_{obsd} \times 10^4$, sec^{-1}	$k_R \times 10^{-5}$, $M^{-1}\ sec^{-1}$
25.0	4.02[a]	0.27	2.5[d]
25.0	5.03[a]	2.63	2.5[d]
25.0	5.68[a]	12.4	2.6[d]
25.0	5.03[a]	2.82	2.6[d]
34.3	5.03[a]	13.9	6.5[e]
15.0	5.03[a]	0.43	
25.0	2.0[b]	0.003	2.8[d]
25.0	2.0[c]	0.009	

[a] 0.2 *M* acetate buffer, $\mu = 1.2\ M$. [b] 0.01 *N* $HClO_4$, $\mu = 1\ M$. [c] 0.01 *N* $HClO_4$. [d] $k_R = k_{obsd}[H^+]/10^{-14}$. [e] $k_R = k_{obsd}[H^+]/1.95 \times 10^{-14}$.

NaOAc–DOAc buffer (0.5 ml, pD 6.4) and the proton exchange rate measured, $t_{1/2} = 4.2$ min. The same buffer was then used to obtain the racemization rate, $t_{1/2} = 7.4$ hr (34°, $\mu \simeq 0.4$). These values give a retention ratio of 106. However, for the Pt(IV) ion the ratio is derived from the exchange rate constant in D_2O at $\mu = 3.4$ and the racemization constant in H_2O at $\mu = 1.0$. Despite this discrepancy in the conditions, it is clear that a substantial retention ratio exists. Moreover, in the Pt(IV) instance racemization at $\mu = 3.4$ should be slower than at $\mu = 1.0$, and the retention ratio would therefore increase if both rates were measured under the same conditions. For the Pt(IV) complex, one rate study was carried out at pH 2 and $\mu = 1\ M$, the highest acidity at which it is practical to follow the rate. The first-order dependence on $[OH^-]$ was still evident. However, for a solution of the complex in 1 *M* $HClO_4$, a condition under which exchange takes place primarily by the acid-independent path, no change in rotation took place in 3 months at 25°. It can be concluded that exchange by the water-catalyzed path either does not lead to racemization or that there is a large retention ratio for this path.

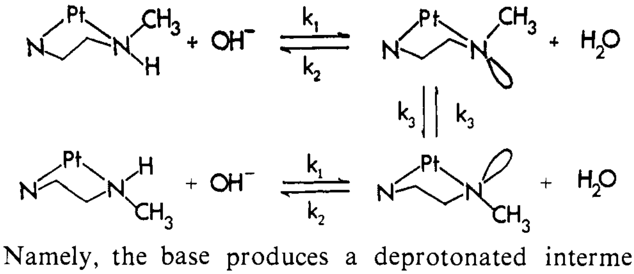
The plots of log k_R against $1/T$ were linear for both complexes and the activation energies for racemization were similar, 18 kcal/mole for Pt(II) and 20 kcal/mole for Pt(IV) (after correction for the enthalpy of dissociation of H_2O; $\Delta H_{av} = 13$ kcal/mole). However, under the same conditions the Pt(IV) ion racemized $\sim 10^3$ times faster than the Pt(II) species. The pK_a for $[Pt^{II}(Meen)(en)]^{2+}$ was too large to allow a measurement to be made in aqueous solution, but the Pt(IV) complex gave $pK_a = 10.6 \pm 0.1$ at 30° and $\mu = 0.01$. The value was largely temperature insensitive (± 0.2) in the range 10–30°, and an estimate of ΔH was not obtained by this method.

Discussion

Although the Pt(II) complex has only one possible geometrical form, the Pt(IV) complex can have a number of structures. The similarities in the method of preparation and the uv spectra of $[Pt^{IV}(Meen)(en)Cl_2]Cl_2$ and the analogous *trans*-$[Pt^{IV}(en)_2Cl_2]Cl_2$[13] suggest that the former species also has a *trans* disposition of the chloride ligands. Furthermore, *cis*-$[Pt^{IV}(en)_2Cl_2]Cl_2$ has two signals in its pmr spectrum which are attributed to the ethylene bridge, whereas the *trans* isomer has only one signal (3.0 ppm)[14] as compared to one (3.0 ppm) for the Meen complex. Also, the *cis*-en species has two N–H signals well separated (4.8 and 6.8 ppm).[14] The Meen complex has only one N–H signal at 7.3 ppm, and from this result it is possible to assign the downfield N–H signal in *cis*-$[Pt^{IV}(en)_2Cl_2]Cl_2$ to the NH_2 groups which are *trans* to each other and the upfield signal to the NH_2 groups which are *trans* to Cl.

Apart from this comparison with the analogous bis(en) complex, the results presented here are best interpreted using the *trans*-diacido structure. For example, only one pmr signal was observed for the methyl group. Since a *cis*-diacido complex would have a number of possible isomers, several methyl signals might be anticipated in the pmr spectrum. However, if the Pt(II) complex were oxidized stereospecifically to one *cis* isomer, some optical rotation would be expected after treatment of such an inert complex with dilute base, and this was not observed. Finally, the complex racemized at only one rate, and it is concluded therefore that the chloride ligands are *trans* to each other.

For cobalt(III) complexes containing these asymmetric N centers the following mechanism has been proposed to account for the large retention ratio.[3]



Namely, the base produces a deprotonated intermediate (k_1) and the rate of reprotonation (k_2) is much greater than the inversion of the intermediate (k_3). The isotope effects for the reaction in the aqueous solution[2,3,5] and the retention ratios in alcohols[8] have both been used as evidence to support this mechanism and the similarity of the results for the Pt complexes with those of Co(III) lead us to the same proposal for the d^6 and d^8 Pt systems.

It has been argued previously[5] that the exchange rate is essentially represented by k_1, since k_2 has been found to be fast (10^9–$10^{10}\ sec^{-1}$) in aqueous solution for reprotonation at oxygen and nitrogen centers.[15] It also seems likely that this situation holds in the present circumstances. However, the racemization rate constant is a composite, $k_R = 2k_3(K_a/K_w)$, involving the proton dissociation constant for the complex. These constants are not available for the cobalt(III) compounds used, but several attempts at measurement require them to be less than 10^{-14}. The same remarks apply to the Pt(II) complex, but K_a has been measured for the Pt(IV) complex ($pK_a = 10.6$). Moreover the proton exchange studies imply that the proton on the $N-CH_3$ group has approximately the same acidity as the others. It follows that the pK_a of the *sec*-N center is ~ 11.5 and the inversion rate constant (k_3) for the deprotonated intermediate at 25° is $\sim 400\ sec^{-1}$ in aqueous solution. This value is not greatly different from those measured for amines[16] and several N-methylaziridines.[17] Also it is in the vicinity of the value proposed for the cobalt(III)

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complexes where only estimates of the pK_a's of these complexes could be made.[2,3,8]

For the Pt(IV) ion k_D and k_R are considerably greater than for the Co(III) complexes ($\sim 10^6$). The larger rates may be attributed to the higher oxidation state of Pt(IV) and consequently to the smaller pK_a. We have estimated the pK_a's of some Co(III) Meen compounds,[2,3,8] and using similar arguments we anticipate a pK_a of $\sim$17 for the analogous cobalt complex *trans*-$[Co(Meen)(en)Cl_2]^+$. The difference between the Pt(IV) value and this estimate then accounts roughly for the rate order difference.

It is also of some interest to consider the enthalpy reaction coordinate profiles for these systems. In the Co(III) complexes, the observed activation energy for H exchange is extraordinarily constant, 28 ± 1 kcal/mole.[2,3,5] We assume, therefore, that the value for $[Pt(Meen)(en)]^{2+}$ is close to that for $Pt(NH_3)_4^{2+}$, *i.e.*, 11 ± 1 kcal/mole.[1] Then an estimate of the inversion barrier can be obtained if ΔH for reprotonation does not differ much from the temperature dependence of the diffusion coefficient for the solvent (1–3 kcal/mole).[18] This leads to an inversion barrier of $\sim$8–10 kcal/mole which does not differ greatly from that deduced by a similar analysis for the deprotonated $[Co(NH_3)_4(sarcosinato)]^{2+}$ ion.[2]

For the *trans*-$[Pt(Meen)(en)Cl_2]^{2+}$ species we know that over the range 10–25° $\Delta pK_a < 0.2$ which means that $\Delta H_a < 7$ kcal/mole. The barrier to inversion in this ion therefore must be >12 and <19.5 kcal/mole. The difference in retention ratio between the Pt(II) and Pt(IV) systems may be accounted for partly by the conformational properties of the two systems. For example, it might be expected that the absence of apical groups in the Pt(II) system could allow either conformation of the en or Meen chelate ring to exist in appreciable concentrations. The Pt(IV) complex, however, has groups of substantial dimensions in the 1 and 6 positions, and under these circumstances the methyl substituent would be expected to adopt its most equatorial form in the most stable configuration. Consequently, inversion at this center also requires inversion of the conformer to attain the most stable configuration. Whether the activation energy for conformational change is included in the inversion barrier or whether it is merely the enthalpy difference between the stable and least stable forms is not yet clear. However, a difference would be expected for the inversion barriers between the Pt(II) and the Pt(IV) systems arising from these conformational properties.

Another factor which may contribute to the difference between the inversion rates of the deprotonated Pt(II) and Pt(IV) ions is the electron-withdrawing capacity of the two oxidation states. It has been shown for organic amine systems that electron-withdrawing groups decrease the inversion rate, possibly by generating more p character in the bond.[19] A similar effect might be anticipated here where the Pt(IV) state is considerably more effective than Pt(II) in reducing the basic character of the N center.

One explanation[2] for the high retention ratio for the $[Co(NH_3)_4(sarcosinato)]^{2+}$ ion arose from the possibility that the axial NH_3 groups on the cobalt atom could hydrogen-bond to the lone pair of electrons on the asymmetric N atom, and thereby stabilize the original configuration. It was suggested[2] that electronegative groups in the 1 and 6 positions would then lead to low retention ratios if this factor was important in the retention mechanism. The present complexes, $[Pt(en)(Meen)]^{2+}$ and *trans*-$[Pt(en)(Meen)Cl_2]^{2+}$, both have this property to differing extents, and it is concluded therefore that the substantial retention factor which is still observed does not arise from this cause.

A study of exchange and inversion in platinum(II)–N,N′-dimethylethylenediamine complexes has appeared recently.[20] The pmr spectrum of the preparative mixture for the $[Pt^{II}(NH_3)_2(N,N'\text{-}Me_2en)]^{2+}$ complex indicated two isomers, assigned as racemate and *meso*.[20] At pH $\sim$10.5 the methyl doublets collapsed to singlets, and at pH $\sim$11 the singlet signals merged. The retention ratio was estimated as approximately equal to the ratio of J_{HNCH_3} ($\sim$6 cps) to the difference in the frequency of the methyl signals ($\sim$2 cps). The k_{ex}/k_{isom} was evaluated as $\sim$3, but when account is taken of the difference in acidity of the two solutions, it is possible to calculate a retention ratio of $\sim$5.

It is not evident why this system should differ appreciably from the complex under study here. It is conceivable that quite small changes in the chemical shifts and/or resolution for the methyl signals with a change in conditions could radically alter the evaluation of the second-order rate constant for isomerization. In the present study such shifts were observed for quite small changes in the solution. Moreover, the explanation that Haake and Turley[20] make for the large retention factor in the $[Co(NH_3)_4(sarcosinato)]^{2+}$ study has been refuted elsewhere[5] and by the present study. In addition, their conclusion that H-exchange proceeds *via* a symmetrical π-bonded species between N and Pt[20] is also not supported by the results of the present investigation. However, Haake and Turley find that at equilibrium the *meso* and racemic forms are present in approximately equal amounts.[20] The racemic form presumably has both methyl groups in their most equatorial condition, while the *meso* form must contain one "axial" and one "equatorial" methyl group. In the absence of apical groups in the 1 and 6 positions, little conformational preference is anticipated for the two possibilities from our analysis of these factors in the foregoing text. However, it would be interesting to see if the equilibrium alters in the *trans*-dichloro Pt(IV) complex where the apical positions are now occupied.

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