Volume 8
Number 11
November 1969

Inorganic Chemistry

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Racemization and Proton Exchange at Asymmetric Nitrogen Centers in Platinum(II) Complexes

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Received March 24, 1969

The platinum complexes Pt(Meen)Cl_2, [Pt(Meen)$(NH_3)_2$]Cl_2, [Pt(Meen)$(NH_3)_2$](BCS)$_2$, [Pt(Meen)(phen)]$Cl_2 \cdot 2H_2O$, and [Pt(Meen)(phen)](BCS)$_2 \cdot H_2O$ have been prepared.[2] The complex ions Pt(Meen)$(NH_3)_2^{2+}$ and Pt(Meen)(phen)$^{2+}$ have been resolved by fractional crystallization of the BCS salts from methanol and water, respectively. In these square-planar complexes the CH_3NH nitrogen atom is the sole center of asymmetry. Racemization rates for these complexes are specific hydroxide ion catalyzed. Rates of exchange of the proton on the N-methyl nitrogen atom were followed by nmr by observing the growth of the methyl singlet on deuteration. These rates, also hydroxide ion catalyzed, were 100 and 2500 times greater than the racemization rates, respectively, for the diammine and phen complexes, indicating mainly a retention of configuration about the nitrogen for the deuteration process.

Introduction

There has been much interest of late in the resolution and kinetics of racemization and proton exchange of transition metal complexes containing asymmetric secondary amine nitrogen atoms. The ability to resolve such complexes depends on the lability of the amine proton and the susceptibility of the deprotonated complex to inversion. A number of rate studies[3-5] performed on simple amine complexes, particularly inert d^6 octahedral and d^8 square-planar complexes, has proved that proton exchange is quite slow in acid media and that the rate of proton exchange is first order in $[OH^-]$. Since inversion at an asymmetric nitrogen atom in these complexes is not expected to occur without prior deprotonation, the resolution of optical isomers was a strong possibility.

Armed with this information, Sargeson, *et al.*,[6-8] have succeeded in resolving the secondary aminecobalt(III) complex ions $Co(NH_3)_4(CH_3NHCH_2COO)^{2+}$, $Co(NH_3)_4(Meen)^{3+}$, and *trans,trans*-$Co(NO_2)_2(Meen)_2^{+}$. The sole center of asymmetry of these complexes is the asymmetric nitrogen atom. They have shown that the rates of racemization and proton exchange are both first order in hydroxide ion concentration and that the rate of proton exchange for a given complex exceeds the rate of racemization by 10^3–10^5; *i.e.*, proton exchange on the asymmetric nitrogen atom is occurring principally without inversion. Once the amido (deprotonated) complex is formed, it must invert rapidly to compete with reprotonation or deuteration even for this limited amount of inversion to be observed. The limiting rate of inversion of the amido complex must equal half the rate of reprotonation.

By nmr coalescence techniques, Haake and Turley[9] have compared the rates of proton exchange and inversion at the amine nitrogen atoms of the two platinum(II) complexes $Pt(Me_2en)(NH_3)_2^{2+}$ and $Pt(Me_2en)(bipy)^{2+}$ (Me_2en = N,N′-dimethylethylenediamine; bipy = bipyridyl). The rates of inversion of each equal half the corresponding rates of proton exchange within experimental error, indicating 100% inversion of the amido complex. The proton-exchange rate for the bipy complex is a factor of 300 greater than that for the diammine.

In contrast, Erickson and Fritz[10] have found that the rate of proton exchange of $Pt(EDDA)(NH_3)_2$ (EDDA = ethylenediaminediacetate) exceeds the rate of inversion by a factor of 200. Buckingham, Marzilli, and

(1) Taken from the Ph.D. thesis of John B. Goddard, Northwestern University, Evanston, Ill., 1969.
(2) Meen = $CH_3NHCH_2CH_2NH_2$; BCS = *d*-α-bromocamphor-π-sulfonate; phen = 1,10-phenanthroline.
(3) F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 1073 (1960).
(4) J. W. Palmer and F. Basolo, *J. Inorg. Nucl. Chem.*, **15**, 279 (1960).
(5) J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).
(6) B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966).
(7) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967).
(8) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 3428 (1967).
(9) P. Haake and P. C. Turley, *ibid.*, **90**, 2293 (1968).
(10) L. E. Erickson and H. L. Fritz, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

Sargeson[11] found a similar factor for the complex Pt(Meen)(en)$^{2+}$, but also found an acetate-catalyzed path and, at very low pH, a water-catalyzed path, revealing that other bases are also effective in removing the proton from the secondary amine nitrogen atom. They have also found[11] that for the octahedral Pt(IV) complex Pt(Meen)(en)Cl_2^{2+} the proton exchange: inversion ratio is 10^4, a value similar to that for the cobalt(III) complexes previously investigated.[6-8]

This paper reports the results of similar investigations on the complexes Pt(Meen)$(NH_3)_2^{2+}$ and Pt(Meen)(phen)$^{2+}$. The results show that the rates of racemization are slower than the rates of hydrogen exchange. This is in agreement with two of the previous studies[10,11] but different from the results of Haake and Turley.[9]

Experimental Section

Materials.—The N-methylethylenediamine (Meen) was purchased from Ames Laboratories, Milford, Conn., and was used without further purification. The 1,10-phenanthroline (phen) and the resolving agent ammonium *d*-α-bromocamphor-π-sulfonate (NH_4BCS) were purchased from Aldrich Chemical Co., Milwaukee, Wis. Deuterium oxide (99.84 mol % D_2O) was obtained from Bio-Rad Laboratories, Richmond, Calif. The nmr calibration standard sodium 3-(trimethylsilyl)propanesulfonate (TPSNa) was from Brinkmann Instruments, Inc., Westbury, N. Y.

Analyses.—C, H, and N analyses were performed by Miss H. Beck of this department, and analyses for Pt were done by burning the complex to the metal.

Spectra.—All uv spectra were taken on a Cary 14 spectrophotometer. Ir spectra were taken as Nujol mulls or KBr disks on a Perkin-Elmer 337 (range 4000–400 cm^{-1}). The pmr spectra were taken either on a Varian A-60 or T-60 nmr spectrometer. Optical rotation measurements were taken on an O. C. Rudolph spectropolarimeter.

Pt(Meen)Cl_2.—Preparation of this complex is analogous to that of Pt(en)Cl_2 by Johnson's method.[12] To 4.144 g of K_2PtCl_4 was added 2.261 g of Meen·2HCl (1:1). The compounds were dissolved in 50 ml of water, the solution was heated with stirring to a gentle boil, and 20 ml of 1.00 *M* NaOH (just enough to neutralize the HCl) was added dropwise over a period of 0.5 hr. A yellow precipitate began to form after 15 ml of the NaOH had been added. The solution was cooled in ice and then filtered. The product was washed with water, acetone, and ether and air dried; crude yield, 2.78 g (84.5%).

The powder was then dissolved in 100 ml of liquid ammonia, in which the pink impurity [Pt(Meen)$_2$][$PtCl_4$] is insoluble. The yellow solution was filtered through a medium-porosity sintered-glass funnel, and the pink residue was washed with water, acetone, and ether and air dried; yield, 0.461 g (of [Pt(Meen)$_2$][$PtCl_4$]).

The liquid ammonia solution was evaporated gently on the steam bath with the aid of an air stream. The yellow solid was washed into a sintered-glass funnel with water, washed with acetone and ether, and air dried; yield, 2.00 g (58.8%). (Optimum yields of this material were around 67%.) The product is a light yellow powder. *Anal.* Calcd for Pt(Meen)Cl_2 and [Pt(Meen)$_2$][$PtCl_4$]: C, 10.59; H, 2.96; N, 8.24. Found for Pt(Meen)Cl_2: C, 10.69; H, 2.66; N, 8.28. Found for [Pt(Meen)$_2$][$PtCl_4$]: C, 10.56; H, 2.84; N, 8.16.

[Pt(Meen)$(NH_3)_2$]Cl_2.—To 3.915 g of Pt(Meen)Cl_2 suspended in 25 ml of water was added 15 ml of concentrated NH_3. The suspension was stirred and warmed 0.5 hr, and the resulting clear solution was evaporated to near dryness. The product was dissolved in 8 ml of water, and the solution was filtered. To the filtrate was added 2 ml of concentrated HCl and 100 ml of acetone; the product readily crystallizes with scratching. After being cooled in ice, the solution was filtered, and the white powder washed with acetone and air dried; yield, 4.10 g (95.0%). *Anal.* Calcd for [Pt(Meen)$(NH_3)_2$]Cl_2: C, 9.63; H, 4.31; N, 14.97; Pt, 52.14. Found: C, 9.77; H, 4.47; N, 14.96; Pt, 52.13. A uv spectrum of the aqueous complex has a maximum at 285 mμ (ϵ 44.3) and a shoulder at 223 mμ (ϵ 947).

The 60-MHz pmr spectra of undeuterated and deuterated [Pt(Meen)$(NH_3)_2$]Cl_2 are given in Figures 1 and 2. In Figure 1, the methyl doublet is clearly seen, along with the two ^{195}Pt satellite doublets. The methylene protons (two nonequivalent pairs) fall mostly downfield of the principal doublet (Figure 2). On deuteration, the methyl singlet grows exactly between the original doublet. The NH_3 protons fall upfield of the HDO peak, whereas the NH_2 and NH proton peaks fall downfield of HDO. All three of these broad peaks disappear on deuteration.

Chemical shifts from internal TPSNa, measured on an A-60, are given in ppm: N-CH_3, 2.7; -CH_2CH_2-, ~2.8; NH_3, 4.08; NH_2, 5.2; NH, 5.7. Coupling constants (cps) are: $J_{^{195}Pt-CH_3}$, 38.5; J_{CH_3-NH}, 6.

AgBCS.—AgBCS was prepared by fractional crystallization from a concentrated solution of NH_4BCS and a twofold excess of $AgNO_3$.

[Pt(Meen)$(NH_3)_2$](BCS)$_2$.—To 1.032 g of [Pt(Meen)$(NH_3)_2$]Cl_2 was added 20 ml of water and 2.307 g of AgBCS (theory). The suspension was warmed and stirred 30 min in the dark and then filtered of AgCl. The filtrate was evaporated to 8 ml, filtered once more through a fine-porosity sintered-glass funnel to remove the remaining AgCl, and then evaporated to near dryness. To the residue was added 20 ml of a 50:50 acetone–ether solution to extract the residual water. The white complex was filtered, washed with acetone and ether, and air dried; yield, 2.25 g (88.3%). *Anal.* Calcd for [Pt(Meen)$(NH_3)_2$]$(C_{10}H_{14}O_4SBr)_2$: C, 29.91; H, 4.80; N, 6.07. Found: C, 29.96; H, 5.16; N, 5.93.

Resolution of [Pt(Meen)$(NH_3)_2$]Cl_2.—The BCS salt prepared as described above (2.252 g) was dissolved in 50 ml of methanol (acidified with a few drops of methanolic 0.1 *N* HCl) and the solution was cooled in ice. When precipitation commenced, it was allowed to continue 15 min, at which time the solution was filtered. The precipitate forms slowly and is quite voluminous. The filtrate was set aside for a second fraction, and the precipitate was washed with acetone and then ether and air dried; yield, 0.738 g (30.5%). This first fraction was recrystallized from 12 ml of methanol containing 6 drops of methanolic 0.1 *N* HCl; yield, 0.570 g (77.2% recovery). To convert to the chloride salt, the product was dissolved in 10 ml of methanol containing 6 drops of concentrated HCl. The volume was reduced to 7 ml with a hot plate, and 5 ml of acetone was added to the warm solution. A white precipitate formed when the solution was cooled. After being cooled in ice, the solution was filtered and the product was washed with acetone and air dried; yield, 0.201 g (89.5%). The chloride was redissolved in 15 ml of methanol containing 5 drops of concentrated HCl, the solution was evaporated to 5 ml, and then 5 ml of acetone was added. The solution was cooled, and the product was filtered, washed, and dried as before; yield, 0.174 g (86% recovery). An ir spectrum revealed the absence of the strong BCS carbonyl stretch at 1760 cm^{-1}.

Optical rotation measurements were made at two Hg wavelengths on a solution of 0.1685 g of this fraction in 10 ml of 0.01 *N* HCl. Values at 365 mμ are α −0.6135° and $[\alpha]^{25}_{365}$ −36.4°; at 404.7 mμ, α −0.4034° and $[\alpha]^{25}_{404.7}$ −23.9°.

A second fraction was obtained with the evaporation to 20 ml of the original aqueous filtrate from the first fraction. The solution was cooled in ice, the [Pt(Meen)$(NH_3)_2$](BCS)$_2$ was filtered, and the filtrate was set aside for a third fraction. The product was washed with acetone and ether and air dried; yield, 0.412 g (18.3% of total). This was converted to [Pt(Meen)$(NH_3)_2$]Cl_2 as before with two precipitations; yield, 0.121 g (72%).

(11) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **91**, 5227 (1969).

(12) G. L. Johnson, *Inorg. Syn.*, **8**, 242 (1966).

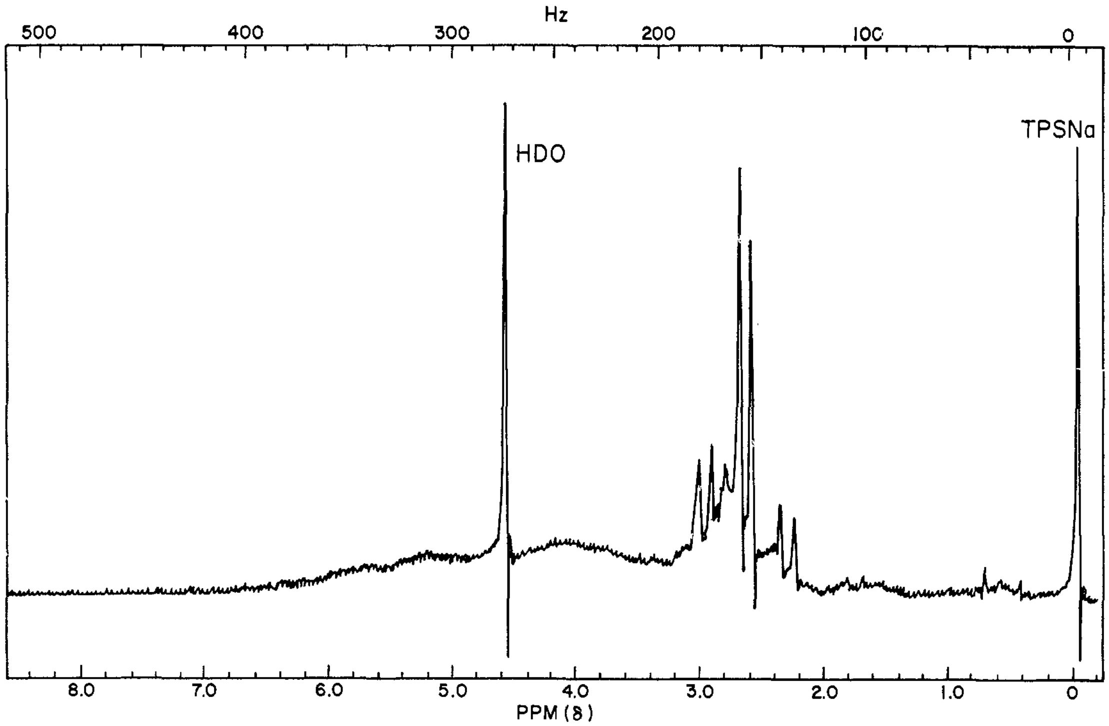


Figure 1.—The 60-MHz spectrum of $[Pt(Meen)(NH_3)_2]Cl_2$ in 0.05 *M* DCl.

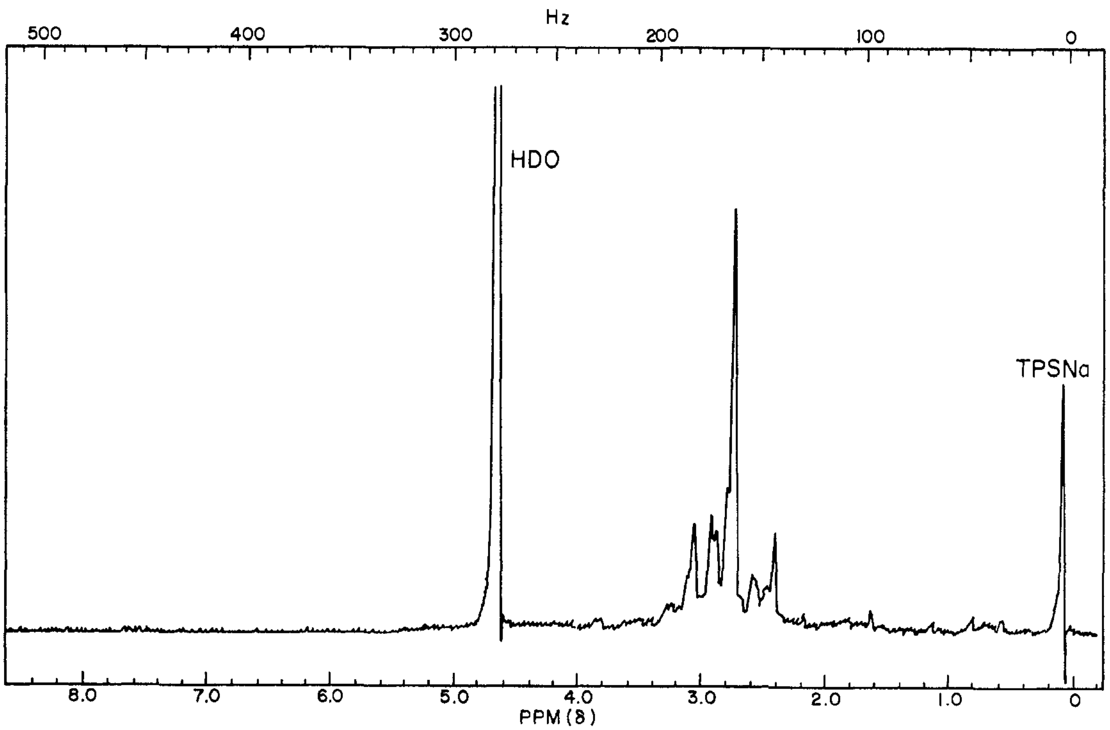


Figure 2.—The 60-MHz spectrum of deuterated (N–D) $[Pt(Meen)(ND_3)_2]Cl_2$ in D_2O.

An optical rotation measurement was made on 0.1205 g of this second fraction of $[Pt(Meen)(NH_3)_2]Cl_2$ in 10 ml of 0.01 *N* HCl at 365 mμ; α −0.3171°, $[\alpha]^{25}_{365}$ −26.3°.

The filtrate from fraction 2 was evaporated to near dryness to yield fraction 3. The residual solvent was extracted with ether, and the product was filtered and air dried; yield, 0.886 g (39.4% of total). This was converted to the chloride salt in the usual way; yield, 0.283 g (79%).

An optical rotation study of 0.2829 g of this third fraction of $[Pt(Meen)(NH_3)_2]Cl_2$ in 10 ml of 0.01 *N* HCl was made at the 365-mμ Hg line; α +0.6844°, $[\alpha]^{25}_{365}$ +24.2°. Evaporation of the filtrate after the first fractions have been removed appears to be the best way of obtaining the (+) isomer, although it is not obtained as optically pure as the (−) enantiomer (*cf.* fraction 1).

[Pt(Meen)(phen)]Cl₂·H₂O.—To 0.933 g of $Pt(Meen)Cl_2$ in 30 ml of water was added 0.952 g of 1,10-phenanthroline (phen) (∼2:1). The suspension was stirred and warmed 2 hr, the resulting yellow solution was evaporated to near dryness, and then the product was redissolved in 30 ml of cold water. The solution was filtered of some unreacted $Pt(Meen)Cl_2$ (0.123 g, 12.9% unreacted). The desired product was precipitated by addition of 150 ml of acetone followed by 200 ml of ether. The

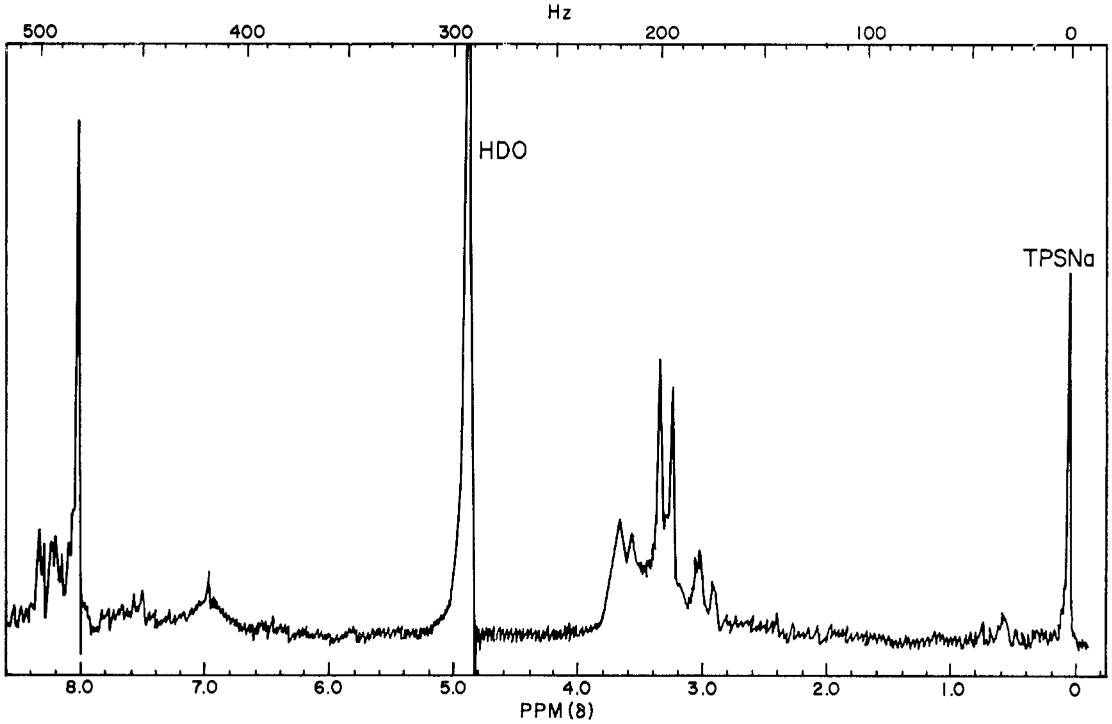


Figure 3.—The 60-MHz spectrum of [Pt(Meen)(phen)]Cl_2 in 0.07 *M* DNO_3.

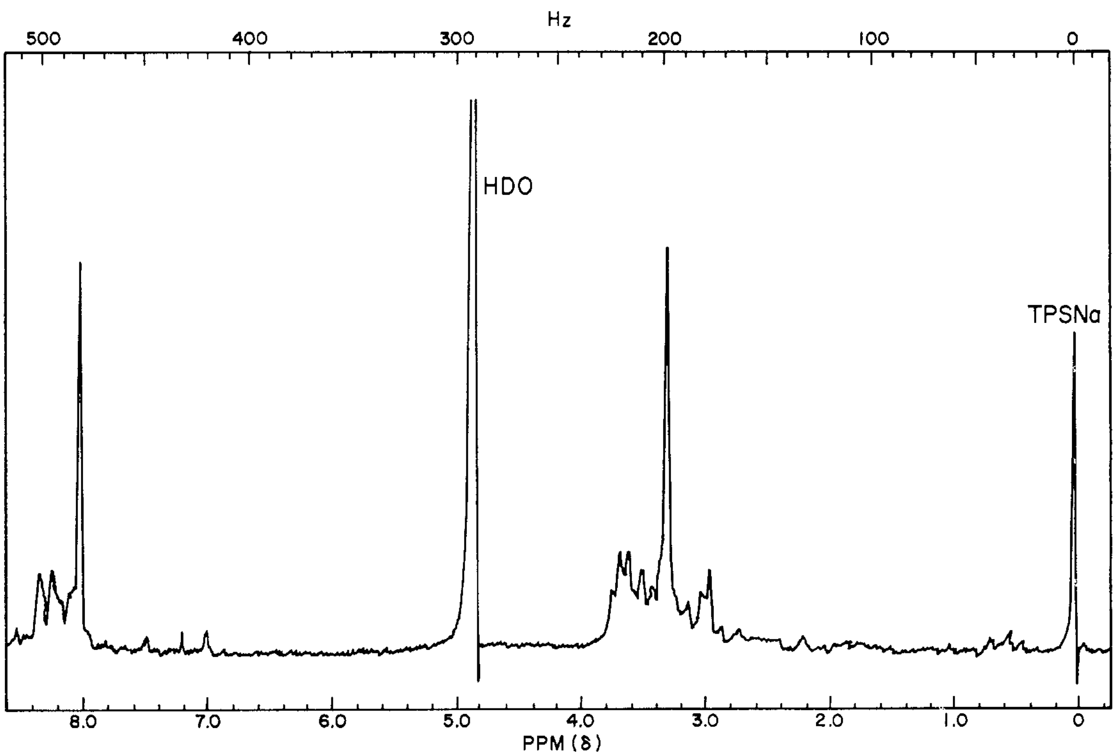


Figure 4.—The 60 MHz spectrum of deuterated (N–D) [Pt(Meen)(phen)]Cl_2 in D_2O.

suspension was cooled in ice and then filtered. The product was washed with acetone and air dried. (The material at this point may be nearly anhydrous and is hygroscopic. Drawing air through the funnel for a few minutes will solidify any oily material that is present.) *Anal.* Calcd for [Pt(Meen)(phen)]$Cl_2 \cdot 2H_2O$: C, 32.38; H, 3.99; N, 10.07; Pt, 35.07. Found: C, 32.16; H, 3.98; N, 10.02; Pt, 35.21. In acidic solutions, the complex reverts slowly to starting materials, Pt(Meen)Cl_2 and 1,10-phenanthroline. An uv spectrum of the aqueous complex has maxima at 359 mμ (ϵ 1503), 342 mμ (ϵ 1870), 298 mμ (ϵ 9440), 277 mμ (ϵ 34,300), and 227 mμ (ϵ 40,500).

The 60-MHz pmr spectra of the undeuterated and deuterated complex are given in Figures 3 and 4. The methyl doublet (Figure 3) collapses to a singlet on deuteration (Figure 4), spaced in the center of the original doublet. The ^{195}Pt satellite doublets are equally spaced on each side of the principal doublet. The $-CH_2CH_2-$ proton peaks for the most part fall downfield of the principal doublet. The NH_2, NH, and phenanthroline protons are relatively far downfield from the HDO peak. The drain of electrons into the π system of 1,10-phenanthroline is seen by the shift of the methyl peak downfield by 0.6 ppm relative to the diammine complex; this effect is more dramatic for the NH_2 and NH peaks, which are shifted almost 2 ppm downfield. Upon deuteration, the broad NH_2 and NH peaks disappear, but the peaks attributed to phenanthroline are unchanged.

Chemical shifts from internal TPSNa, measured on a Varian A-60, are given in ppm: N-CH_3, 3.3; $-CH_2CH_2-$, ~3.5; NH_2, 6.9; NH, 7.5; phenanthroline, 7.0–8.3. Coupling constants (cps) are: $J^{195}{}_{Pt-CH_3}$, 39; J_{NH-CH_3}, 6.

[Pt(Meen)(phen)](BCS)$_2$·H$_2$O. Resolution of Pt(Meen)-(phen)$^{2+}$.—To 0.980 g of [Pt(Meen)(phen)]Cl$_2$·2H$_2$O in 100 ml of water was added 1.473 g of AgBCS (theoretical amount). The solution was warmed and stirred 30 min in the dark. The solution was filtered of AgCl while still warm, then acidified with a few drops of 0.1 N HCl, evaporated to 80 ml, and cooled in ice 1 hr. The resulting precipitate was filtered, washed with acetone and ether, and air dried; yield, 0.652 g (34.0%). *Anal.* Calcd for [Pt(Meen)(phen)](BCS)$_2$·H$_2$O: C, 38.64; H, 4.45; N, 5.15. Found: C, 38.38; H, 4.67; N, 4.92.

This first fraction was recrystallized from 20 ml of water acidified with a few drops of 0.1 N HCl; yield, 0.429 g (65.8% recovery). The product was converted to the chloride salt by stirring with 8 ml of a 1:1:1 ethanol–concentrated HCl–ether solution for 15 min; the partially dissolved chloride salt was then precipitated with a 5-vol portion of acetone. The product was filtered, washed with acetone, and air dried; yield, 0.179 g (80.3%). The BCS peak at 1760 cm^{-1} was absent from an ir spectrum of this complex. An optical rotation measurement was made on 0.1646 g of fraction 1 (as the chloride salt) in 10 ml of 0.01 N HNO$_3$ at the 546-mμ Hg line (the solution is opaque at the higher energy Hg lines); α −0.5400°, $[\alpha]^{25}{}_{546}$ −32.8°.

The original aqueous filtrate from fraction 1 was evaporated to 45 ml and then cooled in ice. The resulting precipitate (fraction 2) was filtered, washed with acetone, and air dried; yield, 0.885 g (46.2%). This was converted to the chloride as before; yield, 0.251 g (54.7%). The optical rotation of 0.246 g of the chloride in 10 ml of 0.01 N HNO$_3$ was taken at 546 mμ; α −0.4953°, $[\alpha]^{25}{}_{546}$ = −20.1°.

The aqueous filtrate from fraction 2 was further acidified with 5 drops of 0.1 N HCl and then evaporated to dryness; yield, 0.286 g (14.9%). Conversion to the chloride yielded 0.140 g (95%). An ir spectrum showed BCS to be absent. Optical rotation values are (0.1352 g/10 ml 0.01 N HNO$_3$): α +0.1499°, $[\alpha]^{25}{}_{546}$ +11.1°. Again, the more soluble (+) isomer is obtained only in an optically impure state.

Kinetics.—Kinetics of racemization were followed with an O. C. Rudolph spectropolarimeter with an oscillating polarizer attachment. An average of several readings would give a reproducibility of ±0.002°, but for individual readings, accuracy was ±0.004°. A 1-dm quartz cell was used in all cases. The polarimeter cell compartment was thermostated to ±0.1°.

Except for the slowest reactions ($t_{1/2}$ > 12 hr), where the infinity reading was taken as the reading for distilled water, kinetics were followed to completion. Plots of log $|\angle_t - \angle_\infty|$ *vs.* time were straight lines in all cases. In no case was any mutarotation seen; all complexes racemized completely.

Kinetics of the exchange of the proton on the N-methyl nitrogen atom in these Pt(Meen)L$_2{}^{2+}$ complexes were followed in buffered D$_2$O solution by nmr. A Varian A-60 was used in most cases, since it was equipped with a variable-temperature probe. A few runs were done on a Varian T-60, which has a constant temperature of 37.5° in the sample chamber. Kinetics were followed by scanning over the methyl doublet at appropriate time intervals to observe the growth of the methyl singlet on deuteration.

For the fastest reactions ($t_{1/2}$ < 10 min), the kinetic samples were left in the nmr sample compartment for the duration of the reaction. Temperature was calibrated with ethylene glycol and is accurate to ±1°. For the intermediate reactions (10 min < $t_{1/2}$ < 6 hr), samples were left in a constant-temperature bath (±0.1°) except when a reading was to be taken. The variable-temperature probe was kept at the approximate temperature (±2°). The slowest reactions ($t_{1/2}$ > 6 hr) were kept in the temperature bath (±0.1°), except for an occasional pmr reading. The variable-temperature probe was left at its normal temperature (~40°) for these readings. All reactions were carried out in nmr tubes.

First-order rate constants were obtained by plotting log $(h_\infty - h_t)$ *vs.* time, where h_t is the height of the methyl singlet at time t, and h_∞ its height after the reaction is completed. This method has been used successfully before.[6-8] The deuteration of Pt(Meen)(NH$_3$)$_2{}^{2+}$ was the reaction studied most extensively, and except for the very slow reactions, these log plots are straight lines. The slow reactions ($t_{1/2}$ > 8 hr) gave straight lines after about one-third of the reaction was completed; for the initial third, plots were curved and the reaction was apparently slower. This curvature may be caused by another reaction, as all nine nitrogen protons exchange with D$_2$O at several different rates. The rate of interest is otherwise easy to follow as the methyl protons stand out well in the pmr spectrum. Kinetic runs under identical conditions were reproducible to ±20%, although reproducibility was not as good for different preparations of the complex. Methyl singlet growth during a kinetic run in D$_2$O is shown by Figure 5.

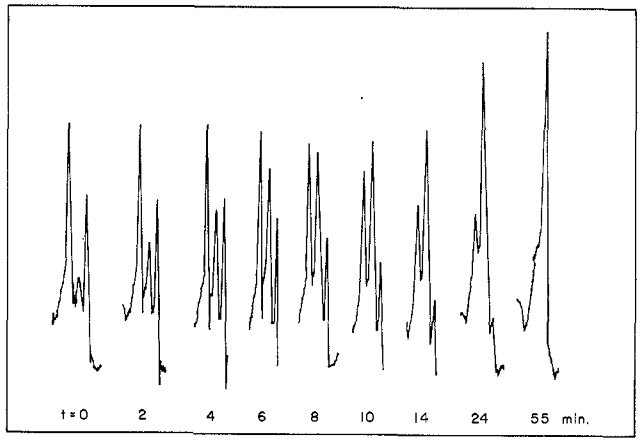


Figure 5.—Deuteration of the N-methyl proton of [Pt(Meen)-(NH$_3$)$_2$]Cl$_2$ in acetate buffer. The reaction was followed with a T-60 nmr spectrometer at 37.5°.

The deuteration of the complex Pt(Meen)(phen)$^{2+}$ was studied less extensively. Runs done at 37.5° on a Varian T-60 gave straight lines for the plot of log $(h_\infty - h_t)$ *vs.* time, again for the growth of the singlet. Resolution of the methyl doublet for this complex is quite good with a T-60, but poorer on an A-60. Consequently, there is much scatter in the points for the runs at 25°. Solubility of the complex is <0.3 M, and kinetic runs were done on nearly saturated solutions.

pH and pD Determinations.—For all racemization studies, the pH of the solution was measured at the temperature of the kinetic runs with a Corning Model 7 pH meter. The pD of the D$_2$O solutions was measured by the method of Glasoe and Long;[13] the pH meter is first calibrated with a standard buffer in H$_2$O, then the "pH" reading of the D$_2$O solution is measured, and 0.40 pH unit is added to it to obtain the pD reading. Glasoe and Long found that this relation (pD = pH + 0.40) holds over a wide range of pD values. These pD measurements were made with a Radiometer Copenhagen pH Meter 25, usually at the temperature of the kinetic runs. It was found that with the buffers used, the variation of pD with temperature was small and within the experimental error of the rate constants. The pD measurements were made on ~0.5 ml of solution, usually before deuteration, but for the faster reactions, the pD was measured after the

(13) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

complex had been deuterated. On reaction solutions that were checked, little, if any, pD change occurred during the reaction.

The ionization constants for H_2O and D_2O at the various temperatures were obtained from the data of Covington, Robinson, and Bates.[14] Second-order rate constants were calculated by dividing the first-order rate constant (k_{obsd}) by $[OH^-]$ or $[OD^-]$.

Results

Racemization rate studies of $[Pt(Meen)(phen)]Cl_2$ (Table I) were performed in buffered aqueous solutions at three temperatures to determine activation parameters. Potassium nitrate was used as the inert electrolyte to maintain ionic strength. Some decomposition, presumably to $Pt(Meen)Cl_2$, was noted toward the end of the higher temperature reactions, but this did not seem to affect the kinetic plots significantly. From a plot of log k_R *vs.* $1/T$ were calculated an activation energy of 17.3 kcal/mol and an activation entropy of +17 eu.

Table I

Kinetics of Racemization of (−)-$[Pt(Meen)(phen)]Cl_2$ in Water, 1.00 M KNO_3, λ 546 mμ

[Complex], M^a	[Buffer], M	Temp, °C	pH	k_{obsd}, sec^{-1}	k_R,^{b} M^{-1} sec^{-1}
0.0099	0.033 (acetate)	25.0	4.84	1.09×10^{-5}	15,750
0.0099	0.033 (phosphate)	25.0	5.62	6.98×10^{-5}	16,730
0.0082	0.033 (phosphate)	25.0	6.26	2.90×10^{-4}	15,930
0.0099	0.033 (phosphate)	25.0	6.74	9.48×10^{-4}	17,240
0.0144	0.033 (acetate)	37.5	4.86	8.77×10^{-5}	49,300
0.0099	0.033 (phosphate)	37.5	5.61	5.57×10^{-4}	55,700
0.0144	0.033 (acetate)	50.0	4.51	2.97×10^{-4}	170,800
0.0144	0.033 (acetate)	50.0	4.87	5.82×10^{-4}	146,000

^{a} Total concentration of complex, not of (−) enantiomer. ^{b} $k_R = k_{obsd}/[OH^-]$.

Racemization rate studies of $[Pt(Meen)(NH_3)_2]Cl_2$, performed in buffered aqueous solutions at three temperatures, are summarized in Table II. An Arrhenius plot yielded an activation energy of 19.8 kcal/mol and an activation entropy of +17 eu.

Table II

Kinetics of Racemization of $[Pt(Meen)(NH_3)_2]Cl_2$ in Water, μ = 1.00 (KCl), λ 365 mμ

[Complex], M^a	(Isomer)	[Buffer], M	Temp, °C	pH	k_{obsd}, sec^{-1}	k_R,^{b} M^{-1} sec^{-1}
0.0150	(−)	0.033 (N-ethylmorpholine (HCl))	25.0	7.93	2.98×10^{-4}	351
0.010^c	(−)	0.033 (N-ethylmorpholine (HCl))	25.0	8.08	4.23×10^{-4}	352
0.0150	(−)	0.033 (N-ethylmorpholine (HCl))	25.0	8.56	1.16×10^{-3}	320
0.0150	(−)	0.033 (phosphate)	25.0	6.68	1.41×10^{-5}	296
0.0252	(+)	0.033 (phosphate)	37.5	6.71	1.66×10^{-4}	1320
0.0252	(+)	0.033 (phosphate)	37.5	7.07	3.38×10^{-4}	1173
0.0252	(+)	0.033 (phosphate)	50.0	6.28	3.87×10^{-4}	4450
0.0252	(+)	0.033 (phosphate)	50.0	6.69	1.07×10^{-3}	4070

^{a} Total concentration of complex, not of optically pure enantiomer. ^{b} $k_R = k_{obsd}/[OH^-]$. ^{c} 1.00 M KBr in place of KCl.

Proton exchange of the N-methyl nitrogen of $[Pt(Meen)(phen)]Cl_2$ was studied in D_2O at 25 and 37.5°; results are presented in Table III. Deuteration in 0.1 N DCl, attempted at 37.5°, resulted in decomposition of the complex to $Pt(Meen)Cl_2$ before completion of the reaction. Because of the poorer resolution of the N-methyl pmr signal compared to that of the diammine complex and the limited pD range available in this case due to decomposition at lower pD and too rapid reactions at higher pD, calculation of activation parameters did not seem warranted.

(14) A. K. Covington, R. A. Robinson, and R. G. Bates, *J. Phys. Chem.*, **70**, 3820 (1966).

Table III

Kinetics of Proton Exchange on the N-Methyl Nitrogen of 0.20 M $[Pt(Meen)(phen)]Cl_2$ in D_2O

Buffer^a (in molar units)	Temp, °C	pD	k_{obsd}, sec^{-1}	k_D, M^{-1} sec^{-1} ^{b}
0.15 D_2MN–0.05 Na_2MN	25.0	3.00	6.22×10^{-5}	4.61×10^7
0.15 D_2MN–0.075 Na_2MN	25.0	3.30	1.11×10^{-4}	4.12×10^7
0.05 NaDT	25.0	3.79	2.49×10^{-4}	3.00×10^7
0.075 D_2ME–0.025 Na_2ME	37.5	2.37	1.30×10^{-4}	1.56×10^8
0.15 D_2MN–0.05 Na_2MN	37.5	3.05	4.83×10^{-4}	1.10×10^8
0.05 NaDT	37.5	3.81	3.10×10^{-3}	1.35×10^8

^{a} Abbreviations: MN, malonate; T, tartrate; ME, maleate. ^{b} $k_D = k_{obsd}/[OD^-]$.

Table IV

Rates of Proton Exchange on the N-Methyl Nitrogen of 0.30 M $[Pt(Meen)(NH_3)_2]Cl_2$ in D_2O at Low pD

Buffer^a (in molar units)	Temp, °C	pD	$10^6 k_{obsd}$, sec^{-1}
0.02 KTOX	25.0	1.98	2.50
0.02 KTOX	25.0	1.94	2.37
0.0782 DCl	25.0	1.11^b	2.34
0.015 Na_2ME–0.030 D_2ME	50.0	2.70	32.3
0.030 Na_2ME–0.060 D_2ME	50.0	2.57	29.4
0.015 K_2OX–0.045 D_2OX	50.0	2.11	24.8
0.030 K_2OX–0.090 D_2OX	50.0	2.00	27.5
0.0646 DCl	50.0	1.19^b	23.1
0.115 DCl	50.0	0.94^b	29.6
0.457 DCl	50.0	0.34^b	27.7

^{a} Abbreviations: KTOX, potassium tetraoxalate ($KDC_2O_4 \cdot D_2C_2O_4$); ME, maleate; OX, oxalate. ^{b} Calculated value.

Because of the stability of the diammine complex and the good resolution of the methyl pmr signal, kinetics of proton exchange for this complex were studied more thoroughly than those for the phen complex. A study at low pD is presented in Table IV. Studies over a wide pD range were made at three temperatures, and the results are given in Tables V–VII. Activation parameters were calculated from plots of log k_D *vs.* $1/T$ for the pD range for which k_D was a constant; E_a = 14.3 kcal and $\Delta S^{\ddagger}$ = +10 eu.

Discussion

The kinetics of racemization of $Pt(Meen)(phen)^{2+}$ and $Pt(Meen)(NH_3)_2{}^{2+}$ are second order, first order in both $[OH^-]$ and concentration of optically active complex. The rate law is given by eq 1. This rate law is

$$\text{rate} = k_R[OH^-][(+)\text{- or }(-)\text{-}Pt(Meen)L_2{}^{2+}] \qquad (1)$$

analogous to that for racemization of the several Co(III)[6–8] and Pt(II) complexes[9–11] which have been investigated. Complex concentration had little effect upon k_R in the range investigated, nor apparently did the inert electrolyte, as a change from KCl to KBr yielded the same rate constant (Table II). The three different buffers used at varying base strengths gave no catalysis other than that attributed to $[OH^-]$, and rates were consistent with one another between two buffers.

TABLE V

RATE CONSTANTS FOR DEUTERATION OF THE N-METHYL NITROGEN ATOM OF 0.30 *M* [Pt(Meen)(NH$_3$)$_2$]Cl$_2$ IN D$_2$O AT 25°

Buffer[a] (in molar units)	pD	$10^5 k_{obsd}$, sec^{-1}	$10^{-5} k_D$,[b] M^{-1} sec^{-1}
0.05 NaDT	3.74	0.94	12.7
0.025 NaDT	3.75	0.94	12.4
0.05 KDP	4.11	1.57	9.0
0.047 DOAc–0.0097 NaOAc	4.25	1.93	8.0
0.027 DOAc–0.0055 NaOAc	4.26	2.01	8.2
0.0115 DOAc–0.0024 NaOAc	4.26	2.05	8.3
0.10 NaOAc–0.044 DOAc	5.30	6.72	2.5
0.026 NaOAc–0.0045 DOAc	5.56	8.28	1.69
0.052 NaOAc–0.0090 DOAc	5.58	8.67	1.69
0.0115 NaOAc–0.0020 DOAc	5.62	9.23	1.64
0.10 NaOAc–0.020 DOAc	5.63	13.9	2.4
0.102 NaOAc–0.0116 DOAc	5.82	10.5	1.17
0.039 NaOAc–0.0044 DOAc	5.84	10.5	1.12
0.021 NaOAc–0.0024 DOAc	5.87	11.1	1.11
0.033 KD$_2$PO$_4$–0.017 Na$_2$DPO$_4$	6.70	86.0	1.27
0.025 KD$_2$PO$_4$–0.025 Na$_2$DPO$_4$	7.03	111	0.77
0.050 KD$_2$PO$_4$–0.050 Na$_2$DPO$_4$	7.04	129	0.88
0.017 KD$_2$PO$_4$–0.033 Na$_2$DPO$_4$	7.38	215	0.66
0.010 KD$_2$PO$_4$–0.030 Na$_2$DPO$_4$	7.58	399	0.78
0.010 KD$_2$PO$_4$–0.040 Na$_2$DPO$_4$	7.81	591	0.68
0.010 borax	9.44	>7000	>0.2[c]

[a] Abbreviations: T, tartrate; P, phthalate; OAc, acetate. [b] $k_D = k_{obsd}/[OD^-]$; $pK_{D_2O} = 14.87$ (25°).[14] [c] Reaction over before first point was taken; $t_{1/2} < 10$ sec.

TABLE VI

RATE CONSTANTS FOR DEUTERATION OF THE N-METHYL NITROGEN OF 0.30 *M* [Pt(Meen)(NH$_3$)$_2$]Cl$_2$ IN D$_2$O AT 37.5°

Buffer[a] (in molar units)	pD	$10^5 k_{obsd}$, sec^{-1}	$10^{-5} k_D$,[b] M^{-1} sec^{-1}
0.050 NaDT	3.69	1.91	11.0
0.050 KDP	4.08	3.97	9.3
0.025 KDP	4.14	4.22	8.6
0.010 KDP	4.16	4.06	7.9
0.0099 NaOAc–0.048 DOAc	4.20	2.94	5.2
0.10 Na$_2$OAc–0.098 DOAc	4.83	6.06	2.5
0.047 NaOAc–0.0082 DOAc	5.56	27.3	2.1
0.106 NaOAc–0.0120 DOAc	5.76	32.9	1.61
0.040 KD$_2$PO$_4$–0.010 Na$_2$DPO$_4$	6.52	221	1.88
0.033 KD$_2$PO$_4$–0.017 Na$_2$DPO$_4$	6.79	437	2.00
0.025 KD$_2$PO$_4$–0.025 Na$_2$DPO$_4$	7.12	975	2.08
0.017 KD$_2$PO$_4$–0.033 Na$_2$DPO$_4$	7.31	1138	1.91

[a] Abbreviations: T, tartrate; P, phthalate; OAc, acetate. [b] $k_D = k_{obsd}/[OD^-]$; $pK_{D_2O} = 14.45$ (37.5°).[14]

Similarity of activation parameters suggests similar mechanisms, the rate difference arising only from the activation energy term. The k_R for Pt(Meen)(phen)$^{2+}$ is 50 times that for Pt(Meen)(NH$_3$)$_2^{2+}$. The π-electron system of phenanthroline can drain electron density from the N-methyl nitrogen atom, creating a more positive center which results in a greater acidity of the N-methyl proton. The pmr spectrum suggests this also (Figure 3), since the N–H peak is shifted 1.8 ppm downfield from its position in the spectrum of the diammine complex. Similarly, it has been shown that the 2,2′-bipyridine ligand acts as an electron sink in the complex [Pt(bipy)(en)]I$_2$, allowing the en ligand to be deprotonated in liquid ammonia even without the aid of added KNH$_2$.[15]

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

TABLE VII

RATE CONSTANTS FOR DEUTERATION OF THE N-METHYL NITROGEN OF 0.30 *M* [Pt(Meen)(NH$_3$)$_2$]Cl$_2$ in D$_2$O AT 50°

Buffer[a] (in molar units)	pD	$10^5 k_{obsd}$, sec^{-1}	$10^{-5} k_D$,[b] M^{-1} sec^{-1}
0.050 NaDT	3.69	11.1	28.5
0.050 NaDT	3.73	12.4	29.1
0.025 NaDT	3.80	10.3	20.5
0.010 NaDT	3.94	10.4	15.0
0.10 NaOAc–0.79 DOAc	3.94	33.9	49.0
0.10 NaOAc–0.59 DOAc	4.08	43.2	45.2
0.05 KDP	4.14	15.5	14.1
0.05 KDP	4.15	20.4	18.2
0.0104 NaOAc–0.050 DOAc	4.21	10.0	7.7
0.050 KDP	4.23	16.2	12.0
0.025 KDP	4.34	15.9	9.2
0.010 KDP	4.53	21.1	7.8
0.10 NaOAc–0.115 DOAc	4.81	34.9	6.8
0.053 NaOAc–0.0091 DOAc	5.58	114	3.8
0.094 NaOAc–0.0106 DOAc	5.80	227	4.5
0.074 NaOAc–0.0099 DOAc	5.90	250	4.0
0.045 KD$_2$PO$_4$–0.005 Na$_2$DPO$_4$	6.29	686	4.4
0.040 KD$_2$PO$_4$–0.010 Na$_2$DPO$_4$	6.48	1120	4.7
0.033 KD$_2$PO$_4$–0.017 Na$_2$DPO$_4$	6.74	1370	3.2

[a] Abbreviations: T, tartrate; OAc, acetate; P, phthalate. [b] $k_D = k_{obsd}/[OD^-]$; $pK_{D_2O} = 14.10$ (50°).[14]

TABLE VIII

COMPARISON OF SECOND-ORDER RATES AND ACTIVATION PARAMETERS OF RACEMIZATION AND PROTON EXCHANGE FOR [Pt(Meen)L$_2$]Cl$_2$ COMPLEXES

Temp, °C	k_R,[a] M^{-1} sec^{-1}	k_D,[b] M^{-1} sec^{-1}	k_D/k_R
	[Pt(Meen)(NH$_3$)$_2$]Cl$_2$		
25.0	322	66,000	200
37.5	1250	190,000	150
50.0	4260	430,000	100
	(E_a = 19.8 ± 1 kcal/mol) ($\Delta S^\ddagger$ = +17 ± 3 eu)	(E_a = 14.3 ± 1 kcal/mol) ($\Delta S^\ddagger$ = +10 ± 3 eu)	
	[Pt(Meen)(phen)]Cl$_2$		
25.0	16,410	3.9×10^7	2400
37.5	52,500	1.34×10^8	2600
	(E_a = 17.3 ± 1 kcal/mol) ($\Delta S^\ddagger$ = +17 ± 3 eu)		

[a] $k_R = k_{obsd}(\text{racem})/[OH^-]$. [b] $k_D = k_{obsd}(\text{deut})/[OD^-]$.

The proton-exchange rate of the phen complex, to the limit of detection, follows a rate law similar to eq 1 for racemization. The proton exchange rate of Pt(Meen)(NH$_3$)$_2^{2+}$, which was followed over a 10^7 *M* concentration range of hydroxide ion, is somewhat more complicated. At low pD, the rate is very slow and is independent of [OD$^-$] (Table IV). The rate law is described simply by eq 2; $k = k_{obsd}$ of Table IV. This

$$\text{rate} = k[\text{Pt(Meen)(NH}_3)_2^{2+}] \quad (2)$$

suggests a water-catalyzed path. Water is a poor base compared to OD$^-$, but the large ratio of D$_2$O to OD$^-$ in these acidic solutions allows it to compete effectively for the amine proton. A very slow water-catalyzed path has also been found in the deuteration of Pt(Meen)(en)$^{2+}$.[11]

In the range of pD ~3–6, the kinetics are not clear. A definite dependence of rate on [OD$^-$] is observed, but it is less than first-order. The actual concentration of OD$^-$ is quite small, eliminating the possibility of significant amounts of an OD^- ion pair, yet some ion association surely exists in these solutions of high concentration. The rates do not depend upon the buffers in the concentration range used, however, as is evident from Tables V–VII. There is also fair agreement between buffers in the same pD range. Consequently, the buffer concentration is not expected to be a part of the rate equation. Varying amounts of chloride ion also had little effect on the rate.

Our primary concern is with the higher pD range which correlates with the pH range of the racemization studies. Here the rate is second order, similar to that for racemization, and is described by eq 3. Nmr co-

$$\text{rate} = k_D[\text{Pt(Meen)(NH}_3)_2{}^{2+}][\text{OD}^-] \quad (3)$$

alescence studies have proved useful for obtaining inversion rates which are too fast to determine by the more conventional kinetic approach used in this study.[9,16] Coalescence studies were performed with $[Pt(Meen)(NH_3)_2]Cl_2$ in H_2O solution; the methyl doublet was found to coalesce to a singlet at pH ~10.1 at 37°. Second-order rate constants of $\sim 1 \times 10^5$ M^{-1} sec^{-1} were calculated, a factor of ~2 below those at pD ~6–7 (Table VI).[17] This is fair agreement considering the difference in method and in range of concentration of hydroxide ion.

The mechanism for racemization and proton exchange of both $Pt(Meen)(phen)^{2+}$ and $Pt(Meen)(NH_3)_2{}^{2+}$ (proton exchange of the diammine above pD ~6) is given by eq 4–6. The rate constant for proton ex-

$$d\text{-[Pt(CH}_3\text{NHCH}_2\text{CH}_2\text{NH}_2)\text{L}_2{}^{2+} + \text{OH}^- \underset{k_1}{\overset{k_D}{\rightleftharpoons}} d\text{-Pt(CH}_3\ddot{\text{N}}\text{CH}_2\text{CH}_2\text{NH}_2)\text{L}_2{}^+ + \text{H}_2\text{O} \quad (4)$$

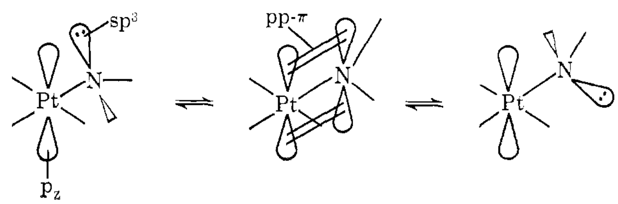
$$d\text{-Pt(CH}_3\ddot{\text{N}}\text{CH}_2\text{CH}_2\text{NH}_2)\text{L}_2{}^+ \underset{k_2}{\overset{k_2}{\rightleftharpoons}} l\text{-Pt(CH}_3\ddot{\text{N}}\text{CH}_2\text{CH}_2\text{NH}_2)\text{L}_2{}^+ \quad (5)$$

$$l\text{-Pt(CH}_3\ddot{\text{N}}\text{CH}_2\text{CH}_2\text{NH}_2)\text{L}_2{}^+ + \text{H}_2\text{O} \underset{k_D}{\overset{k_1}{\rightleftharpoons}} l\text{-Pt(CH}_3\text{NHCH}_2\text{CH}_2\text{NH}_2)\text{L}_2{}^{2+} + \text{OH}^- \quad (6)$$

change is k_D; rate of reprotonation (k_1) is very great. The actual rate of inversion of the amido complex is k_2 and is pH independent. Although the inversion rate is great, the reprotonation rate is even greater, resulting largely in retention of configuration. The measured rate constant for racemization, $k_{obsd} = 2k_2K_a[OH^-]/K_w$, is pH dependent since the rate depends on the amount of amido complex present. Here K_a is the acid dissociation constant for the proton on the N-methyl nitrogen atom. The value of K_a is unknown, but for the complex $Pt(Meen)(en)^{2+}$, it has been assumed[11] that $K_a < 10^{-14}$ based on the fairly constant rates of reprotonation of nitrogen unshared electron pairs.

A comparison of racemization and proton-exchange rates for both the diammine and phen complexes is made in Table VIII, where k_R and k_D are average values. Retention of configuration (or deuteration) is favored over inversion for $Pt(Meen)(phen)^{2+}$ by a factor of 2500, whereas this factor is only 100 for Pt(Meen)-$(NH_3)_2{}^{2+}$. The greater rate separation for the phen complex may result from a faster rate of reprotonation or a slower rate of inversion, or a combination of the two. If the reprotonation rate is constant, as has been assumed previously,[8] then the actual rate of inversion of the phen complex (eq 5) must be a factor of 12–25 slower than that of the diammine complex. In that case, differences in observed proton-exchange rates (k_D) for the two complexes result strictly from a difference in the K_a's.

The k_D/k_R ratios for four other Pt(II) complexes with asymmetric secondary amine nitrogen atoms are known also: k_D/k_R = 240 for $Pt(Meen)(en)^{2+}$;[11] 200 for $Pt(EDDA)(NH_3)_2$;[10] and ≥2 for $Pt(Me_2en)(NH_3)_2{}^{2+}$ and $Pt(Me_2en)(bipy)^{2+}$.[9] These ratios are all substantially less than the factors of 10^5 found for certain Co(III) complexes.[8] This could result from an increased stabilization of the amido intermediate through π bonding from a filled nitrogen 2p orbital to a vacant platinum 6p orbital. Once this π bond is formed, a symmetrical intermediate exists and racemization results.



(7)

It should be noted that this type of π bonding is not possible with the low-spin d^6 systems of Co(III). Furthermore, if the relatively smaller k_D/k_R ratio in these low-spin d^8 systems is due to pp-π bonding, then even a smaller ratio of rates is expected if the N ligand atom is replaced by P and/or the Pt is replaced by Pd. This is currently under investigation.

Acknowledgment.—We wish to thank Drs. D. A. Buckingham and A. M. Sargeson for discussion of their work on $Pt(Meen)(en)^{2+}$. The receipt of a National Institutes of Health fellowship by J. B. G. is gratefully acknowledged. This research was supported in part by National Institutes of Health Grant GM-07488.

(16) M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **8**, 795 (1969).
(17) The authors are indebted to Dr. M. Jouan for these measurements.