Ir Spectra of Pt(IV) Complexes of Trimethylenediamine Derivatives Compared with Those of Pt(II) Complexes.—For complexes Pt(diamine)Cl_4 there are differences in band structure and relative intensities from the spectra of the corresponding Pt(diamine)Cl_2 complexes, but it is not difficult in most cases to trace a 1:1 correspondence of bands, most shifting by a few tens of wave numbers or less. It cannot necessarily be concluded from this that the "axial" chloro groups coordinated to the Pt atom have little effect on the chelate ring conformation, since this correspondence applies to Pt((±)dptn)Cl_2 and Pt((±)dptn)Cl_4 where the ring conformations are probably different (chair with axial and equatorial methyl groups and skew-boat with equatorial methyl groups, respectively[5]). ν_{N-H} bands remain sharp in Pt(diamine)Cl_4 complexes. The Pt–Cl stretching bands in Pt(IV) complexes do not show any clear splitting due to the presence of two different types of coordinated chloride ion but occur at slightly higher frequencies (330–350 cm^{-1}) than in Pt(II) complexes. For c-Pt(tn)Cl_2 peaks probably corresponding predominantly to asymmetric and symmetric Pt–N stretching[8] occur at 535 and 482 cm^{-1}, respectively. The corresponding peaks for Pt(tn)Cl_4 occur at 532 and 470 cm^{-1}. For other Pt(diamine)Cl_4 complexes where corresponding bands are easily distinguished only small frequency shifts are again observed (*e.g.*, for b-Pt(tnCl)Cl_2, 562 and 515 cm^{-1}; for Pt(tnCl)Cl_4, 575 and 508 cm^{-1}).

For complexes of the type *trans'*-Pt(diamine)Cl_2(OH')$_2$ a band corresponding to O–H stretching, usually moderately sharp, is observed slightly below 3500 cm^{-1}. The N–H stretching bands are usually broadened, probably due to H bonding with the coordinated hydroxide. Pt(tnCl)$Cl_2(OH)_2$ is exceptional in giving a very sharp ν_{O-H} peak at the comparatively high frequency of 3550 cm^{-1}, with the N–H stretching bands showing an unusual pattern with both moderately broad and sharp bands (Figure 7b). The hydroxide ions are apparently not involved in H bonding here, possibly because the axial N–H atoms are already engaged in H bonding with the chloro group of the coordinated tnCl. As mentioned previously, for Pt(tnCl)$Cl_2(OH)_2$, the two ν_{O-H} bands merge into one broad band. For these trans dihydroxo complexes in general some correspondence with the Pt(diamine)Cl_2 spectra is usually present, though this is less marked than for the Pt(diamine)Cl_4 complexes. They all show an intense broad band near 550 cm^{-1}, possibly corresponding to Pt–O stretching. The ν_{Pt-Cl} bands occur only slightly (<10 cm^{-1}) to higher frequencies than those for Pt(diamine)Cl_2.

In the spectra of *trans*-[Pt(tn)$_2Cl_2$]Cl_2 and [Pt(tnOH)$_2Cl_2$]Cl_2, a sharp peak at 348 cm^{-1} in each complex probably corresponds to Pt–Cl stretching.

Acknowledgments.—T. G. A. acknowledges the award of a CSIRO postgraduate studentship. The 100-MHz spectrum of [Pt(tnOH)$_2$]Cl_2 was run by Dr. S. R. Johns, of the Division of Applied Chemistry, CSIRO.

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Complexes with Six Membered Chelate Rings. VI. A Proton Magnetic Resonance Study of Some Platinum(II) Complexes of *N,N'*-Dimethylpropane-1,3-diamine, *N,N,N',N'*-Tetramethylpropane-1,3-diamine, and *N,N,N',N'*-Tetramethylethylenediamine

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The preparations of a number of complexes of *N,N'*-dimethylpropane-1,3-diamine (dimetn), *N,N,N',N'*-tetramethylpropane-1,3-diamine (tetrametn), and *N,N,N',N'*-tetramethylethylenediamine (tetrameen) are described, and pmr spectra of water-soluble complexes are discussed. The geometric isomers of [Pt(dimetn)$(NH_3)_2$]Cl_2 are present in aqueous solution in the ratio meso/racemic = 2.8. The rate of N-deuteration in D_2O solution and the effect of increasing pH on the pmr spectrum in H_2O of this complex are discussed. N-Deuteration of the racemic isomer is significantly faster than for the meso isomer. The retention ratio for this complex is of the order of 10–30.

Introduction

Continuing our investigation of the complexes of platinum and palladium with trimethylenediamine and its derivatives,[2] we now describe the preparation and pmr spectra of some platinum(II) complexes of the *N*-methyl substituted trimethylenediamines, *N,N'*-dimethylpropane-1,3-diamine ($CH_3NH(CH_2)_3NHCH_3$, dimetn) and *N,N,N',N'*-tetramethylpropane-1,3-diamine ($(CH_3)_2N(CH_2)_3N(CH_3)_2$, tetrametn). Proton magnetic resonance spectroscopy has been used to study the kinetics of N-deuteration and inversion about nitrogen for some related complexes of platinum(II) with *N*-methylethylenediamines,[3–5] but as yet no information is available on rates of N-deuteration and inversion for complexes with six-membered chelate rings. Consequently, we have studied these reactions for the complex [Pt(dimetn)$(NH_3)_2$]Cl_2.

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(1) Address correspondence to this author.

(2) Part V: T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **11**, 117 (1972).

(3) P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, **90**, 2293 (1968).

(4) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **91**, 5227 (1969).

(5) L. E. Erickson, *ibid.*, **91**, 6284 (1969).

TABLE I

Compound	Pt, %		C, %		H, %		N, %		Cl, %	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
(dimetn)$(HCl)_2$			34.3	34.2	9.2	9.2	16.0	16.2		
(tetrameen)$(HCl)_2$			38.1	38.2	9.6	9.6	14.8	15.1		
(tetrametn)$(HCl)_2$			41.4	41.5	9.9	9.9	13.8	13.3		
Pt(dimetn)Cl_2	53.0	52.8	16.3	16.2	3.8	3.8	7.6	7.7	19.3	19.4
Pt(tetrameen)Cl_2			18.9	18.7	4.2	4.2	7.3	7.5	18.6	18.9
Pt(tetrametn)Cl_2	49.2	49.3	21.2	21.2	4.6	4.5	7.1	6.9	17.9	18.2
[Pt(dimetn)$(NH_3)_2$]$Cl_2 \cdot H_2O$	46.4	46.3	14.3	14.4	5.3	5.3	13.3	13.4		
[Pt(dimetn)$(NH_3)_2$][$PtCl_4$]$\cdot H_2O$	56.9	57.2	8.8	8.8	3.2	3.1	8.2	8.2	20.7	20.7
[Pt(tetrameen)$(NH_3)_2$]$(ClO_4)_2$			13.2	14.1	4.1	4.2	10.3	10.1	13.0	13.2
[Pt(tetrameen)$(NH_3)_2$][$PtCl_4$]$\cdot H_2O$	55.7	56.3	10.3	10.3	3.5	3.4	8.0	8.3	20.2	19.7
[Pt(tetrametn)$(NH_3)_2$][$PtCl_4$]$\cdot H_2O$			11.8	11.4	3.7	3.3	7.9	7.9		

TABLE II

PROTON MAGNETIC RESONANCE SPECTRA

Compound	τ'_{CH_3}	$J_{Pt-N-CH_3}$, Hz	τ'-CH_2-		$J_{Pt-N-CH_2-}$, Hz	$J_{CH_2-CH_2}$, Hz	J_{NH-CH_3}, Hz
			Outer	Inner			
(tetrameen)$(HCl)_2$	6.99	...	6.33	...	...	...	...
[Pt(tetrameen)$(NH_3)_2$]$(ClO_4)_2$	7.10	33.5	7.09	...	27.0	...	...
(dimetn)$(HCl)_2$	7.24	...	6.82	7.87	...	7.5	0
[Pt(*meso*-dimetn)$(NH_3)_2$]Cl_2	7.28	36.5	7.1[a]	8.04	*a*	*a*	6.0
[Pt($\pm$dimetn)$(NH_3)_2$]Cl_2	7.43	38.5	7.1[a]	8.04	*a*	*a*	6.0
(tetrametn)$(HCl)_2$	7.05	...	6.72	7.79	...	7.5	...
[Pt(tetrametn)$(NH_3)_2$]Cl_2	7.19	32.3	7.13	7.98	30	5.0	...

[a] Not clearly resolved.

Although several platinum[6,7] and palladium[6,8,9] complexes of *N,N,N′,N′*-tetramethylethylenediamine ($(CH_3)_2N(CH_2)_2N(CH_3)_2$, tetrameen) have been prepared, as yet pmr spectra have not been reported. Consequently, some complexes of this ligand have been included in this paper.

Experimental Section

Diamines and Dihydrochlorides.—dimetn was obtained from Koch-Light, tetrametn from Fluka, and tetrameen from BDH. All were used without further purification. Dihydrochlorides were prepared in the usual way.[10] Analyses are listed in Table I.

Dichloro(diamine)platinum(II) Complexes, Pt(diamine)Cl_2.—Pt(dimetn)Cl_2 was prepared by the general method for complexes Pt(diamine)Cl_2.[10] Free dimetn (1.3 mol) was added to 1 mol of K_2PtCl_4 in the minimum volume of water. Care was required in this reaction, since warming of the mixture was necessary for the reaction to occur, but excess heating caused ready decomposition. Characteristically, the reaction mixture turned dark brown rather suddenly after heating on a steam bath for a few minutes. Warming was immediately discontinued and the solution acidified with HCl. The complex was obtained as very pale yellow microcrystals which were filtered off, washed with cold water and then acetone, and air-dried. Typical yield was 54%. The infrared spectrum of this complex shows no bands near 1600 cm^{-1} (characteristic of $-NH_2$ deformation). There is a single sharp N–H stretching band at 3205 cm^{-1}.

Pt(tetrameen)Cl_2 was obtained as a yellow powder by the method of Mann and Watson,[6] by addition of excess free diamine to a solution of H_2PtCl_6.

Since attempts to prepare Pt(tetrametn)Cl_2 from K_2PtCl_4 gave metallic platinum as the major product, this complex was prepared by an adaptation of the method used for Pt(tetrameen)Cl_2. To a quantity of H_2PtCl_6 solution (10 ml) prepared from 0.4 g of Pt was slowly added a twofold excess of free tetrametn. An orange solid (probably [tetrametn H_2][$PtCl_6$]) was initially formed, then redissolved as the mixture was stirred and warmed to give an orange-yellow solution. Little further reaction seemed to occur on standing on a steam bath (under these conditions with tetrameen, Pt(tetrameen)Cl_2 formed readily). A small volume of ethanol (~5 ml) was added to aid reduction. Warming was continued for 24 hr, small quantities of ethanol (~5 ml) and free ligand (~0.5 ml) being added from time to time. A yellow solid was obtained, suspended in a pale yellow solution. After cooling, the precipitate was filtered off, washed well with cold water and then acetone, and air-dried (yield 62% based on Pt). This complex could be recrystallized from a large volume of boiling water, but prolonged boiling caused deposition of Pt metal. The corresponding palladium complex has been reported.[9] Pt(tetrameen)Cl_2 and Pt(tetrametn)Cl_2 showed no infrared bands attributable to N–H groups.

Analytical results for these complexes are listed in Table I.

Bis(ammine)(diamine)platinum(II) Complexes.—The chloride salts, [Pt(diamine)$(NH_3)_2$]Cl_2, were prepared in the usual way.[10] The dimetn complex, when precipitated from concentrated aqueous solution by excess acetone, was obtained as a well-defined monohydrate, [Pt(dimetn)$(NH_3)_2$]$Cl_2 \cdot H_2O$, either as a white powder or fine colorless plates. A typical yield was 84% based on Pt(dimetn)Cl_2. However, as often occurs for complexes of this type,[2,10] the corresponding complexes of tetrameen and tetrametn could not be easily characterized in the solid state, being hygroscopic and tending to partially decompose to Pt(diamine)Cl_2. However, pmr spectra of D_2O solutions of these salts are consistent with the presence of Pt(diamine)$(NH_3)_2^{2+}$ as the only cation in solution, and tetrachloroplatinate salts obtained by addition of K_2PtCl_4 solution to aqueous solutions of [Pt(diamine)$(NH_3)_2$]Cl_2 were completely characterized. Infrared spectra and analytical results (Table I) indicated that water of crystallization was present in these salts. [Pt(dimetn)$(NH_3)_2$][$PtCl_4$]$\cdot H_2O$ was violet-pink, while the tetrameen and tetrametn complexes were pink.

The perchlorate salt, [Pt(tetrameen)$(NH_3)_2$]$(ClO_4)_2$, was prepared from Pt(tetrameen)Cl_2 by the usual method[10] (yield 42%). Corresponding complexes of dimetn and tetrametn were difficult to obtain pure.

Instrumentation and Experimental Methods.—pH measurements were made on a PYE pH meter and are reliable to ±0.1 pH unit. These measurements were carried out at 25°. The slightly warmer temperature of the nmr probe (30°) would have a small effect on the pH of the solution. Other instrumentation was described in previous papers.

Chemical shifts are reported on a τ' scale (relative to DSS, 2,2-dimethyl-2-silapentane-5-sulfonate) using *tert*-butyl alcohol (τ' = 8.77) as internal standard.

Unless otherwise stated, solutions used for nmr studies contained approximately 0.05 g in 0.5 ml of solvent. However, the spectra did not show marked concentration dependence.

Results

Pmr Spectra of Diamine Dihydrochlorides.—The spectrum of (tetrameen)$(HCl)_2$ in D_2O consists of two sharp singlets corresponding to the methylene protons (4) and the methyl protons (12) (Table II).

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(6) F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 2722 (1958).

(7) A. J. Poe and D. H. Vaughan, *J. Amer. Chem. Soc.*, **92**, 7537 (1970).

(8) D. W. Meek, *Inorg. Chem.*, **4**, 250 (1965).

(9) D. A. Baldwin and G. J. Leigh, *J. Chem. Soc., A*, 1431 (1968).

(10) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **9**, 1800 (1970).

The spectra of (dimetn)(HCl)$_2$ and (tetrametn)(HCl)$_2$ are similar. Each consists of a sharp methyl singlet superimposed on a pattern from the methylene groups (Figure 1a shows the spectrum of (tetrametn)(HCl)$_2$).

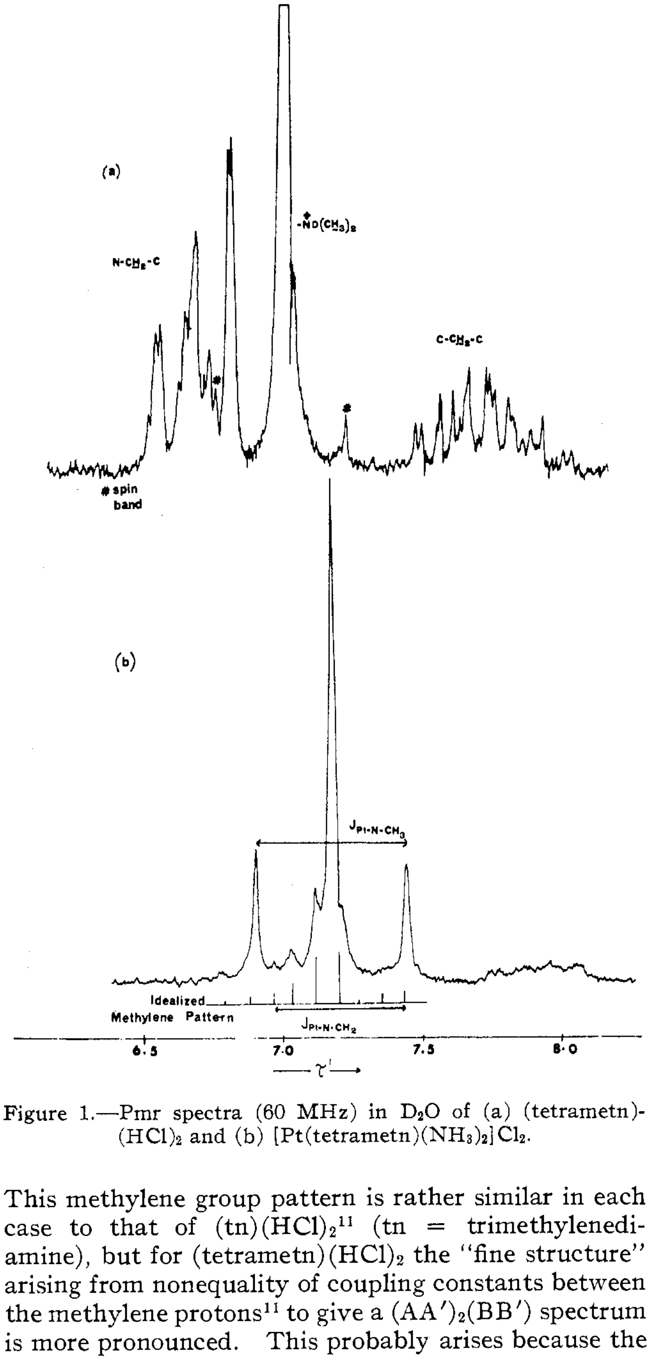
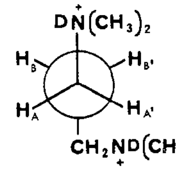


Figure 1.—Pmr spectra (60 MHz) in D$_2$O of (a) (tetrametn)(HCl)$_2$ and (b) [Pt(tetrametn)(NH$_3$)$_2$]Cl$_2$.

This methylene group pattern is rather similar in each case to that of (tn)(HCl)$_2$[11] (tn = trimethylenediamine), but for (tetrametn)(HCl)$_2$ the "fine structure" arising from nonequality of coupling constants between the methylene protons[11] to give a (AA′)$_2$(BB′) spectrum is more pronounced. This probably arises because the preference for the particular rotamer is greater than the preference for the corresponding rotamer of (tn)(HCl)$_2$. (dimetn)(HCl)$_2$ can exist in two geometric isomers, meso and racemic. One isomer can be converted into the other by inversion about one of the nitrogen atoms. The presence of only one methyl peak in the spectrum of (dimetn)(HCl)$_2$ indicates that this inversion is rapid. Since proton exchange in diamine dihydrochlorides is very rapid,[11] this is not unexpected. Details of the spectra are given in Table II.



Pmr Spectra of Pt(tetrameen)(NH$_3$)$_2$$^{2+}$ and Pt(tetrametn)(NH$_3$)$_2$$^{2+}$.—The spectrum of [Pt(tetrameen)(NH$_3$)$_2$](ClO$_4$)$_2$ in D$_2$O consists of two sharp peaks (almost coincident) with "satellites" from coupling with ^{195}Pt ($I = {}^1/_2$, 34% abundance). The relative intensities of the two peaks enable the assignments in Table II to be made. This spectrum indicates that, as for other platinum–diamine complexes,[11] conformational inversion of the chelate ring is rapid. The spectrum in (CD$_3$)$_2$C=O at room temperature is similar to that in D$_2$O, but below −50° the usual broadening[11] occurs.

The spectrum of [Pt(tetrametn)(NH$_3$)$_2$]Cl$_2$ in D$_2$O is reproduced in Figure 1b, and details are given in Table II. A sharp peak (corresponding to the *N*-methyl groups) and its "satellites" are superimposed on the characteristic pattern from the methylene groups. The pattern from the other methylene groups is partially obscured by the *N*-methyl resonance and its "satellites," but it is possible to assign the peaks of the expected "triplet" with its "satellites" to give the idealized pattern centered at τ′ 7.13, shown in Figure 1b. The inner methylene group gives a complex, comparatively weak pattern centered at τ′ 7.98. The spectrum is consistent with rapid conformational interconversion, probably between two equivalent chair-type conformations.

Pmr Spectra of Pt(dimetn) (NH$_3$)$_2$$^{2+}$.—This complex can exist in two distinct geometrical isomers, meso and racemic, illustrated (in the conformations probably preferred) in Figure 2. The spectrum of N-deuterated [Pt(dimetn)(NH$_3$)$_2$]Cl$_2$ in D$_2$O is illustrated in Figure 3. There are two sharp *N*-methyl peaks (intensity ratio 2.8:1), each with "satellites," superimposed on a complex pattern from the methylene groups (an (AB)$_2$-CD pattern for the meso isomer and (AA′)$_2$CC′ from the racemic isomer, with additional peaks from coupling with ^{195}Pt). The spectrum does not change appreciably over a period of several weeks. The kinetic data discussed later suggest that the equilibrium Pt(*meso*-dimetn)(NH$_3$)$_2$$^{2+}$ ⇌ Pt(racemic dimetn)(NH$_3$)$_2$$^{2+}$ would be established after this time. Thus the system is already in equilibrium shortly after dissolution. It is not possible from the spectrum to assign the methyl peaks to particular isomers. However, provided that the other ligands attached to the Pt atom are not sufficiently bulky to interact sterically with an equatorial *N*-methyl group (*e.g.*, NH$_3$),[12] it would be expected that an equatorial *N*-methyl group would be

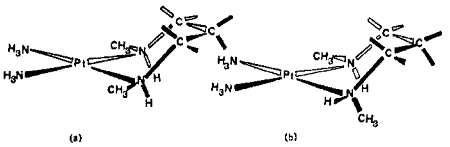


Figure 2.—Geometric isomers of Pt(dimetn) (NH$_3$)$_2$$^{2+}$: (a) meso, (b) racemic.

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[11] T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **9**, 1807 (1970).

[12] This condition may not apply to a ligand such as 2,2′-bipyridine, which is relatively bulky in the "equatorial" plane of the complex.

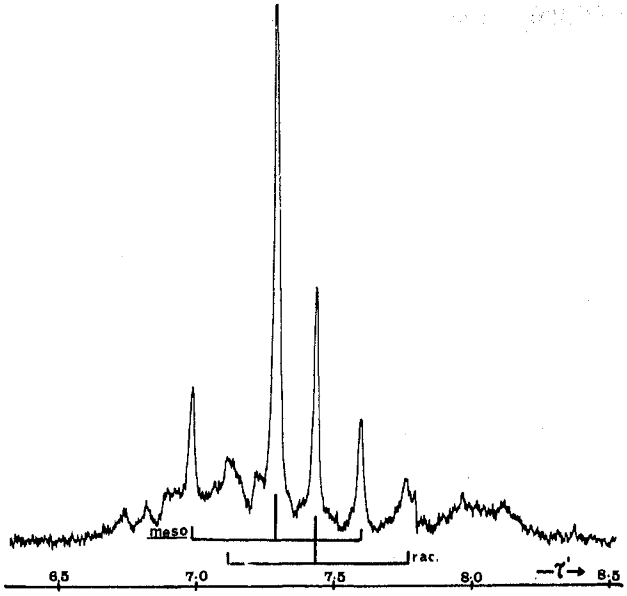

Figure 3.—Pmr spectrum (60 MHz) of N-deuterated [Pt(dimetn)$(NH_3)_2$]Cl_2 in D_2O.

preferred to an axial group. The meso isomer can exist in a chair-type conformation with both methyl groups equatorial, which would be preferred much more than the alternative chair conformation with both methyl groups axial. It would be expected that, at equilibrium, the isomer with both methyl groups capable of being equatorial (meso) would be preferred to the racemic isomer for which the ring conformation will be either a chair-type conformation in which one methyl group is axial at any instant or (less likely) a skew-boat conformation (the conformational possibilities are similar to those for the corresponding isomers of pentane-2,4-diamine[11,13]). Thus, the stronger (downfield) methyl peak has been assigned to the meso isomer, and the concentration of meso isomer is 2.8 times that of the racemic isomer. This fairly marked preference for a particular isomer contrasts with the behavior of the corresponding complex of *N*,*N'*-dimethylethylenediamine (dimeen), where meso and racemic isomers are present in almost equal proportions,[3] perhaps reflecting the fact that N substituents on five-membered chelate rings approximate to "axial" and "equatorial" less closely than for six-membered rings.

The spectrum of the undeuterated complex in H_2O is reproduced in Figure 4a. The methyl peaks and their "satellites" are now split by the N–H atoms (J_{NH-CH_3} = 6.0 Hz in each case). The spectrum in ~8 *N* DCl is rather similar, except that the methyl resonances have shifted slightly upfield, the meso signal (τ' 7.28 → 7.32) more so than the signal from the racemic isomer (τ' 7.43 → 7.44). The two resonances are thus closer together than in neutral solution, and the high-field peak of the meso doublet overlaps the low-field peak of the racemic doublet. In the DCl solution a broad band from the amine protons is centered at τ' 6.02. Since inversion about the N atoms would be very slow in concentrated acid, the observation of equilibrium proportions of the two isomers indicates that they exist in these proportions in the solid state. This is not surprising, since during preparation the complex is in a basic (ammoniacal) solution where inversion would be fast.

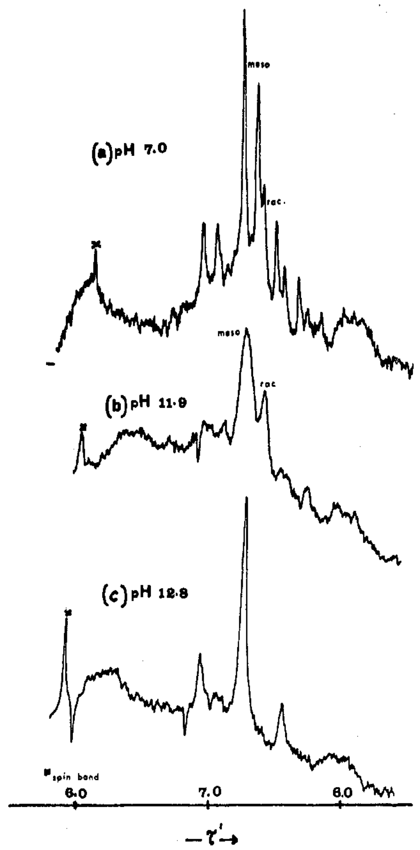

Figure 4.—Dependence of the 60-MHz pmr spectrum of [Pt(dimetn)$(NH_3)_2$]Cl_2 in H_2O on pH of the solution.

Rates of N-Deuteration of [Pt(dimetn)$(NH_3)_2$]Cl_2 in Neutral D_2O.—When the spectrum of this complex in D_2O was run immediately after dissolution, the spectrum was similar to that of the complex in H_2O (Figure 4a), with the signals from the *N*-methyl groups split into doublets. After a few minutes, the sharp peaks corresponding to $-ND-CH_3$ were present in the centers of these doublets (Figure 5). After 2 hr the spectrum corresponded to that of the completely deuterated complex (Figure 3). If h_1 and h_3 are the heights of the low-field and high-field peaks, respectively, of the meso doublet, and h_2 is the height of the central singlet (Figure 5)

$$h_1 + h_3 \propto [\text{undeuterated species}]$$
$$h_2 \propto [\text{deuterated species}]$$

Thus

$$\frac{h_1 + h_2 + h_3}{h_1 + h_3} = \frac{\text{total concentration}}{[\text{undeuterated species}]}$$

and

$$\log\left[\frac{h_1 + h_2 + h_3}{h_1 + h_3}\right] = (k/2.303)t \qquad (1)$$

where k is the rate constant for N-deuteration (assumed first order) and t is time in seconds since dissolution. Thus a plot of log $(h_1 + h_2 + h_3)/(h_1 + h_3)$ against t should be linear, with slope k/2.303. This method has the advantage over using the change in a single peak

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(13) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **10**, 1717 (1971).

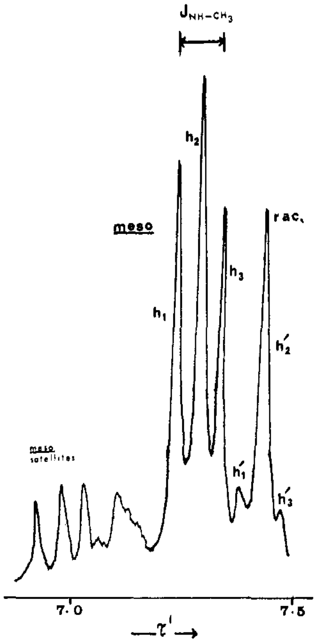

Figure 5.—Pmr spectrum of partially N-deuterated [Pt(dimetn)$(NH_3)_2]Cl_2$ in D_2O: h_i = heights of peaks of meso isomer; h_i' = heights of peaks of racemic iosmer.

height, or a difference between peak heights, that any change in spectrometer tuning during the experiment should not affect a ratio of peak heights. Similarly, the heights of the peaks from the racemic isomer (h') were used to determine this rate constant. There was an experimental difficulty in the measurement of peak heights since methyl peaks are superimposed on the complex methylene group spectrum, and it was not always clear where the "base line" for peak height measurements should be. This uncertainty is probably the reason why the plots do not quite pass through the origin (Figure 6) and may affect the accuracy of the rate constants found. However, the plots are linear, and the rate constants should be at least of the right order. For solutions of 0.1 g of [Pt(dimetn)$(NH_3)_2]Cl_2 \cdot H_2O$ in 0.5 ml of D_2O (measured pD 7.0), at 30°, $k_{\text{meso}} = 4.9 \times 10^{-4}$ sec^{-1} and $k_{\text{rac}} = 11.7 \times 10^{-4}$ sec^{-1}. The usual form of the rate constant (where there are no anions except OH^- or OD^- which catalyze the exchange) is

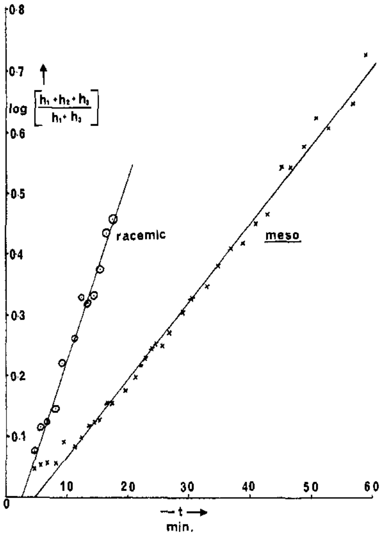

Figure 6.—First-order rate plots for N-deuteration of [Pt(dimetn)$(NH_3)_2]Cl_2$ in D_2O.

$$k_{\text{obsd}} = k_{D_2O} + k_{OD} - [OD^-] \qquad (2)^4$$

where $k_{D_2O} \ll k_{OD^-}$. Ignoring k_{D_2O}, $k_{OD^-(\text{meso})} = 4.9 \times 10^3$ l. M^{-1} sec^{-1} and $k_{OD^-(\text{rac})} = 11.7 \times 10^3$ l. M^{-1} sec^{-1}.

Effect of pH on the Spectrum of [Pt(dimetn)$(NH_3)_2]Cl_2$ in H_2O.—Rates of N–H exchange and inversion about N atoms increase as the concentration of OH^- increases. For *N*-methyldiamine complexes of platinum, these processes become rapid on the nmr time scale at high pH. Haake and Turley[3] studied the effect of increasing pH on the spectrum of [Pt(dimeen)$(NH_3)_2]Cl_2$ in H_2O. At pH 10.5 their methyl signals, originally doublets (J_{NH-CH_3} = 5.9 Hz), became singlets (rapid exchange of N–H atoms) and at pH 10.8 the signals from the two isomers coalesced (originally separated by 2.2 Hz—rapid inversion about N atoms).

We have carried out analogous studies with the dimetn complex. The spectrum of the solution obtained by dissolving 0.355 g of complex in 3 ml of H_2O (pH 7.0) is reproduced in Figure 4a. The pH was then increased by addition of sodium hydroxide solution. By pH 11.5 the peaks of the two doublets had begun to broaden. At pH 11.7 the signal from the racemic isomer had coalesced to a broad singlet, and at pH 11.9 both methyl peaks were broad singlets (Figure 4b). At pH 12.2 the meso peak had sharpened considerably and the racemic signal remained well separated from it. At pH 12.5 the peak from the racemic isomer had broadened, and by pH 12.8 the two peaks had completely coalesced (Figure 4c). When the pH was increased still further to 13.1 the peak sharpened considerably. The value of $J_{Pt-N-CH_3}$ at this pH was 36.5 Hz.

For two species A and B, which are present in equal concentrations and undergoing exchange, the rate constant for the exchange process at coalescence is given by

$$k = \pi \Delta\nu_{AB}/\sqrt{2} \qquad (3)^{14}$$

For the coalescence of the methyl doublets, this equation becomes

$$k = \pi(J_{NH-CH_3})/\sqrt{2} = 13.3 \text{ sec}^{-1}$$

Taking pH 11.6 and 11.9 for coalescence of racemic and meso doublets, respectively, and K_w = 13.8 30°, $k_{OH^-(\text{meso})} = 1.1 \times 10^4$ l. M^{-1} sec^{-1} and $k_{OH^-(\text{rac})} = 2.1 \times 10^4$ l. M^{-1} sec^{-1}. These values are greater by a factor of 2 than those obtained for k_{OD^-} earlier. However, no attempt has been made to keep conditions such as concentration and ionic strength constant. As well, there could be a significant isotope effect.

The coalescence for the inversion process takes place about one pH unit above that required for exchange. The fact that one isomer is present in greater proportion than the other prevents an accurate estimate of the rate constant for inversion. The results suggest a retention ratio (*i.e.*, the ratio of the second-order rate constants for exchange and inversion) between 10 and

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[14] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 223.

30. This is greater than that reported by Haake and Turley[3] for $Pt(dimeen)(NH_3)_2^{2+}$, but rather less than values reported for *N*-methylethylenediamines by Buckingham, *et al.*,[4] and Erickson.[5] However, as pointed out by Buckingham, *et al.*,[4] values of the inversion rates and retention ratios obtained by this method could easily be in error (especially in this case where there is a considerable increase in the concentration of NaOH to change the pH from 11.9 to 12.8).

Discussion

Rates of N-Deuteration.—The rate of N-deuteration for the racemic isomer of $Pt(dimetn)(NH_3)_2^{2+}$ is almost twice that for the meso isomer. This can be rationalized if it is assumed that in a six-membered ring an axial proton attached to a N atom which also carries an equatorial methyl group is somewhat shielded from the attack by an hydroxide ion which initiates the exchange. The equatorial methyl group and the axial H atom on the central carbon atom would be chiefly responsible for this steric hindrance. For the meso isomer, both amino protons would be in this sheltered axial orientation in the preferred conformation. For the racemic isomer, both chair conformations are equivalent and each amino proton would spend 50% of its time in the less sheltered equatorial orientation, where attack by OH^- can occur more readily. For five-membered chelate rings, the substituents on the N atoms are rather less decisively "axial" or "equatorial" in character than their counterparts in six-membered (chair) chelate rings, and "axial" amino protons do not appear to be protected from the attack appreciably more than "equatorial" protons. Thus, there appears to be little difference in rates of N-deuteration between the isomers of $Pt(dimeen)(NH_3)_2^{2+}$, and the exchange rate is greater than for the dimetn complexes.[3]

Platinum-Proton Coupling Constants.—Erickson[5] pointed out that the Pt–N bond strength was considerably reduced when the N atom carried two methyl groups (*e.g.*, such bonds could be broken in concentrated KOH solution). This was reflected in low values of $J_{Pt-N-CH_2-}$ and $J_{Pt-N-CH_3}$ compared with complexes of less substituted diamines. A similar effect is observed for $J_{Pt-N-CH_2-}$ of $Pt(tetrameen)(NH_3)_2^{2+}$ and $Pt(tetrametn)(NH_3)_2^{2+}$. The values of $J_{Pt-N-CH_2-}$ for these complexes (27 and 30 Hz, respectively) are much lower than for the corresponding ethylenediamine (41.5 Hz) and trimethylenediamine (43.0 Hz) complexes.[11] The exact orientations of the methylene protons in the preferred conformations may also have some effect on the coupling constants.[13] The values of $J_{Pt-N-CH_3}$ for these complexes (33.5 and 32.3 Hz for tetrameen and tetrametn complexes, respectively) are also low compared with the corresponding complexes of dimeen (39.9, 39.2 Hz) and dimetn (meso 36.5 Hz, racemic 38.5 Hz).

If $J_{Pt-N-CH_3}$ in the isomers of $Pt(dimetn)(NH_3)_2^{2+}$ is governed by the orientation of the *N*-methyl groups in the preferred conformation, then the coupling constant in the meso isomer represents the coupling to an equatorial *N*-methyl group, while the coupling in the racemic isomer will be the average of the couplings to axial and equatorial *N*-methyl groups. This leads to the conclusion that $J_{Pt-N-CH_3(ax)}$ is greater than $J_{Pt-N-CH_3(eq)}$ by 4 Hz. The comparatively small difference in coupling constants for the isomers of $Pt(dimeen)(NH_3)_2^{2+}$ again probably illustrates the less distinct "axial" and "equatorial" nature of N substituents in five-membered chelate rings.

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Effect of Basicity of Nonreacting Ligands on the Rate of Reaction of Dithiooxamide with Dichloro(phenanthroline)platinum(II) Derivatives

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An examination has been made of the kinetics of the displacement by dithiooxamide (DTOA) of chloride from $Pt(phenX)Cl_2$ to give $[Pt(phenX)(DTOA)]Cl_2$ (phenX is one of a series of ten substituted phenanthroline ligands). The reaction is carried out in nitromethane solution at 25° and is followed by conductivity. The displacement of the first chloride is rate determining, and the rate law is of the usual form, rate $= k_1[\text{complex}] + k_2[\text{complex}][\text{entering ligand}]$. First-order rate constants are small and without apparent pattern. There is a linear free energy relation between the second-order rate constant and the basicity of the phenanthroline, complexes with the least basic phenanthrolines reacting most rapidly. The most reactive complexes are found to have the strongest bonds to the leaving groups. These results are taken to indicate: (1) that the activation energy is expended on making the bond to the incoming nucleophile; (2) that decreasing the basicity of phenanthroline increases the electrophilicity of platinum through σ bonding; (3) the σ-bonding effect is the same whether it operates cis or trans to the leaving group.

In the extensively studied substitution reactions of square-planar complexes, the ligand trans to the leaving group has received the bulk of the attention.[1,2] Its ability to promote substitution is considered to have two aspects, one arising from its σ bonding ability and the other arising from its π bonding ability. The σ trans effect is generally ascribed to a weakening of the bond to the leaving group. Strong σ bonding ligands in the trans position get a large share of the p character

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(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 351.

(2) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 18.