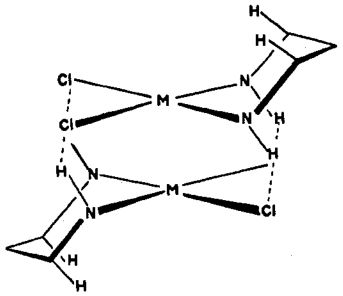

Figure 5.—Possible "molecular pair" in solid Pt(diamine)Cl_2.

Tetrachloroplatinate Salts.—In a previous paper,[2] colors of a number of tetrachloroplatinate salts, [Pt(diamine)$(NH_3)_2$][$PtCl_4$] and [Pt(diamine)$_2$][$PtCl_4$], were correlated with the probable ring conformations in the cations. Violet colors indicate some cation–anion electronic interaction; pink colors indicate the lack of such interaction.

The pink color of [Pt(tnOH)$(NH_3)_2$][$PtCl_4$] corresponds to little anion–cation interactions. The chelate ring in this complex probably takes up a chair conformation with the hydroxyl group axial (Figure 4), since such a conformation is preferred for Pt(tnOH)$(NH_3)_2{}^{2+}$ in solution (see following paper). The axial hydroxyl group would not sterically hinder close anion approach below the PtN_4 plane but, by H bonding to the axial amino protons, could hinder formation of N–H···Cl H bonds (probably an important factor when anion–cation proximity is favored).

Although the conformation of Pt(tnCl)$(NH_3)_2{}^{2+}$ in aqueous solution is analogous to that of the hydroxy compound, this cation gives a violet-pink tetrachloroplatinate. This may correspond to a mixture of two different crystal structures, one with close anion–cation approach and the other without, or to a weak perturbation of the anion in a single-crystal structure.

Of the two geometrical isomers of Pt(tnOH)$_2{}^{2+}$, the trans isomer (Figure 3) would not permit close anion approach, but this would be possible for the cis isomer. However, [Pt(tnOH)$_2$][$PtCl_4$], which probably contains almost equal quantities of the two isomers, is pink, indicating that close cation–anion approach actually occurs for neither. Analogous geometrical isomers exist for [Pt(tnCl)$_2$][$PtCl_4$], and this salt is also pink.

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Complexes with Six-Membered Chelate Rings. V. Nuclear Magnetic Resonance and Infrared Spectra of Some Complexes of 1,3-Diaminopropan-2-ol and 2-Chloropropane-1,3-diamine with Platinum and Palladium

BY T. G. APPLETON AND J. R. HALL*

Received March 1, 1971

Proton magnetic resonance spectra are reported for the compounds (diamine)$(HCl)_2$, Pt(diamine)$(NH_3)_2{}^{2+}$, [M(tnOH)$_2$]Cl_2, [Pt(tnCl)$_2$]Cl_2, and *trans*′-[Pt(tnOH)$(NH_3)_2Cl'_2$]Cl_2 in D_2O solutions. The spectra of the complexes are consistent with a preference for a chair-type conformation of the chelate ring with the chloro or hydroxy substituent axial. Such a conformation is probably stabilized by intramolecular hydrogen bonding. Some aspects of the infrared spectra of the complexes M(diamine)Cl_2, [M(diamine)$_2$][MCl_4], *trans*′-Pt(diamine)$Cl_2(OH')_2$, and Pt(diamine)Cl_4 are discussed. (M = Pt or Pd, diamine = 1,3-diaminopropan-2-ol, tnOH, or 2-chloropropane-1,3-diamine, tnCl.)

Introduction

X-Ray diffraction studies[1–3] and proton magnetic resonance spectra[4–6] of a number of complexes containing six-membered diamine chelate rings have shown that in many respects the conformational behavior of these rings is analogous to that of the corresponding cyclohexane derivatives. This paper discusses the conformational behavior and some aspects of infrared and pmr spectra of Pt(II), Pd(II), and Pt(IV) complexes of the diamines 1,3-diaminopropan-2-ol ($NH_2CH_2CHOHCH_2NH_2$, tnOH) and 2-chloropropane-1,3-diamine ($NH_2CH_2CHClCH_2NH_2$, tnCl). The chelate rings in these complexes are analogs of cyclohexanol and chlorocyclohexane, respectively.

Experimental Section

Preparation of complexes[7] and instrumentation[4,8] have been previously described. Nmr spectra were run on N-deuterated samples in D_2O at 60 MHz using *tert*-butyl alcohol as internal standard, unless otherwise stated. Variable-temperature spectra were run using a V-6040 attachment on the A-60. The 100-MHz spectra were recorded by Dr. S. R. Johns on a Varian HA-100 instrument. Solutions for nmr usually contained about 80 mg/ml. Spectra were not significantly concentration dependent. Chemical shift data are reported on a τ' scale (relative to DSS, 2,2-dimethyl-2-silapentane-5-sulfonate) using τ' 8.77 for *tert*-butyl alcohol in D_2O. N-Deuterated b-Pt(tnCl)Cl_2 was prepared by recrystallization of Pt(tnCl)Cl_2 from boiling D_2O.

Results

Proton Magnetic Resonance Spectra.—The pmr spectrum of (tnOH)$(HCl)_2$ at room temperature is

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(1) T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jap.*, **42**, 1016 (1969).

(2) A. Pajunen, *Suom. Kemistilehti B*, **41**, 232 (1968).

(3) A. Pajunen, *ibid.*, *B*, **42**, 15 (1969).

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

(5) T. G. Appleton and J. R. Hall, *ibid.*, **10**, 1717 (1971).

(6) W. J. Kasowski and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **91**, 3212 (1969).

(7) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **11**, 112 (1972).

(8) T. G. Appleton and J. R. Hall, *ibid.*, **9**, 1800 (1970).

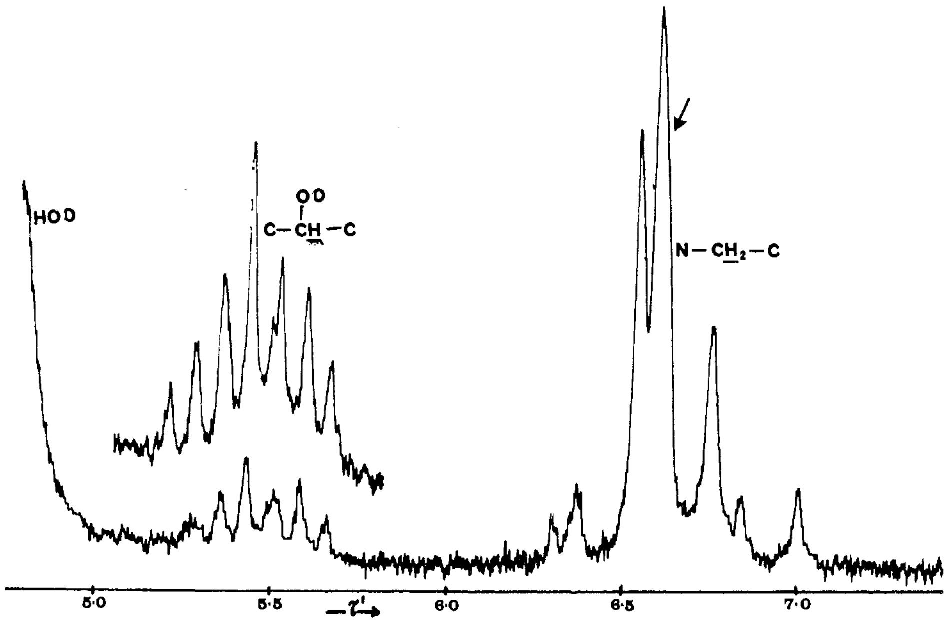

Figure 1.—The 60-MHz pmr spectrum of $(tnOH)(HCl)_2$ in D_2O at 30°.

reproduced in Figure 1. When the temperature is varied, the spectrum shows minor changes (the most noticeable being the splitting of a peak which is single at 30° (arrowed in Figure 1) into two peaks at higher temperatures). The spectrum approximates to $(AB)_2M$ (X is reserved for designating the ^{195}Pt nucleus in platinum complexes). Provided, as here, there is no discernible coupling between the two AB groups, the AB part of the spectrum is similar to that of the well-known ABX spectrum and may be easily analyzed by hand.[9] The only approximation involved is the assumption that H_M is shifted infinitely from H_AH_B. The coupling constants and chemical shifts obtained from this analysis are listed in Table I.

TABLE I

60-MHz PMR SPECTRA[a] OF $(tnOH)(HCl)_2$, $(tnCl)(HCl)_2$, AND $(tnBr)(HBr)_2$ IN D_2O

Compd	Temp, °C	τ'_M	τ'_A	τ'_B	Hz $\Delta\nu_{AB}$	$\lvert J_{AB}\rvert$	$\lvert J_{AM}\rvert$	$\lvert J_{BM}\rvert$
$(tnOH)(HCl)_2$	5	5.55	6.61	6.68	15.0	13.7	2.9	10.5
$(tnOH)(HCl)_2$	14	5.54	6.59	6.83	14.3	14.0	2.5	10.1
$(tnOH)(HCl)_2$	30	5.53	6.57	6.81	13.9	14.0	2.2	10.8
$(tnOH)(HCl)_2$	56	5.50	6.57	6.79	13.3	14.0	2.8	10.3
$(tnOH)(HCl)_2$	90	5.47	6.56	6.77	12.6	14.0	3.4	9.4
$(tnCl)(HCl)_2$	30	5.36	6.39	6.62	13.8	14.0	2.7	10.1
$(tnBr)(HBr)_2$	30	5.44	6.33	6.55	12.9	14.0	3.2	10.1

[a] Values accurate to ±0.5 Hz.

$(tnCl)(HCl)_2$ and $(tnBr)(HBr)_2$ in D_2O gave similar spectra (except that the H_M patterns were partly obscured by the HOD peaks) ($tnBr = NH_2CH_2CHBrCH_2NH_2$). Values obtained from these spectra are also listed in Table I. In all these compounds J_{AM} and J_{BM} have the same sign.

The spectrum of N- and O-deuterated $[Pt(tnOH)(NH_3)_2]Cl_2$ in D_2O is reproduced in Figure 2. The $>CH_M$–OD signal is a quintet (τ' 5.73) and the methylene protons give a central doublet (τ' 7.09) with "satellites" arising mainly from coupling of these protons with ^{195}Pt ($I = {}^1/_2$, 34% abundance). The methylene pattern is a superposition of the AB parts of an $(AB)_2M$ and an $(AB)_2MX$ pattern, where $X = {}^{195}Pt$. Little information can be gained from the $(AB)_2M$ pattern, essentially a "deceptively simple" doublet plus quintet. The peaks in each multiplet are separated by the average coupling, ${}^1/_2(\lvert J_{AM} + J_{BM}\rvert)$. However, as illustrated schematically in Figure 3, the $(AB)_2MX$ pattern could be analyzed to give values of $\lvert J_{AB}\rvert$, $\lvert J_{AM}\rvert$, $\lvert J_{AX}\rvert$, $\lvert J_{BX}\rvert$, and $\Delta\nu_{AB}$. $\lvert J_{BM}\rvert$ could not be obtained accurately from the "satellite" $(AB)_2MX$ pattern, but once J_{AM} was known its value could be obtained using the average coupling observed in the $(AB)_2M$ spectrum. These values are listed for various temperatures in Table II.

TABLE II

60-MHz PMR SPECTRA[a] OF SOME Pt^{II} AND Pt^{IV} COMPLEXES OF tnOH AND tnCl

Complex	Temp, °C	Hz $\lvert J_{AM}\rvert$	$\lvert J_{BM}\rvert$	$\lvert J_{AX}\rvert$	$\lvert J_{BX}\rvert$	$\lvert J_{AB}\rvert$	$\Delta\nu_{AB}$[b]
$[Pt(tnOH)(NH_3)_2]Cl_2$	20	5.2	0.8	66.4	22.1	13.0	1.4
$[Pt(tnOH)(NH_3)_2]Cl_2$	40	5.2	1.8	63.7	21.8	13.0	1.0
$[Pt(tnOH)(NH_3)_2]Cl_2$	90	5.3	2.2	61.2	23.8	12.8	0.0
$[Pt(tnOH)_2]Cl_2$	8	5.5	0.5	65.1	21.1	13.0	1.5
$[Pt(tnOH)_2]Cl_2$	16	5.3	1.5	63.9	21.6	12.8	0.9
$[Pt(tnOH)_2]Cl_2$	30	5.1	1.9	63.3	22.3	12.8	0.9
$[Pt(tnOH)_2]Cl_2$	59	4.7	2.3	61.3	24.3	12.5	0.5
$[Pt(tnOH)_2]Cl_2$	93	5.0	2.0	59.4	24.0	12.5	0.2
$[Pt(tnCl)(NH_3)_2](NO_3)_2$	30	5.0	2.6	65.2	18.2	13.5	5.4
$[Pt(tnOH)(NH_3)_2Cl_2]Cl_2$[d]	30	5.3	≤ 2[c]	46.2	9.6	13.5	−27.8

[a] All values accurate within ±0.5 Hz. [b] Positive when H_A is downfield from H_B. [c] Not resolved. [d] τ'_{H_M} 5.54, τ'_{H_A} 7.31, τ'_{H_B} 6.84.

The spectrum of $[Pt(tnOH)_2]Cl_2$ in D_2O at 30° is reproduced in Figure 2b. It is similar to that of $[Pt(tnOH)(NH_3)_2]Cl_2$, except that each peak of the central doublet is now split by 1.3 Hz. No splitting is resolved in the "satellites." This splitting may be explained in terms of two distinct overlapping $(AB)_2M$ patterns, differing only in the chemical shifts of H_A and H_B. At 100 MHz and 30° the splitting increases to 2.5 Hz. In this spectrum, the peaks in the $(AB)_2MX$ spectrum from H_A (outer "satellites") do not show appreciable splitting, but those from H_B are broadened. Thus it appears that the chemical shift differences in the

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[9] B. Gestblom and S. Rodmar, *Acta Chem. Scand.*, **18**, 1767 (1964).

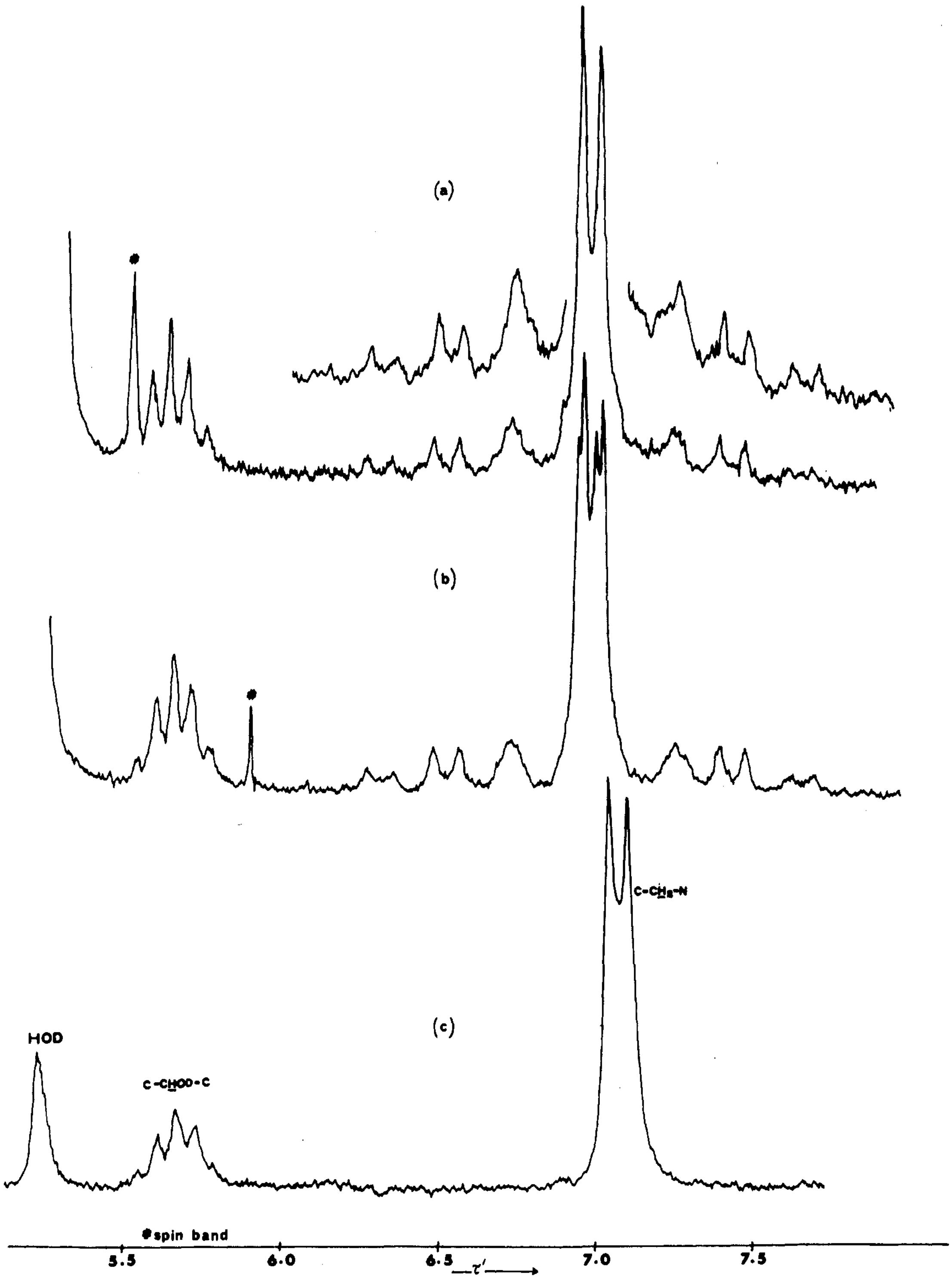


Figure 2.—The 60-MHz pmr spectra of tnOH complexes in D_2O at 30°: (a) $[Pt(tnOH)(NH_3)_2]Cl_2$; (b) $[Pt(tnOH)_2Cl_2$; (c) $[Pd(tnOH)_2]Cl_2$.

"doublets" of the two $(AB)_2M$ patterns are due chiefly to differing shifts of H_B. When the temperature is increased to 93° (at 60 MHz), the central AB signal simplifies to a doublet, and at lower temperatures the splitting increases (1.5 Hz at 16°, 2.0 Hz at 8°). Coupling constants obtained from analysis of the $(AB)_2MX$ "satellite" patterns are listed in Table II.

At 30° $[Pd(tnOH)_2]Cl_2$ gives a "simple" quintet–doublet spectrum (τ' 5.79 and 7.20; $^1/_2|J_{AM} + J_{BM}| =$ 3.5 Hz) (Figure 2c). When the temperature is increased, the doublet sharpens, and when it is lowered, it begins to broaden, but no distinct splitting is observed, as in the platinum complex.

The spectra of $[Pt(tnCl)_2]Cl_2$ and $[Pt(tnCl)(NH_3)_2](NO_3)_2$ in D_2O are essentially similar to that of $Pt(tnOH)(NH_3)_2^{2+}$. The $>CH$-Cl signal at τ' 5.3 is obscured by the residual HOD peak. The methylene protons give a doublet at τ' 6.88, with "satellites" from coupling with ^{195}Pt forming the AB part of an $(AB)_2MX$ spectrum. The parameters obtained from the spec-

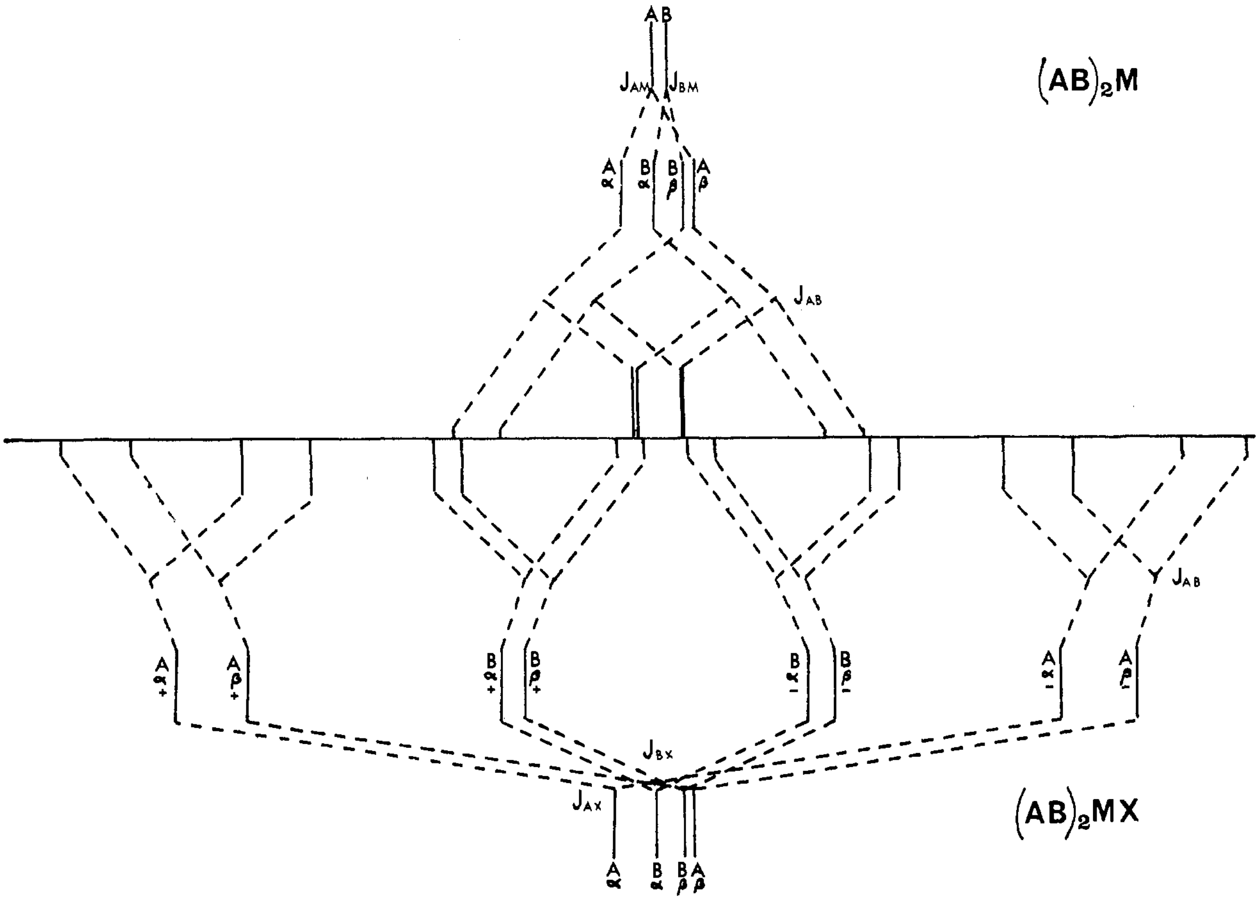


Figure 3.—AB part of $(AB)_2M$ + $(AB)_2MX$ pattern for $[Pt(tnOH)(NH_3)_2]Cl_2$ in D_2O at 40°. Total intensity of $(AB)_2M$ is twice that of $(AB)_2MX$. α, β spin states of M; +, − spin states of X.

trum of $[Pt(tnCl)(NH_3)_2](NO_3)_2$ are listed in Table II. At 60 MHz the spectrum of $[Pt(tnCl)_2]Cl_2$ was almost identical with that of the diammine complex, and no additional splitting of the central methylene doublet was observed.

The spectrum of *trans'*-$[Pt(tnOH)(NH_3)_2Cl'_2]Cl_2$ in D_2O is reproduced in Figure 4. Although quite different in appearance from the pattern obtained for Pt(II) complexes, the methylene pattern could be analyzed in terms of $(AB)_2M$ + $(AB)_2MX$ (Figure 5) to give the values listed in Table II. The main cause of the greater complexity of this spectrum is the much greater chemical shift difference between H_A and H_B (the usual convention of labeling the low-field proton "A" has not been followed for this complex to keep nomenclature consistent with the Pt(II) complexes).

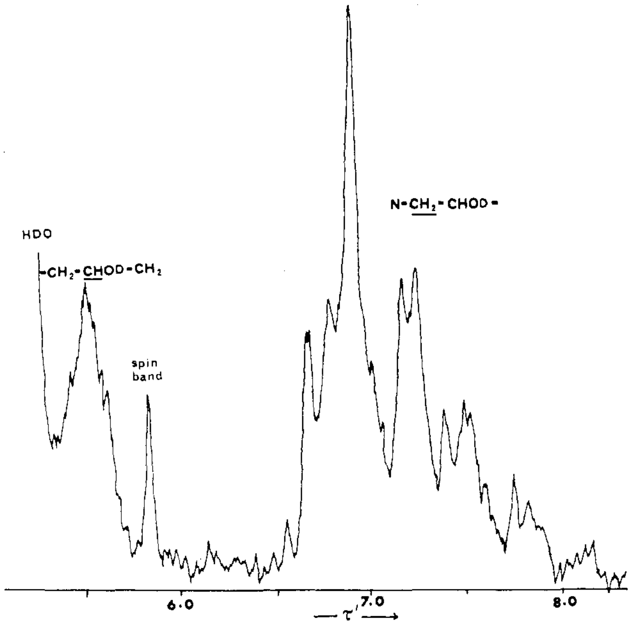


Figure 4.—The 60-MHz pmr spectrum of $[Pt(tnOH)(NH_3)_2Cl_2]Cl_2$ in D_2O.

Infrared Spectra.—Most of the general features of ir spectra of platinum and palladium complexes of substituted trimethylenediamines[8] are observed for complexes of tnOH and tnCl. However, complexes of these ligands give characteristic infrared bands. Complexes of tnOH show OH stretching peaks, listed in Table III for some typical complexes. Since none of

TABLE III

O–H STRETCHING FREQUENCIES OF tnOH COMPLEXES OF Pt(II), Pd(II), AND Pt(IV)

Complex	ν_{O-H}, cm^{-1}	Band type[b]
$Pt(tnOH)Cl_2$	3420	m sp
$Pd(tnOH)Cl_2$	3418	m sp
$[Pt(tnOH)_2][PtCl_4]$	3450	m sp
N- and O-deuterated $[Pt(tnOH)_2][PtCl_4]$	2560	m sp
$[Pd(tnOH)_2][PdCl_4]$	3445	m sp
$[Pt(tnOH)_2]Cl_2$	3340	b
$Pt(tnOH)Cl_4$	3555	v sp
trans'-$Pt(tnOH)Cl_2(OH')_2$	3550–3300	b[a]
trans-$[Pt(tnOH)_2Cl_2)Cl_2$	3500	v b

[a] Overlaps with band from PtOH. [b] Key: m, moderately; v, very; sp, sharp; b, broad.

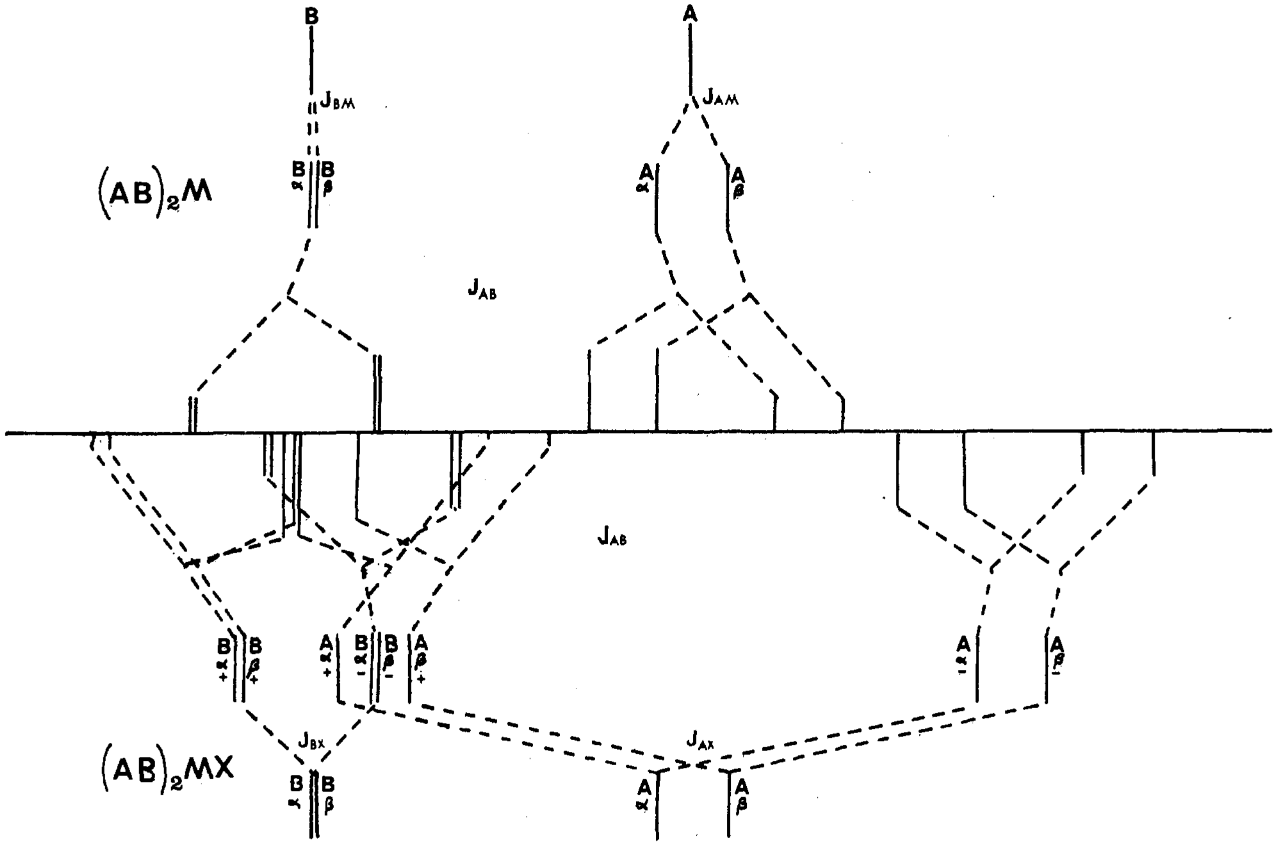


Figure 5.—AB part of $(AB)_2M$ + $(AB)_2MX$ pattern for $[Pt(tnOH)(NH_3)_2Cl_2]Cl_2$ at 30° in D_2O. Total intensity of the $(AB)_2M$ pattern is twice that of $(AB)_2MX$. α, β spin states of M; +, − spin states of X.

these complexes contained water of crystallization, assignment of ν_{O-H} was not difficult. Complexes of tnCl all show a characteristic sharp peak near 700 cm^{-1}. Some of these frequencies are listed in Table IV. The infrared spectra of the two forms of Pd(tnCl)Cl$_2$, a typical complex of tnCl, were reproduced in the preceding paper.

Table IV

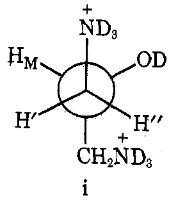
Frequencies of Characteristic Band (near 700 cm^{-1}) of tnCl Complexes with Pt(II), Pd(II), and Pt(IV)

Complex	Freq, cm^{-1} a form[a]		b form[a]
Pt(tnCl)Cl$_2$	710		690
Pt(tnCl)Cl$_2$ (N-deuterated)			615
Pd(tnCl)Cl$_2$	698		670
Pt(tnCl)Br$_2$	710		699
Pd(tnCl)Br$_2$		690	
[Pt(tnCl)$_2$][PtCl$_4$]		700	
Pt(tnCl)Cl$_4$		711	
Pt(tnCl)Cl$_2$(OH)$_2$		728	

[a] Where two forms exist.

Discussion

Proton Magnetic Resonance Spectra of Diamine Dihydrohalides.—The nonequivalence of the two protons in each methylene group of (tnOH)(HCl)$_2$ is not surprising, since in none of the rotamers can H′ be equivalent to H″. This nonequivalence is analogous to that observed for $(NH_2CH_2CH(CH_3)CH_2NH_2)(HCl)_2$.[4] From Table I, $J_{BM} \gg J_{AM}$. From the Karplus equation,[4,10] these values suggest a preferred rotamer for which $\phi_{BM} \simeq$ 180° and $\phi_{AM} \simeq 60°$ (where, in a fragment H_X–C–C–H_Y, ϕ_{XY} is the dihedral angle between the planes H_X–C–C and C–C–H_Y). Of the three possible rotamers iii is thus excluded. The spectrum does not allow a decision to be made between i with H′ = H_A and ii with H″ = H_A, but it would be expected that i would be preferred to ii, since in i the ND_3^+ group is trans to the bulky charged $CH_2ND_3^+$ group. The figures quoted in Table I are reliable only to ±0.5 Hz, but small trends with temperature are observed. J_{AB} is almost constant; $\Delta\nu_{AB}$ decreases with increasing temperature; J_{AM} is greatest and J_{BM} is least at higher temperatures. These changes are consistent with the expected decreasing preference for a particular rotamer with increasing temperature. There does seem to be some reversal in the trends in coupling constants at lower temperatures. If this effect is genuine, it may reflect small changes with temperature of the coupling constants within a particular rotamer.



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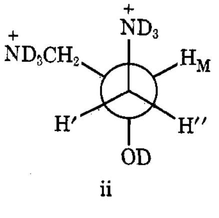

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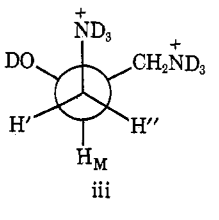

iii

The essential similarity of the spectra obtained for (tnCl)(HCl)$_2$ and (tnBr)(HBr)$_2$ indicate that the preferred rotamer is similar to that of (tnOH)(HCl)$_2$.

Pmr Spectra of Complexes.—Possible conformations of the chelate ring in the complex $[Pt(tnOH)(NH_3)_2]Cl_2$ are depicted in Figure 6. Using the Karplus equation for proton–proton couplings and an analogous angular dependence for Pt–N–C–H couplings,[5,11] some fea-

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(10) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(11) L. E. Erickson, J. W. McDonald, J. E. Howie, and R. P. Clow, *J. Amer. Chem. Soc.*, **90**, 6371 (1968).

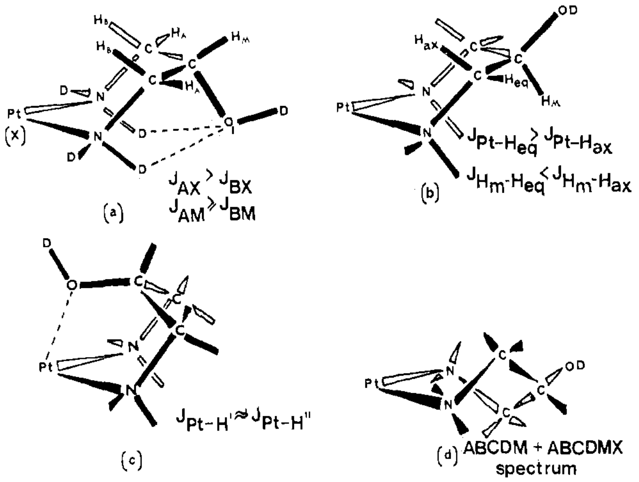


Figure 6.—Possible conformations of the tnOH chelate ring.

tures of the pmr spectra which would be expected from each conformational type can be predicted. These predictions are included in Figure 6 and arise from the following argument.

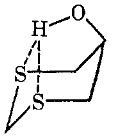
If a chair-type conformation with the hydroxyl group axial (Figure 6a) is preferred (with nomenclature as in the figure), H_A is equatorial, with $\phi_{AX} \simeq 180°$, and H_B is axial, with $\phi_{BX} \simeq 60°$. With Karplus-type angular dependence of the platinum–proton coupling constants, J_{AX} would be expected to be considerably greater than J_{BX}. Also, for this conformation, $\phi_{AM} \leqslant \phi_{BM} < 90°$, so that both J_{AM} and J_{BM} would be expected to be small, with J_{AM} greater than J_{BM}. As can be seen from Table II, this order of coupling constants is actually observed.

If the chair-type conformation with the hydroxyl group equatorial (Figure 6b) were preferred, then it would be expected that $J_{Pt-H_{eq}} > J_{Pt-H_{ax}}$ and that $J_{H_{eq}-H_M} < J_{H_{ax}-H_M}$; *i.e.*, the methylene proton with the greater coupling to Pt would have the lesser coupling to H_M. This is not the observed order of coupling constants.

It is conceivable that a boat-type conformation, stabilized by a weak interaction between the metal ion and the hydroxyl group, might be preferred (Figure 6c). However, for this conformation there is comparatively little difference between the platinum–proton dihedral angles, and little difference in platinum–proton coupling constants would be expected.

There are two equivalent skew-boat conformations possible, one of which is illustrated in Figure 6d. If this type of conformation were preferred, these two equivalent conformations would be expected to be in rapid equilibrium, and little difference would be seen in the platinum–proton coupling constants. If a skew-boat conformation were preferred without such rapid interconversion, the two methylene groups would no longer be related by symmetry, and a more complicated spectrum than that observed would be expected.

Thus the chelate ring conformation may be unambiguously assigned to that shown in Figure 6a. The preference for this conformation probably arises from intramolecular hydrogen bonding between the hydroxy group and the axial amine hydrogen atoms. Although the hydroxy group prefers the equatorial orientation in cyclohexanol,[12] intramolecular H bonding causes the axial conformer to be preferred in some heterocyclic compounds, *e.g.*[13]



Some distinct changes occur in the various coupling constants with temperature (Table II). With increasing temperature (i) J_{AX} decreases, (ii) J_{BX} increases, (iii) J_{BM} increases, (iv) J_{AM} remains almost constant, (v) J_{AB} decreases slightly, and (vi) $\Delta\nu_{AB}$ decreases. These changes are consistent with a decreasing preference for the axial conformer as the temperature increases. The couplings with ^{195}Pt (X) change toward the average value for axial and equatorial protons (~40 Hz[5]), and thus J_{AX} decreases and J_{BX} increases. The proton–proton coupling constants will change toward the average value for interconverting equivalent chair conformations (5.5 Hz for trimethylenediamine complexes[4]). Thus J_{BM} increases toward this value, and J_{AM}, already close to it, changes little. The chemical shift differences between the methylene protons is at least partially dependent on the existence of a preferred conformation, and as the preference decreases, $\Delta\nu_{AB}$ also decreases. The value of J_{AX} at lower temperatures is comparable to that previously predicted for platinum coupling to an equatorial proton, 65 Hz,[5] but J_{BX} is somewhat higher than the platinum–axial proton coupling, 15 Hz, observed with [Pt(*meso*-dptn)$_2$]Cl$_2$ (dptn = pentane-2,4-diamine, $NH_2CHCH_3CH_2CHCH_3NH_2$).[5] An accurate estimate of the degree of conformational preference cannot be made from these figures, but at 20°, at least 80–90% of the chelate rings would be in the axial conformation at any instant.

The extra splittings observed in the spectra of [Pt(tnOH)$_2$]Cl$_2$ are probably due to the presence, in almost equal quantities, of the two geometric isomers illustrated in Figure 3 of the preceding paper. Since, as mentioned earlier, the splitting arises chiefly from differing chemical shifts of H_B, these (predominantly axial) protons must experience significantly different environments in the different isomers. The splitting decreases with increasing temperature. This decreasing importance of environmental differences for H_B is probably associated with decreasing conformational preference and increasing rate of conformational interconversion.

The absence of metal–proton coupling in the spectrum of [Pd(tnOH)$_2$]Cl$_2$ prevents the direct determination of the preferred conformation in this complex, but from the similarity of its (AB)$_2$M spectrum to the (AB)$_2$M part of the spectra of the platinum complexes, especially the low-average coupling constant, it is probable that the ring conformation is similar to that in the platinum complexes. Geometric isomers exist for this complex, but this affects the spectrum less than for [Pt(tnOH)$_2$]Cl$_2$.

From the coupling constants listed in Table II it is clear that the preferred conformation in the tnCl complexes is analogous to that in the tnOH complexes and in contrast to chlorocyclohexanes where the chloro group prefers the equatorial orientation. Again, the existence of geometric isomers has little effect on the 60-MHz spectrum of [Pt(tnCl)$_2$]Cl$_2$.

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The increased oxidation state of the metal in $[Pt(tnOH)(NH_3)_2Cl_2]Cl_2$ causes a reduction in the platinum–proton coupling constants, but the large difference between J_{AX} and J_{BX} together with the proton–proton couplings indicates that the preferred conformation is still chair type with the hydroxy group axial. An attempt can be made to compensate for the changed oxidation state by multiplying the coupling constants for the Pt(IV) complex by the factor 41.5/26.0.[5] The "compensated" values of J_{AX} and J_{BX} thus obtained are 73.5 and 15.5 Hz, respectively (*cf.* 66.4 and 22.1 Hz for $[Pt(tnOH)(NH_3)_2]Cl_2$). This suggests that the presence of the coordinated chloro groups may enhance the preference for the conformation with the hydroxy group axial, perhaps by sterically reducing competition by solvent molecules for H bonding to the axial amino H atoms. However, effects such as probable flattening of ∠Pt–N–C may also affect these coupling constants. It will be noticed that the axial protons (H_B) are much more deshielded than the equatorial protons (H_A). This contradicts the usual rule that equatorial protons resonate at lower fields than axial.

trans-$[Pt(tnOH)_2Cl_2]Cl_2$ is not sufficiently water soluble for a good spectrum to be obtained in D_2O. However, it is clear that the spectrum is similar to that of $[Pt(tnOH)(NH_3)_2]Cl_2$, the existence of geometric isomers having no major effect.

Infrared Spectra. Complexes of tnOH.—From Table III it will be seen that $M(tnOH)Cl_2$ and $[M(tnOH)_2][MCl_4]$ give moderately sharp ν_{O-H} bands. If the conformation preferred in solution (*i.e.*, chair type, with the axial hydroxy group H bonding to the axial amino protons) is present in these solids, this intramolecular H bonding does not cause the O–H stretching bands to be excessively broad. The N–H stretching bands also are not greatly broadened although the rather complex splitting in the complexes $M(tnOH)Cl_2$ (Figure 7a) may arise, at least partly, from this intramolecular hydrogen bonding. In $Pt(tnOH)Cl_4$, the ν_{O-H} peak is even sharper and occurs at a higher frequency. For N- and O-deuterated $[Pt(tnOH)_2][PtCl_4]$, ν_{O-D} occurs at 2565 cm^{-1}, ν_{O-H}/ν_{O-D} = 1.35 (*cf.* 1.41 calculated for the mode involving hydrogen motion only).

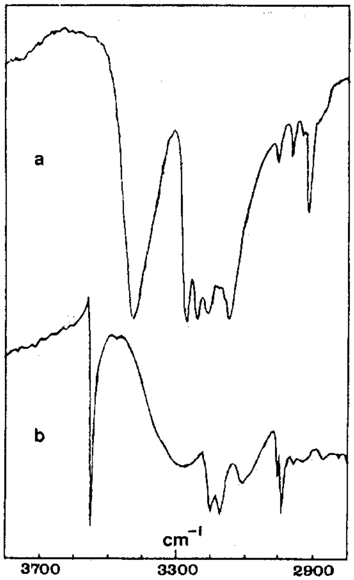

Figure 7.—Ir spectrum (3800–2800 cm^{-1}) of (a) $Pt(tnOH)Cl_2$ and (b) $Pt(tnCl)Cl_2(OH)_2$ (hexachlorobutadiene mulls).

In salts $[Pt(diamine)_2]Cl_2$ anion–cation interactions usually cause N–H stretching bands to be broadened.[8,14,15] With $[Pt(tnOH)_2]Cl_2$, both ν_{N-H} and ν_{O-H} bands are very broad. For $[Pt(tnOH)_2Cl_2]Cl_2$ the O–H stretching band is extremely broad. The ν_{N-H} pattern of this complex consists of a very sharp peak at 3275 cm^{-1} with broad bands at lower frequencies. Anhydrous $[Pt(tn)_2Cl_2]Cl_2$ gives a similar N–H stretching pattern—a sharp peak at 3215 cm^{-1} and lower frequency broad peaks.

Complexes of tnCl.—Molecules containing a C–Cl bond characteristically show a moderately strong peak in their ir spectra in the range 600–800 cm^{-1}, usually near 700 cm^{-1}.[16] For $(tnCl)(HCl)_2$ there are sharp bands at 845 and 618 cm^{-1}. On N-deuteration the peak at 845 cm^{-1} appears to shift to 730 cm^{-1}, which would be consistent with a mode arising predominantly from $-NH_3$ rocking. The band at 618 cm^{-1} shifts only slightly, to 616 cm^{-1}, suggesting that this lower frequency band arises predominantly from C–Cl stretching. Best evidence for this conclusion comes from comparison with the ir spectrum of $(tnBr)(HBr)_2$. This spectrum is almost identical with that of the chloro compound, except that the band at 618 cm^{-1} has shifted to 537 cm^{-1}. By comparison, the peak at 845 cm^{-1} shifts only to 836 cm^{-1}. Thus, ν_{C-Cl} occurs at 618 cm^{-1} and ν_{C-Br} at 537 cm^{-1} in these salts.

The complexes $M(tnCl)X_2$ have a strong, sharp band in the range 670–710 cm^{-1} and a medium to strong band in the range 780–810 cm^{-1}. At first sight, by comparison with $(tnCl)(HCl)_2$ these would be thought to correspond to C–Cl stretching and $-NH_2$ rocking, respectively. However, on N-deuteration of b-$Pt(tnCl)Cl_2$[17] the peak at 798 cm^{-1} shifts only to 782 cm^{-1}, while that at 690 cm^{-1} shifts to 615 cm^{-1}. The only conclusion that can be made from these observations is that in the undeuterated tnCl complex, there is no band which may be regarded as due dominantly to CCl stretching but that extensive mixing occurs with other modes, including some involving motions of the NH_2 groups. The frequency of this band in deuterated b-$Pt(tnCl)Cl_2$ (615 cm^{-1}) is close to that of ν_{C-Cl} in $(tnCl)(HCl_2)$ (618 cm^{-1}), which may indicate that such mixing no longer occurs in the deuterated complex. The CCl bond is relatively isolated from the NH_2 groups in terms of chemical bonds, but if the chloro group is axial and hydrogen bonded to axial NH atoms (as in the conformation preferred for tnCl complexes in aqueous solution), the vibrational coupling may occur *via* this H bonding.

The tnBr complexes studied did not show any bands which could easily be assigned to C–Br stretching. They did give moderately strong peaks near 700 cm^{-1} (725 cm^{-1} for $Pd(tnBr)Cl_2$, 670 cm^{-1} for $Pt(tnBr)Br_2$).

Like some tnOH complexes, many complexes of tnCl showed considerable complexity in the N–H stretching region, which may be partly attributable to intramolecular H bonding.

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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(($\pm$)dptn)Cl$_2$ and Pt(($\pm$)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]). $\nu_{\mathrm{N-H}}$ 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 $\nu_{\mathrm{O-H}}$ 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 $\nu_{\mathrm{O-H}}$ 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 $\nu_{\mathrm{Pt-Cl}}$ bands occur only slightly (<10 cm^{-1}) to higher frequencies than those for Pt(diamine)Cl$_2$.

In the spectra of *trans*-[Pt(tn)$_2$Cl$_2$]Cl$_2$ and [Pt(tnOH)$_2$Cl$_2$]Cl$_2$, a sharp peak at 348 cm^{-1} in each complex probably corresponds to Pt–Cl stretching.

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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$_2$O solution and the effect of increasing pH on the pmr spectrum in H$_2$O 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$_3$NH(CH$_2$)$_3$NHCH$_3$, dimetn) and *N,N,N',N'*-tetramethylpropane-1,3-diamine ((CH$_3$)$_2$N(CH$_2$)$_3$N(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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