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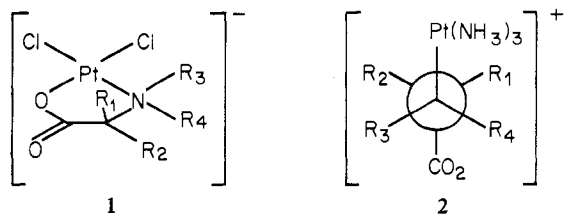
Conformational Effects on Three-Bond and Four-Bond Platinum-Hydrogen Coupling Constants in Platinum Complexes of Methylglycines

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Proton nmr spectra of platinum(II) complexes of glycine and nine *N*- and *C*-methylglycines (AA), including both chelate, Pt(AA)Cl₂, and N-coordinated, Pt(AA)(NH₃)₃⁺, species, have been analyzed. Relative energies and rotamer populations of several N-coordinated species were estimated on the basis of data for glycine and *N*-methylalanine species, which showed that both three-bond (³J_{Pt-H}) and four-bond (⁴J_{Pt-H}) platinum-proton spin coupling constants reach a maximum when Pt and H (70–90 Hz) or CH₃ (7–10 Hz) are trans and are much smaller (20–30 and <1 Hz) when Pt and H or CH₃ are gauche. For chelate species, the preferred conformations of the chelate rings were deduced from vicinal spin coupling constants while the shape of the conformational energy profile, especially near the planar eclipsed conformation, was related to ⁴J_{Pt-H} coupling to C-CH₃ groups.

Our earlier nmr investigations of platinum(II) complexes of amino acids established the pronounced effect of ligand conformation on three-bond coupling (³J_{Pt-H}) between the central ¹⁹⁵Pt and ligand protons of Pt-N-C-H fragments.^{2,3} More recently, Appleton and Hall reported substantial, conformation-dependent four-bond coupling (⁴J_{Pt-H}) in Pt-N-C-CH₃ moieties of six-membered ring diamine chelates of platinum.^{4–6} They concluded, not surprisingly, that both ³J_{Pt-H} and ⁴J_{Pt-H} are largest when the C-H or C-CH₃ is trans to platinum. Since we had earlier failed to observe measurable four-bond Pt-H coupling in the two *C*-methylglycine chelates we had investigated (alanine and α-aminoisobutyric acid), we decided to examine the spectra of the other members of the series. In this paper, we report nmr data for Pt(II) complexes of glycine and the nine *N*- and *C*-methyl derivatives.⁷ Both the chelate species Pt(AA)Cl₂, **1**, and the N-coordinated species Pt(AA)(NH₃)₃⁺, **2**, were investigated.



1 **2**
R₁, R₂, R₃, R₄ = H, CH₃ in 10 combinations

From a conformational viewpoint, the N-coordinated species can be considered to be substituted methylammonium ions, whose observed properties are essentially a weighted average over the three classic staggered rotamers observed in one complete rotation about the C-H bond. Thus the techniques which have been applied so successfully to determine relative rotamer populations and coupling constants of staggered forms of substituted ethanes can be applied to these compounds.⁸ Methyl substitution could be expected to have

a pronounced effect on the relative energies of these rotamers and, hence, on the observed average values of the spectral parameters. In addition, a C-CH₃ group could act as a probe with ⁴J_{Pt-H} indicating the conformational situation of the C-CH₃ group.

Although the glycinate chelate ring is more nearly planar than the ethylenediamine chelate ring, considerable evidence (including our earlier nmr studies^{2,9}) indicates significant preference for nonplanar conformations of substituted glycinate chelates, especially in the solid state.¹⁰ Hawkins has recently reviewed the relevant data and has reported conformational energy calculations which support the conclusion that a considerable range of nonplanar puckered and envelope conformations of chelated alanine are essentially equal in energy in Co(ala)(NH₃)₄²⁺.¹¹ It was our hope that this nmr study would provide a reliable experimental approach for establishing the conformational energy profile of glycinate chelates in solutions.

Experimental Section

Preparation of Amino Acids. Commercially available amino acids were used whenever possible. Of the four amino acids which were not commercially available, three (meala, meaba, and dmala) were synthesized by condensation of the appropriate α-chloro or bromo acid with an excess (20%) of methylamine or dimethylamine and a stoichiometric amount (2 mol/mol of acid) of KOH. The solution was kept at room temperature to avoid hydrolysis of the acid and the progress of reaction was followed by nmr. The free amino acids were isolated after adjustment of the pH to 6 and were subsequently purified by recrystallization from ethanol or dimethylformamide. *N,N*-Dimethyl-α-aminoisobutyric acid (dmaba) was synthesized from α-aminoisobutyric acid by reaction with formaldehyde and formic acid.¹²

Preparation of Chelates. The bright yellow amino acid chelates of general formula KPt(AA)Cl₂ were prepared by reaction of the free amino acid with K₂PtCl₄ in a 1:1 mole ratio as described earlier.² Details of the separation procedure varied slightly with solubility of the complex but all were obtained in 30–50% yield.

Nmr Samples of Chelates. For complexes whose potassium salts were sufficiently soluble in H₂O or D₂O, nmr samples were prepared by simply dissolving about 0.5 mmol of solid in 0.5 ml of H₂O or D₂O. If the potassium salt was not sufficiently soluble in water to obtain good spectra (~1 mmol/ml of solvent), K⁺ ion was replaced by H⁺, NH₄⁺, or TMA⁺ (tetramethylammonium ion) by passing the solu-

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(7) Abbreviations: glycine, gly; alanine, ala; α-aminoisobutyric acid, aba; *N*-methylglycine = sarcosine, sarc; *N*-methylalanine, meala; *N*-methyl-α-aminoisobutyric acid, meaba; *N,N*-dimethylglycine, dmgly; *N,N*-dimethylalanine, dmala; *N,N*-dimethyl-α-aminoisobutyric acid, dmaba.

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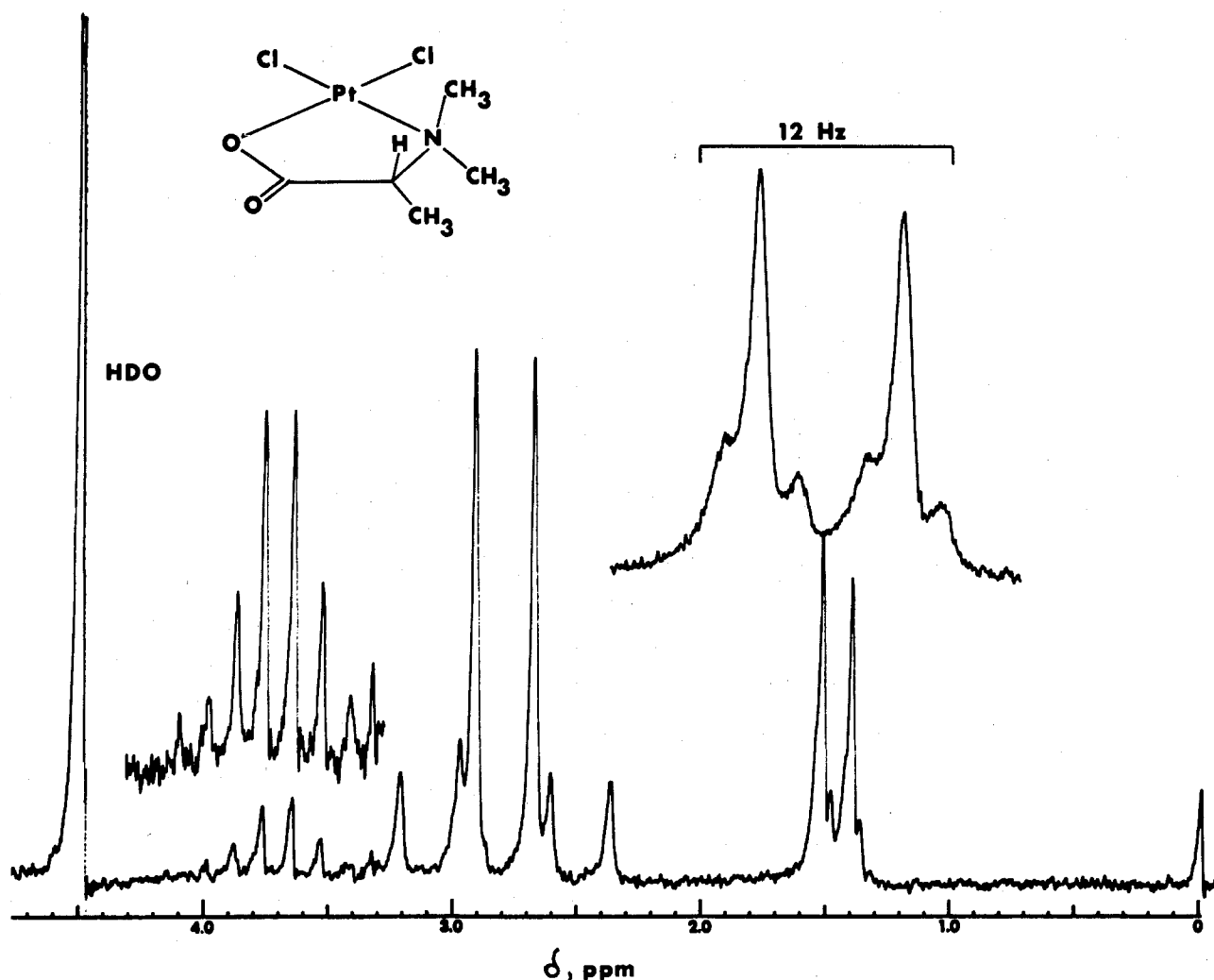


Figure 1. The 60-MHz proton nmr spectrum of 1 M KPt(dmala)Cl₂ in D₂O.

tion through a Dowex 50W-X8 cation-exchange resin in the appropriate form and evaporating the solution to dryness.

Preparation of N-Coordinated Species. N-Coordinated species of general formula [Pt(AA)(NH₃)₃]Cl were prepared from the corresponding chelates by gently warming about 0.5 mmol of the chelate salt in 5 ml of concentrated aqueous ammonia at 60–70° for a 10–15-min period and evaporating to dryness to yield a colorless, glassy solid. The solid was dissolved in about 0.5 ml of D₂O and spectra were recorded. In some cases, a second treatment was required to discharge all of the initial yellow color and to produce complete ring opening. However, none of the *N,N*-dimethyl species could be converted to N-coordinated species by this technique. In attempting to prepare these species gentle treatment with ammonia apparently only displaced the two Cl's. This was indicated by the loss of yellow color and only minor changes in nmr spectra compared to the dichloro chelate. Heating the samples for a longer time with excess concentrated NH₃ resulted in displacement of free amino acid. The comparative lability of the Pt–N(CH₃)₂ bond relative to the Pt–NH₃ bond in the presence of a nucleophilic reagent is not unexpected.¹³

Results

Chelate Species. The spectral features of the chelates are illustrated by the spectrum of KPt(dmala)Cl₂, which is shown in Figure 1. It consists of a C-CH₃ doublet at 1.45 ppm, with its platinum-195 satellites (⁴J_{Pt-H} = 3.3 Hz); a pair of *N*-CH₃ peaks at 2.63 and 2.88 ppm, each flanked by platinum-195 satellites (³J_{Pt-H} = 37.5 Hz); and a C-H quartet at 3.72 ppm, with its platinum-195 quartet satellites (³J_{Pt-H} = 27.3 Hz). Absorption signals for *N*-CH₃, C-CH₃, and C-H protons of the other chelates, when present in the compound,

generally fall in about the same region of the spectrum.

Spectra of the two isomers of *N*-methylalanine are shown in Figures 2 and 3. Figure 2a is the spectrum of a D₂O solution of the less soluble isomer. It was isolated from the reaction mixture as the potassium salt, but the spectrum is that of the more soluble H⁺ form. It is assumed to be the *trans* isomer. The spectrum closely resembles that of KPt(dmala)Cl₂, except that only one *N*-CH₃ absorption is present and additional coupling due to the *N*-H proton is evident in the *N*-CH₃ and C-H regions. Upon standing for several days, *N*-H proton exchange was almost complete and the spectrum simplified to that shown in Figure 2b.

When the solid *trans*-KPt(meala)Cl₂ was dissolved in water and kept at pH > 7 for a few minutes before passage through the H⁺ cation exchange column, additional peaks were observed in all parts of the spectrum (Figure 3a). These are attributed to the less favored *cis* isomer. At mid-pH, *N*-H proton dissociation would permit equilibration of the isomers.^{3,14} The equilibrium ratio of *trans* to *cis* isomers, calculated from relative peak areas in the C-CH₃ part of the spectrum, is about 8:1. A *cis*-enriched HPt(meala)Cl₂ sample was obtained by precipitation of part of the *trans* isomer from an aqueous solution of the equilibrated mixture (H⁺ form) by addition of KNO₃. After enrichment, the solution was evaporated to dryness, and dissolved in D₂O. The

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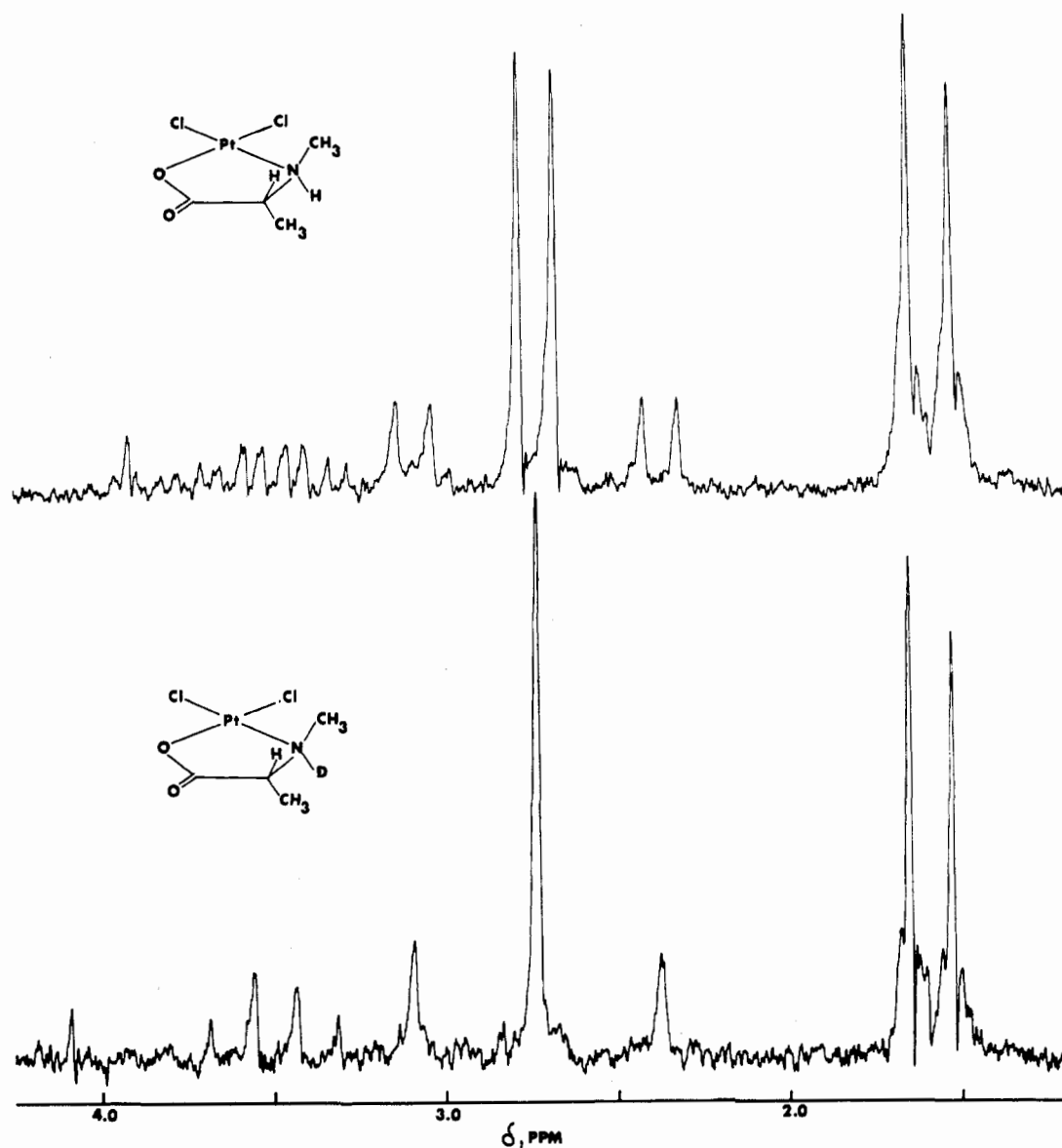


Figure 2. The 60-MHz proton nmr spectra of *trans*-HPt(meala)Cl₂ in D₂O: top (a), freshly dissolved solid; bottom (b), after several days to permit exchange of *N*-H proton.

spectrum is shown in Figure 3b. The platinum-195 satellites of the C-CH₃ ($^4J_{\text{Pt-H}} = 2.7$ Hz) and *N*-CH₃ ($^3J_{\text{Pt-H}} = 43.5$ Hz) signals are clearly evident, but the spectrum amplitude is too low to show complete details of the C-H region. Several traces of this sample at maximum spectrum amplitude revealed enough details of the C-H quartet (split by *N*-H) to permit evaluation of $J_{\text{H-N-C-H}}$ (4.3 ± 0.3 Hz). On standing at room temperature, *N*-H protons of both isomers exchanged with solvent D₂O, with the exchange rate of the *trans* isomer being greater by a factor of about 6. After exchange was complete, 100-MHz spectra of the sample were obtained, from which the value of $^3J_{\text{Pt-H}}$ (21 ± 1 Hz) was determined.

Chemical shifts and spin-coupling constants at magnet temperature for the ten chelates are given in Table I. The chemical shifts differ slightly from some of the values reported earlier.² This results from using an internal reference standard (TMS*). In the earlier work, values were measured with respect to (CH₃)₄NCl and the observed difference between TMS* and (CH₃)₄NCl was added to obtain TMS* shifts.

The temperature dependence of the spectrum of each compound was investigated. Except for a sometimes sizable downfield shift for C-H proton signals (up to 0.2 ppm/100°) the effects on all parameters were generally small and will not be discussed further.

N-Coordinated Species. Spectra of most of the compounds are comparable to those of corresponding chelate species and require no detailed description. As noted for chelate species, C-H, *N*-CH₃, and C-CH₃ regions of the spectra are well separated, are clearly resolved, and are found in the regions expected. A detailed analysis of the more complex Pt(sarc)-(NH₃)₃⁺ spectrum has been given earlier.³ Only complexes of *N*-methylalanine provide significant complications.

The spectrum of a D₂O solution of Pt(meala)(NH₃)₃⁺, prepared by treating *trans*-KPt(meala)Cl₂ with excess aqueous NH₃, is shown in Figure 4. The spectrum is consistent with that expected for an approximately equimolar mixture of the two diastereomers corresponding to the *cis* and *trans* chelates, whose stereochemistry (for (*R*)-alanine) is shown in Scheme I. The C-CH₃ region has two separate doublets ($J_{\text{H-C-CH}_3} = 7.0$ Hz), one with prominent ¹⁹⁵Pt satellites ($^4J_{\text{Pt-H}} = 7.0$

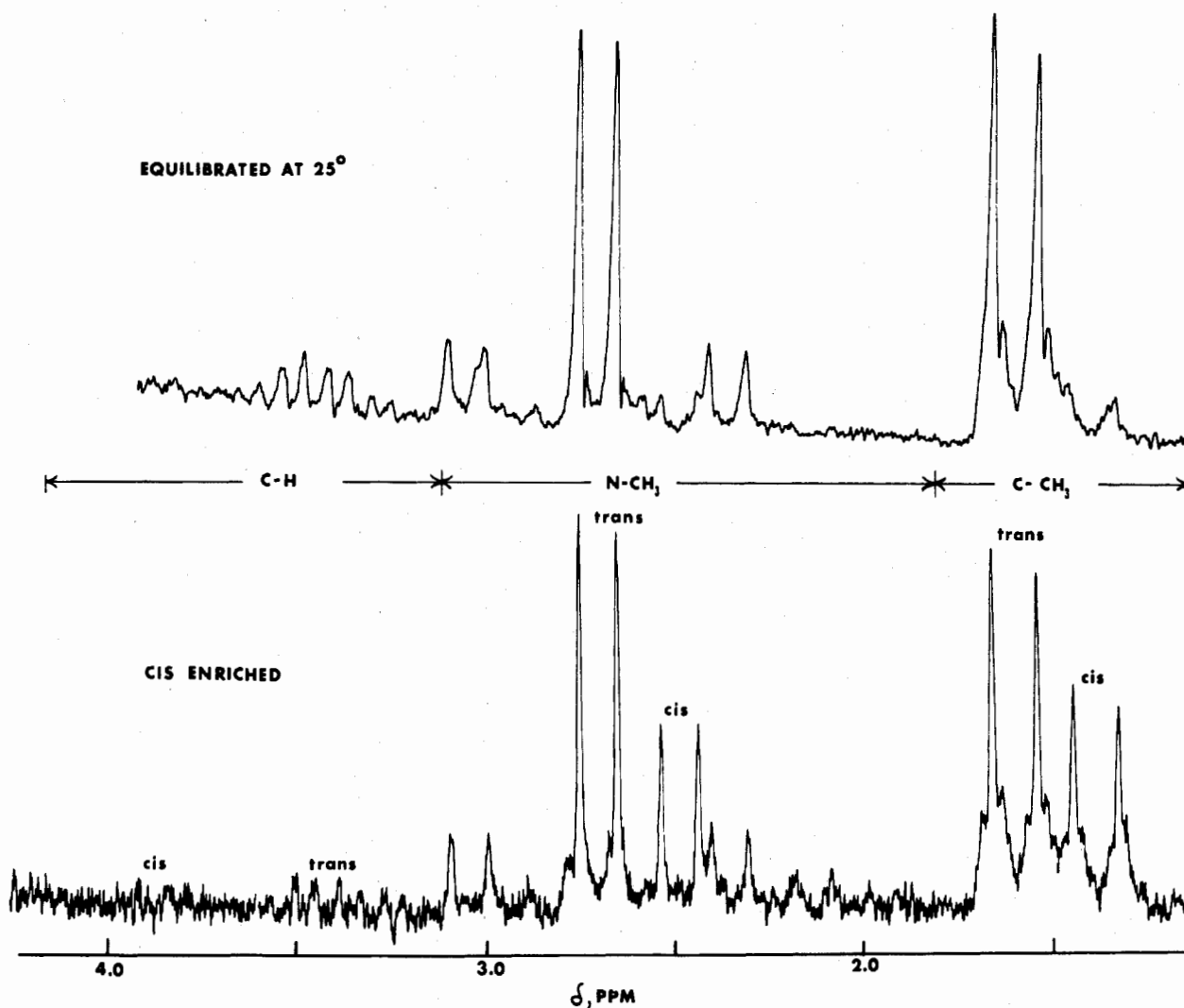


Figure 3. The 60-MHz proton nmr spectra of freshly dissolved HPT(meala)Cl₂ samples: top (a), after equilibration at mid-pH before conversion to H⁺ form, to permit equilibration of cis and trans isomers; bottom (b), cis-enriched sample.

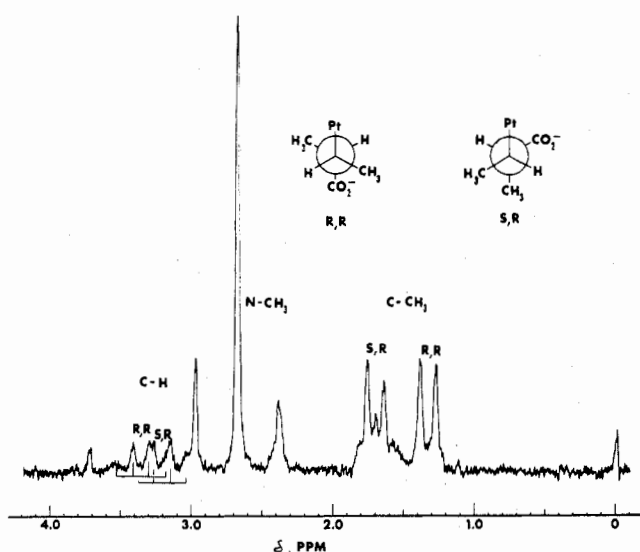
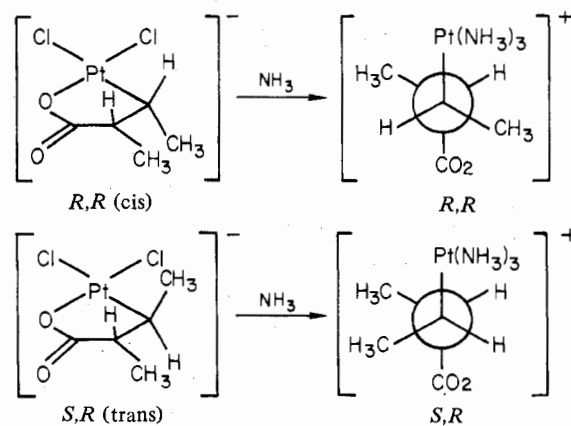


Figure 4. The 60-MHz proton nmr spectrum of an equilibrium mixture of isomers of [Pt(meala)(NH₃)₃]Cl in D₂O.

H_z). The total intensity of the upfield doublet is slightly less than that of the downfield doublet including its satellites. The N-CH₃ signals of the two isomers are nearly superimpos-

Scheme I



ed, but the $^3J_{\text{Pt-H}}$ values are slightly different (34.5 vs. 35.5 Hz). The central peaks of the two C-H quartets are resolved with their centers separated by about 8 Hz at 60 Mz. The downfield quartet is slightly less intense. The location of the downfield platinum satellite quartet of the downfield C-H quartet is also indicated. Assignment of the peaks to particular species is based on the reasonable assumption that the conformation with the C-CH₃ group trans to Pt pre-

Table I. Chemical Shifts and Spin-Coupling Constants of Pt(gly)Cl₂⁻ and Methyl Derivatives

Compd	Structure	Proton chem shifts, ppm			Spin-coupling constants, Hz					
		δ_{C-H}	δ_{N-CH_3}	δ_{C-CH_3}	$J_{H-N-C-H}$	$J_{Pt-N-C-H}$	$J_{Pt-N-C-CH_3}$	J_{H-C-CH_3}	J_{H-N-CH_3}	$J_{Pt-N-CH_3}$
Pt(gly)Cl ₂ ⁻		3.58			6.5 (av)	38.5				
Pt(sarc)Cl ₂ ⁻		3.38 (A) 3.88 (B)	2.67		4.3 (AX) 6.6 (BX)	38.5 (H _A) 33.5 (H _B)		5.9	43	
Pt(dmgly)Cl ₂ ⁻		3.68	2.86			32.9			35.5	
Pt(ala)Cl ₂ ⁻		3.82		1.43	?	28.0	<1	7.0		
<i>cis</i> -Pt-(meala)Cl ₂ ⁻		3.97	2.48	1.38	4.3	21	2.7	7.1	5.9	43.5
<i>trans</i> -Pt-(meala)Cl ₂ ⁻		3.46	2.70	1.60	3.4	41.8	3.2	7.1	5.9	41.5
Pt(dmala)Cl ₂ ⁻		3.72	2.63 (A) 2.88 (B)	1.45		27.3	3.3	6.9		37.5
Pt(aba)Cl ₂ ⁻				1.53			<1			
Pt(meaba)Cl ₂ ⁻			2.56	1.45 (A) 1.73 (B)			2.2 (H _A) 2.8 (H _B)	5.9	41.5	
Pt(dmaba)Cl ₂ ⁻			2.73	1.58			3.1		35.9	

Table II. Chemical Shifts and Spin-Coupling Constants of Pt(gly)(NH₃)₃⁺ and Methyl Derivatives

Compd	Structure	Proton chem shifts, ppm			Spin-coupling constants, Hz				
		δ_{C-H}	δ_{N-CH_3}	δ_{C-CH_3}	$J_{H-N-C-H}$	$J_{Pt-N-CH_3}$	$J_{Pt-N-C-H}$	$J_{Pt-N-C-CH_3}$	J_{H-C-CH_3}
Pt(gly)(NH ₃) ₃ ⁺		3.37 (3.68)			?		37.5 (31.1)		
Pt(sarc)(NH ₃) ₃ ⁺		3.33 (3.67) (A) 3.53 (3.85) (B)	2.67 (2.75)		5.2 (AX) 7.2 (BX) 6.0 (CH ₃)	36.0 (36.0)	52.8 (57.6) (A) 27.6 (23.2) (B)		
Pt(ala)(NH ₃) ₃ ⁺		3.43 (3.70)		1.43 (1.58)	?		23.6 (21.6)	<1 (<1)	7.0
(<i>R,R</i>)-Pt(meala)(NH ₃) ₃ ⁺		3.37 (3.62)	2.68 (2.75)	1.33 (1.42)	9.0 6.0 (CH ₃)	34.5 or 35.5 (same)	29.6	<1 (<1)	7.0
(<i>S,R</i>)-Pt(meala)(NH ₃) ₃ ⁺		3.22 (3.62)	2.68 (2.78)	1.71 (1.85)	9.6 6.0 (CH ₃)	34.5 or 35.5 (same)	29.6	7.0 (7.0)	7.0
Pt(aba)(NH ₃) ₃ ⁺				1.50 (1.61)				~1.5 (~1.5)	
Pt(meaba)(NH ₃) ₃ ⁺			2.65 (2.73)	1.37 (1.53) (A) 1.52 (1.65) (B)	6.0 (CH ₃)	33.4 (33.4)		<1 (<1) (A) 3.2 (2.8) (B)	

dominates for the *S,R* isomer while the conformation with CO₂⁻ trans to Pt predominates for the *R,R* isomer. When the sample was evaporated to dryness and redissolved in H₂O, additional splitting was observed for both C-H and N-CH₃ signals. This splitting yielded the $J_{H-N-C-H}$ values given in Table II. The J_{Pt-H} values for both isomers were obtained from a 100-MHz spectrum of a D₂O solution of the mixture which revealed the major components of the quartet side bands of C-H quartets of both isomers.

The C-CH₃ signals of the five N-coordinated species that could be obtained are presented in Figure 5. Significant coupling (7.0 Hz) is evident for (*S,R*)-Pt(meala)(NH₃)₃⁺. Slight coupling (~1.5 Hz) is present in Pt(aba)(NH₃)₃⁺ and none (<1 Hz) was observed in Pt(ala)(NH₃)₃⁺ and (*R,R*)-Pt(meala)(NH₃)₃⁺. For Pt(meaba)(NH₃)₃⁺, significant coupling (3.2 Hz) is observed for one of the two C-CH₃ groups.

Spectral parameters for the seven N-coordinated species

which could be prepared are summarized in Table II. Where reliable values were obtained, chemical shifts and coupling constants of the corresponding acidified (CO₂⁻ protonated) samples are also listed. The magnitude of the downfield shift was taken as clear evidence that the Pt-O bond of the chelate had been broken by the NH₃ treatment.

Temperature Dependence. The temperature dependence of J_{Pt-H} of Pt(gly)(NH₃)₃⁺ was investigated in detail. Results are given in Table III. The temperature dependence of the spectra of most of the other complexes was also investigated, but the effects were generally smaller and the data are not included in this report.

Discussion

Conformation-Independent Spin-Coupling Constants. Of the six ¹H-¹H and ¹H-¹⁹⁵Pt coupling constants which characterize the spectra of these complexes, J_{H-N-CH_3} , J_{H-C-CH_3} ,

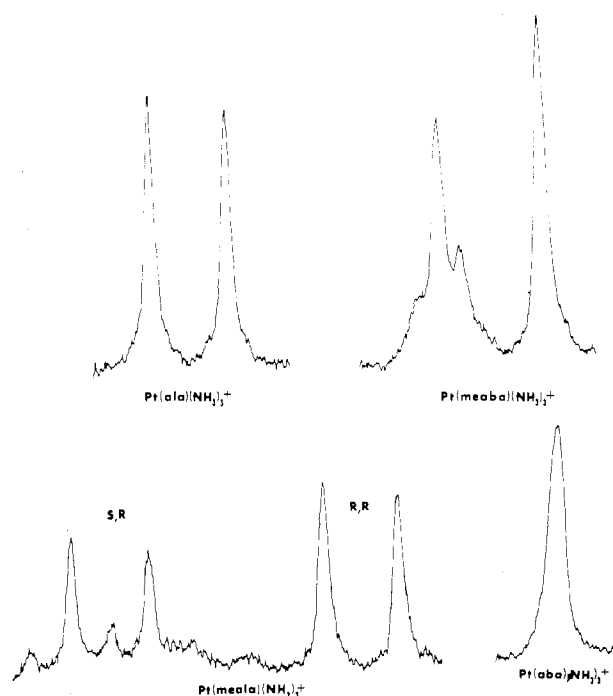


Figure 5. The C-CH₃ portion of the 60-MHz proton nmr spectra of N-coordinated amino acids.

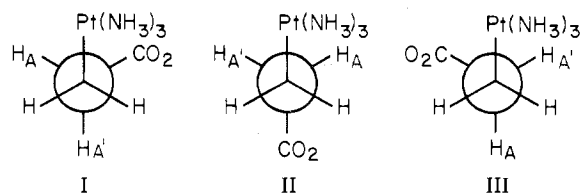
Table III. The Temperature Dependence of ${}^3J_{\text{Pt-H}}$ for Pt(gly)(NH₃)₃⁺

Temp., °C	$J_{\text{obsd.}}$ Hz	$J_{\text{calcd.}}^a$ Hz	Temp., °C	$J_{\text{obsd.}}$ Hz	$J_{\text{calcd.}}^a$ Hz
7	36.4	36.4	61	38.2	38.1
15	36.7	36.7	71	38.5	38.5
23	37.0	36.9	81	38.7	38.8
41	37.5	37.5	90	39.0	39.0
52	37.9	37.9			

^a Based on ${}^3J_t = 90.0$ Hz, ${}^3J_g = 30.9$ Hz, and $\Delta E = 1200$ cal/mol.

and $J_{\text{Pt-N-CH}_3}$ would not be expected to be sensitive to the conformation of the ligand. The first two are remarkably constant, 6.0 ± 0.1 and 7.0 ± 1 Hz, in both chelate and N-coordinated species, while $J_{\text{Pt-N-CH}_3}$ depends on the extent of substitution at the nitrogen. For all species containing -NHCH₃, ${}^3J_{\text{Pt-H}} = 35.5 \pm 2$ Hz; for -N(CH₃)₂, 42 ± 2 Hz. A similar decrease with methyl replacement of an N-H proton has been reported in several diamine complexes.¹⁵ It provides a measure of the weakening of the Pt-N bond which needs to be taken into account in interpreting conformational implications of other three-bond ¹⁹⁵Pt-¹H coupling constants. On the basis of these average values, a reduction in ${}^3J_{\text{Pt-H}}$ of about 15% per N-methyl replacement would be indicated. The effect of methyl substitution on average coupling to CH₂ protons in ethylenediamine complexes, from 40 Hz for en to 35 Hz for N,N'-diamine to 30 Hz for N,N',N'-tmen,¹³ supports the view that the effect of two methyl groups is approximately twice that of one methyl group. However, the corresponding effect on average coupling to CH₂ protons in gly complexes is smaller (39 Hz for gly to 33 Hz for dmgly), so that a reduction in ${}^3J_{\text{Pt-H}}$ of 10% per methyl substitution is perhaps more reasonable.

${}^3J_{\text{Pt-H}}$ and Conformational Analysis of N-Coordinated Species. Conformational analysis of these species is based on the assumption that the observed spectral parameters are weighted averages over three staggered conformations I-III (for glycine). For glycine, I and III are equivalent so that



$H_A = H_{A'}$. The relatively small value for ${}^3J_{\text{Pt-H}}$ at magnet temperature (37.5 Hz) indicates that conformation II predominates, *i.e.*, that conformation II with CO₂⁻ trans to Pt(NH₃)₃ is the low-energy form. Furthermore, the temperature dependence is sufficient to permit an evaluation of ${}^3J_{\text{Pt-H}}$ for conformations in which H is trans, 3J_t , and gauche, 3J_g , to Pt and ΔE , the energy difference between I (or III) and II. With I = III, the observed coupling constant ${}^3J_{\text{obsd}}$ is given

$${}^3J_{\text{obsd}} = ({}^3J_t - {}^3J_g)f_t + {}^3J_g \quad (1)$$

where the fractional population in which H is trans to Pt, f_t , is given by

$$f_t = e^{-\Delta E/RT} / (1 + 2e^{-\Delta E/RT}) \quad (2)$$

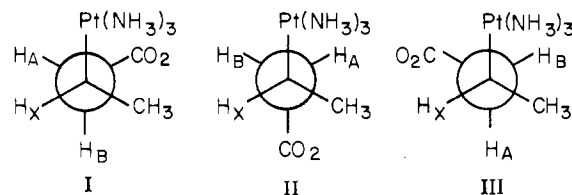
A standard linear least-squares program was used to calculate the intercept (3J_g) and the slope (${}^3J_t - {}^3J_g$) of a plot of ${}^3J_{\text{obsd}}$ vs. f_t for a range of ΔE values. The "best fit" was then taken to be the value of ΔE which produced the smallest standard deviation in 3J_g and 3J_t . By this method 3J_t and 3J_g were calculated to be 90.0 ± 1.0 and 30.9 ± 0.8 Hz, respectively, for $\Delta E = 1200 \pm 50$ cal mol⁻¹. These values were used to calculate ${}^3J_{\text{Pt-H}}$ at each temperature from eq 1 and 2 and the results are included in Table III.

These values of 3J_t and 3J_g can be compared with ${}^3J_{\text{eq}}$ and ${}^3J_{\text{ax}}$ deduced from spectra of six-membered ring chelates by Appleton and Hall.^{5,15} They concluded that $J_{\text{ax}} \cong 15$ Hz and $J_{\text{eq}} \cong 65$ Hz. For 2-hydroxy- or 2-chloropropane-1,3-diamine chelates, observed ${}^3J_{\text{Pt-H}}$ values for the two methylene protons lie close to these values (~ 65 and ~ 22 Hz at room temperature) which led them to conclude that preference for the chair conformation of the six-membered chelate ring is almost complete. There appears to be little doubt that 3J_t (or ${}^3J_{\text{eq}}$) is 3-4 times 3J_g (or ${}^3J_{\text{ax}}$) and that the dihedral angle dependence of ${}^3J_{\text{Pt-H}}$ can be estimated with reasonable confidence by a Karplus-type equation¹⁶ of the form

$${}^3J_{\text{Pt-H}} = K \cos^2 \phi \quad (3)$$

where $K = {}^3J_t = 70$ -90 Hz. This predicts ${}^3J_g = 18$ -22 Hz. Since observed average values for ${}^3J_{\text{Pt-H}}$ reported by Appleton and Hall and for some of the other N-coordinated species are significantly less than the 30 Hz for 3J_g obtained from our analysis, that value for 3J_g (or ${}^3J_{\text{ax}}$) is probably too high, in spite of the excellent fit obtained for the temperature dependence of ${}^3J_{\text{Pt-H}}$ of Pt(gly)(NH₃)₃⁺.

Examination of the three possible rotamers for sarcosine suggests that II and III might be nearly equally populated

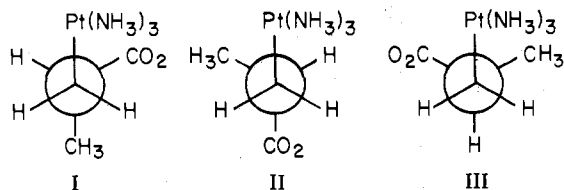


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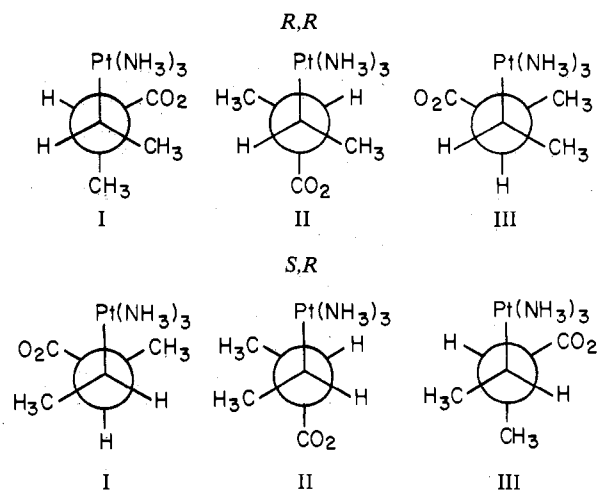
while unfavorable steric interaction of the three bulky groups would make I less favorable. Assuming the $^3J_{\text{Pt-H}}$ values calculated for glycine, one would expect $J_{\text{Pt-HB}}$ to be about 30 because H_B is gauche to the platinum in both II and III. Similarly, $^3J_{\text{Pt-HA}}$ would be estimated to about $60 = \frac{1}{2}(90 + 30)$ since H_A would spend half its time gauche and half its time trans to the platinum. Initial examination of the data agrees with these expectations; *i.e.*, $^3J_{\text{Pt-HB}}$ is about 27 Hz and $^3J_{\text{Pt-HA}}$ is about 53 Hz at magnet temperature. But analysis of the H-H coupling constants in H_2O reveals that III is preferred over II. As noted in a previous analysis of the spectrum, the methylene proton which is more strongly coupled to the platinum is less strongly coupled to the *N*-H proton (H_X).³ This situation would exist in III. Relative values of both $^3J_{\text{Pt-H}}$ and $^3J_{\text{H-H}}$ can be accounted for approximately on the basis of a ratio of I:II:III = 0.1:0.4:0.5. Assuming $^3J_\text{t} = 80$ and $^3J_\text{g} = 20$ Hz for $^3J_{\text{Pt-H}}$, $^3J_\text{t} = 11$ and $^3J_\text{g} = 3$ Hz for $^3J_{\text{H-H}}$, and this population ratio, $J_{\text{Pt-HA}} = 50$ (*vs.* 53), $J_{\text{Pt-HB}} = 26$ (*vs.* 27), $J_{\text{BX}} = 6.2$ (*vs.* 7.2), and $J_{\text{AX}} = 3.8$ (*vs.* 5.2) Hz. The rotamer energy differences calculated from this ratio are $E_{\text{II}} - E_{\text{III}} = 138$ cal/mol and $E_{\text{I}} - E_{\text{III}} = 900$ cal/mol. Qualitatively, the effect of temperature on $^3J_{\text{Pt-H}}$ corresponds to this model; *i.e.*, $^3J_{\text{Pt-HA}}$ decreases and $^3J_{\text{Pt-HB}}$ increases with increased temperature. However, the model predicts that $J_{\text{Pt-HA}}$ should decrease more slowly than $J_{\text{Pt-HB}}$ increases, whereas, the opposite is observed.

Inspection of the possible rotamers of alanine suggests that III would be the least favored rotamer with I and II of about



equal population. In I and II the C-H hydrogen is gauche to the platinum; consequently $^3J_{\text{Pt-H}}$ should be small. The experimental $^3J_{\text{Pt-H}}$ value is small, 23.6 Hz at 40°, indicating that the C-H hydrogen is nearly always gauche to the platinum. The slight increase of 1.4 Hz over a 60° range indicates the more frequent occurrence of rotamer III at increased temperatures, but it is not sufficient to permit evaluation of energy differences between forms. Relative energies of I and II cannot be determined on the basis of $^3J_{\text{Pt-H}}$ but can be estimated from the conformation dependence of $^4J_{\text{Pt-H}}$ which was established on the basis of the other members of the series.

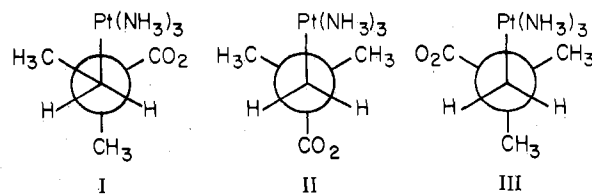
$^4J_{\text{Pt-H}}$ and the Conformational Analysis of N-Coordinated Species. The dihedral angle dependence of $^4J_{\text{Pt-H}}$ in this series was established by analysis of the spectra of the two isomers of $\text{Pt}(\text{meala})(\text{NH}_3)_3^+$ whose rotamers for *N*-methyl-*(R)*-alanine are shown below. The conformational preference of the two isomers can be established independently on the basis of $^3J_{\text{Pt-H}}$ and $^3J_{\text{H-H}}$ coupling constants. Since $^3J_{\text{Pt-H}}$ is relatively small for both isomers while $^3J_{\text{H-H}}$ is relatively large, conformation III must predominate for the *S,R* isomer and conformation II for the *R,R* isomer. In conformation III of the *S,R* isomer, C-CH₃ is trans to Pt; in conformation II of the *R,R* isomer, C-CH₃ is gauche to Pt. Therefore, the large $^4J_{\text{Pt-H}}$ coupling observed for the *S,R* isomer (7.0 Hz) must correspond to a lower limit for the trans coupling constant, ^4J_t , while the small $^4J_{\text{Pt-H}}$ coupling observed for the *R,R* isomer (<1 Hz) must correspond to an upper limit for the gauche coupling constant, ^4J_g .



The conclusion that ^4J_t is about 7 Hz and that ^4J_g is very small (<1 Hz) agrees well with Appleton and Hall's conclusions for six-membered ring chelates. They concluded that ^4J_eq , which corresponds to ^4J_t , is at least 6.5 Hz while ^4J_ax , which corresponds to ^4J_g , is very small. This requires that $^4J_{\text{Pt-H}}$ decreases more rapidly with dihedral angle than the corresponding $^3J_{\text{Pt-H}}$.

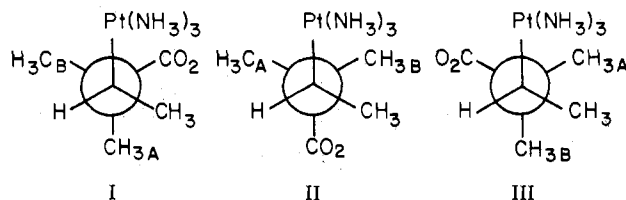
The establishment of the conformation dependence of $^4J_{\text{Pt-H}}$ permits an assessment of relative conformational energies of $\text{Pt}(\text{aba})(\text{NH}_3)_3^+$, $\text{Pt}(\text{meaba})(\text{NH}_3)_3^+$, and $\text{Pt}(\text{ala})(\text{NH}_3)_3^+$. For $\text{Pt}(\text{ala})(\text{NH}_3)_3^+$, for which $^3J_{\text{Pt-H}}$ indicates strong preference for I or II over III, $^4J_{\text{Pt-H}}$ is <1 Hz. Therefore, conformation II, in which C-CH₃ is gauche to Pt and CO₂⁻ is trans to Pt, must also be strongly preferred over I.

Two of the rotamers of $\text{Pt}(\text{aba})(\text{NH}_3)_3^+$ (I and III) are



equivalent. Any sizable population in these conformations would be expected to result in significant long-range coupling between ¹⁹⁵Pt and the C-CH₃ protons. The fact that this coupling remains less than 1.5 Hz over an 80° temperature range indicates that the preferred conformation is II. A lower limit on $\Delta E = E_{\text{I}} - E_{\text{II}} = E_{\text{III}} - E_{\text{II}}$ can be estimated as follows. Assuming $^4J_\text{t} = 8$ Hz and $^4J_\text{g} = 0$ Hz, a 60% population for I and III yields $^4J_{\text{Pt-H}} = 0.2(^4J_\text{g}) + 0.2(^4J_\text{t}) + 0.6(^4J_\text{t}) = 1.6$ Hz. Thus, $\Delta E = RT \ln 3 = 650$ cal/mol.

Replacement of one *N*-H proton of $\text{Pt}(\text{aba})(\text{NH}_3)_3^+$ by a methyl group yields $\text{Pt}(\text{meaba})(\text{NH}_3)_3^+$ and alters the conformational situation appreciably. If conformation II of Pt-



(meaba)(NH₃)₃⁺ prevailed strongly, $^4J_{\text{Pt-H}}$ would be very small for both C-CH₃ groups. This coupling is in fact substantial (~3 Hz) for the downfield C-CH₃ group but is <1

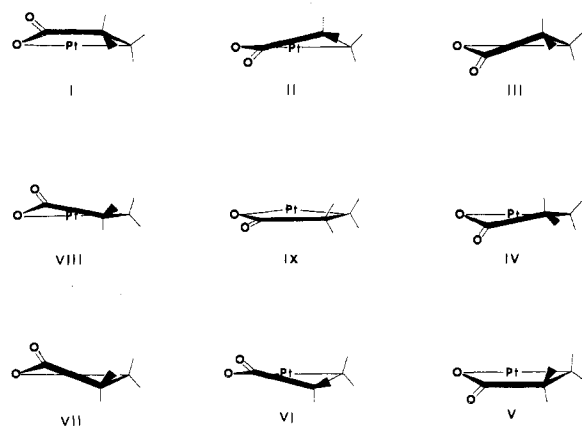


Figure 6. Some of the low-energy conformations available to chelated glycinate.

Hz for the upfield C-CH₃ group. This nonequality requires that I > III or III > I. On the basis of the data for Pt(ala)-(NH₃)₃⁺, it is clear that III should be preferred over I. On the basis of the model applied to Pt(aba)(NH₃)₃⁺, the relative populations of I, II, and III can be estimated. Since, ${}^4J_{\text{Pt-H}} = f_{\text{I}}(8) + f_{\text{II}}(0) + f_{\text{III}}(0) < 1$, $f_{\text{I}} < 1/8$. Similarly, ${}^4J_{\text{Pt-HB}} = f_{\text{I}}(0) + f_{\text{II}}(0) + f_{\text{III}}(8) = 3$ or $f_{\text{III}} = 3/8$ which requires that $f_{\text{II}} \cong 1/2$. Relative energies calculated from these fractional populations are $(E_{\text{III}} - E_{\text{II}}) = RT \ln 4/3 = 170$ cal/mol and $(E_{\text{I}} - E_{\text{II}}) = RT \ln 4 = 830$ cal/mol, or more.

Effects of Protonation. Protonation of CO₂⁻ has two effects. It uniformly shifts all of the signals downfield an amount which depends on the distance from the protonation site (C-H, ~20 Hz; C-CH₃, ~10 Hz; N-CH₃, ~5 Hz). In addition, it changes ${}^3J_{\text{H-H}}$, ${}^3J_{\text{Pt-H}}$, and ${}^4J_{\text{Pt-H}}$ which can be attributed to a change in rotamer populations. The direction of this change is usually toward a greater contribution from rotamer II in which the CO₂H is trans to Pt(NH₃)₃. For example, average values of ${}^3J_{\text{Pt-H}}$ decreased with protonation for both Pt(gly)(NH₃)₃⁺ (~6 Hz) and Pt(ala)(NH₃)₃⁺ (~2 Hz). The larger change observed for the former is not unexpected. The comparatively small value for ${}^3J_{\text{Pt-H}}$ of Pt(ala)(NH₃)₃⁺, 23.6 Hz, indicates a very strong preference for II even before protonation. Similarly, acidification of Pt(aba)(NH₃)₃⁺ had little effect on ${}^4J_{\text{Pt-H}}$, which is undetectably small (<1 Hz) in the CO₂⁻ form. However protonation did decrease ${}^4J_{\text{Pt-H}}$ for CH₃A of Pt(meaba)(NH₃)₃⁺ perceptibly (from 3.2 to 2.8 Hz) which is consistent with an increase in the population of II. Apparently protonation of CO₂⁻ reduces favorable gauche interaction between CO₂⁻ and Pt(NH₃)₃. Such favorable interaction could include hydrogen bonding between CO₂⁻ and Pt(NH₃)₃ protons.

Model for Analysis of Chelate Data. Although a simple equilibrium between puckered conformations suffices to describe certain properties of glycinate chelates better than the assumption of planar rings,⁹ Hawkins' analysis, which also recognizes the importance of envelope and eclipsed conformations is clearly more realistic. A useful way of representing the full range of available conformations is given in Figure 6. In addition to the planar eclipsed conformation IX, the puckered conformations I and V, and the envelope conformations III and VII, four other envelope conformations which relieve eclipsed H-H interactions (II, IV, VI, and VIII) are included. A useful way of describing these different conformations and interconversion pathways is to specify the vertical displacement of the center of the C-C bond from the coordination plane (denoted *z*) and the angle of inclination of the C-C bond to the coordination plane,

Table IV. Comparison of Calculated and Observed Spin-Coupling Constants for Glycine Chelates

Coupling const	Assumed dihedral angle dependence	J_{calcd}^a	J_{obsd}
Cis ${}^3J_{\text{H-H}}$	$10 \cos^2 \phi$	6.6	3.3-6.6
Trans ${}^3J_{\text{H-H}}$	$11 \cos^2 \phi$	4.3	3.4-4.3
${}^3J_{\text{Pt-H}}(\text{NH}_2)$	$90 \cos^2 \phi$	37	28-38
${}^3J_{\text{Pt-H}}(\text{NHCH}_3)$	$81 \cos^2 \phi$	33	21-42
${}^3J_{\text{Pt-H}}(\text{N}(\text{CH}_3)_2)$	$72 \cos^2 \phi$	29	27-33

^a Based on model described in text. Coupling constants are all in Hz.

referred to as the ring-puckering angle, ω . To the extent that available conformations can be described by these two parameters, the conformers shown in Figure 6 can all be located on a surface in 3-space; *i.e.*, a plot of $E(z, \omega)$ vs. z and ω . Hawkins' calculations suggest that this surface is essentially a flat-bottomed bowl with the planar eclipsed conformation, IX, in the center and the other eight conformations arranged in roughly a circle around the base. Thus the orientation of a given substituent (H or CH₃) on the N or C atom is readily interconverted among several conformations, each having a different dihedral angle between coupled nuclei. The data for the 10 glycine chelates fit this model reasonably well, with observed *J* values lying close to those expected for such a surface. Deviations can be attributed to modifications of the energy surface.

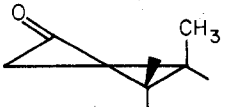
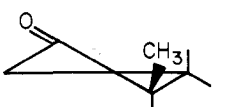
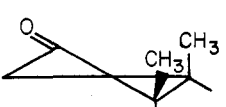
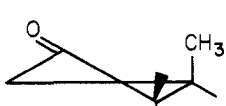
Dreiding models were used to estimate ω , z , and the appropriate dihedral angles between Pt and H or H and H for the nine conformations shown in Figure 6. Values of the corresponding coupling constants were calculated assuming a $\cos^2 \phi$ dihedral angle dependence and J_{trans} estimated from the literature or from the data for N-coordinated species.¹⁷ Average values for the nine conformations were calculated and are given in Table IV.

Conformational Implications of ${}^3J_{\text{Pt-H}}$ and ${}^3J_{\text{H-H}}$. The 3J values calculated for this simple model generally lie within the range of values observed for these 10 complexes. Deviations from the average values can be taken as evidence for some preference for particular nonplanar conformations. In assessing the conformational implications of the nmr data, it should be recognized that the dihedral angles responsible for variation in ${}^3J_{\text{Pt-H}}$, ${}^3J_{\text{H-H}}$, and ${}^4J_{\text{Pt-H}}$ will be similar for a given substituent in III, IV, V, and VI and in VII, VIII, I, and II. An intermediate value will be found for IX. Thus, it is only possible to state with confidence that there is some (usually slight) preference for conformations III-VI or VII-II. For simplicity, conformations I and V will be used to illustrate the conclusions but it should be emphasized that these are only representative of the range of conformations VII-II and III-VI. Excluding the four compounds which have a plane of symmetry, there are six compounds to consider. Conformational preferences for the six are summarized in Table V. The arguments which led to these conclusions are elaborated below.

The six compounds can best be considered in pairs, in increasing order of complexity, beginning with the monomethyl species Pt(ala)Cl₂⁻ and Pt(sarc)Cl₂⁻. The agreement between observed and calculated values for ${}^3J_{\text{H-H}}$ for Pt(sarc)Cl₂⁻ argues for very little conformational preference for the glycinate ring. However the small difference between ${}^3J_{\text{Pt-H}}$ for the two methylene protons requires a slight preference for conformations in which N-CH₃ is pseudoaxial. By contrast, for Pt(ala)Cl₂⁻, the comparatively small value for ${}^3J_{\text{Pt-H}}$

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Table V. Conformational Preferences of Glycinate Chelates

Compd	Preferred conformn indicated by nmr data
Pt(sarc)Cl ₂ ⁻	
Pt(ala)Cl ₂ ⁻	
cis-Pt(meala)Cl ₂ ⁻	
trans-Pt(meala)Cl ₂ ⁻	
Pt(dmala)Cl ₂ ⁻	Puckered; planar eclipsed form insignificant; no significant preference for puckering in either sense
Pt(meaba)Cl ₂ ⁻	Puckered; planar eclipsed form insignificant

(28 Hz) requires preference for the conformation in which C-CH₃ is pseudoequatorial.

The tendencies suggested by these data are more pronounced in the two isomers of Pt(meala)Cl₂⁻. For the cis isomer, unfavorable interaction between eclipsed N-CH₃ and C-CH₃ is apparently relieved most effectively by puckering in the sense suggested by the monomethyl derivatives; *i.e.*, with the C-CH₃ pseudoequatorial and the N-CH₃ pseudoaxial. This reduces ³J_{Pt-H} and ³J_{H-H} from corresponding values for the monomethyl species and indicates a greater conformational preference than that of either Pt(ala)Cl₂⁻ or Pt(sarc)Cl₂⁻. However, for *trans*-Pt(meala)Cl₂⁻, the large value of ³J_{Pt-H} indicates a preference for conformations in which both CH₃ groups are pseudoaxial. Apparently, the gauche CH₃-CH₃ interaction is too unfavorable to permit the C-CH₃ group to achieve its "normal" equatorial preference.

The equilibrium isomer ratio of *trans*- to *cis*-Pt(meala)Cl₂⁻ (~8) gives an indication of the magnitude of the unfavorability of the CH₃-CH₃ interaction. For the cis isomer, puckering in either sense fails to relieve this unfavorable interaction; for the *trans* isomer, puckering in the preferred sense provides that relief. If the rings were confined to the planar eclipsed conformation, the energy difference would be expected to be comparable to that between the two eclipsed forms of butane, which has been estimated to be 1.1-2.6 kcal mol⁻¹.¹⁸ The free energy difference calculated from the isomer ratio is ΔG° = RT ln 8 = 1.3 kcal mol⁻¹. In Co(III) complexes of *meala*, unfavorable interactions with axial groups produce essentially complete stereospecificity.¹⁹ By contrast, for the N-coordinated species availability of one rotamer which minimizes steric interactions for each isomer makes the two species essentially equally probable.

For the two trimethyl derivatives, Pt(dmala)Cl₂⁻ and Pt(maba)Cl₂⁻, the conformational situation seems to be similar. The chemical shift difference between the two N-CH₃ groups of Pt(dmala)Cl₂⁻ is approximately the same as that

between the two C-CH₃ groups of Pt(maba)Cl₂⁻. Since the magnetic anisotropies of the C-C or C-N bond, which are largely responsible for these differences, are similar,²⁰ the average orientation of the lone methyl group with respect to the pair of methyls on the adjacent atom must be similar. For Pt(dmala)Cl₂, the relatively small J_{Pt-H} (27 Hz) can be attributed entirely to the effect of the N-CH₃ groups and preference for either extreme conformation is not significant.

⁴J_{Pt-H} and the Conformational Energy Profile of Glycinate Chelates. On the basis of the data for N-coordinated species, it seems reasonable to expect that there should be a significant correlation between ⁴J_{Pt-H} and the conformational preference of C-CH₃ groups. The greater the pseudoequatorial preference for C-CH₃, the closer the Pt-N-C-C-H moiety approaches the favorable planar-W conformation²¹ and the larger ⁴J_{Pt-H} should be. If propeller rotation about the C-CH₃ bond is assumed to give a similar average orientation of CH bonds for all conformations and a cos² φ dependence is assumed for the Pt-N-C-CH₃ dihedral angle (⁴J_{Pt-H} = 8 cos² φ), the average ⁴J_{Pt-H} of the nine conformations shown in Figure 6 is 3.2 Hz. Observed values for several compounds lie close to this value, suggesting that the no-preference model and assumed dihedral angle dependence is reasonably sound. However, there are several discrepancies. The coupling in Pt(ala)Cl₂⁻ is immeasurably small in spite of evidence (³J_{Pt-H}) which shows clearly that the preferred orientation of C-CH₃ is pseudoequatorial. The two symmetric C-CH₃ species, Pt(aba)Cl₂⁻ and Pt(dmaba)Cl₂⁻, for which a preferred orientation is ruled out have both one of the smallest (~1 Hz) and one of the largest (3.1 Hz) ⁴J_{Pt-H} values. For the pseudoequatorial favoring C-CH₃ of *cis*-Pt(meala)Cl₂⁻, ⁴J_{Pt-H} is less than for the pseudoaxial favoring C-CH₃ of *trans*-Pt(meala)Cl₂⁻. Finally, the data for (*R,R*)-Pt(meala)(NH₃)₃⁺ and of Appleton and Hall show clearly that ⁴J_{Pt-H} decreases much more rapidly with dihedral angle than the cos² φ relation which was used in the above calculation. An alternative interpretation does not require rejection of conclusions based on ³J_{Pt-H} values and provides additional insight into the details of the potential energy surface.

A model which can account for the wide variation in ⁴J_{Pt-H} in these compounds is the following. (1) The three-dimensional potential energy surface is featureless (*i.e.*, shaped like a flat-bottomed bowl) for chelated glycine and is only tilted a little for monomethyl derivatives. (2) The energy of the planar eclipsed conformation increases more than that of puckered conformations (with either sense of puckering) whenever methyl substituents replace H's of both N and C. The extent of this upward "dent in the bowl" increases with methyl substitution. (3) ⁴J_{Pt-H} is very small (<1 Hz) for the planar eclipsed conformation and for any conformation in which C-CH₃ is pseudoaxial and reaches a significant value (~6 Hz) only for relatively large dihedral angles (CH₃ close to equatorial orientation).

In terms of this model, the effect of methyl substitution is to decrease the contribution from conformations close to the planar eclipsed conformation and, if the ligand is not symmetric, to produce some preference for particular puckered or envelope conformations. Thus ⁴J_{Pt-H} for Pt(aba)Cl₂⁻ is heavily weighted by contributions from the planar eclipsed conformation (⁴J_{Pt-H} < 1 Hz) while ⁴J_{Pt-H} for Pt(dmaba)Cl₂⁻ can be looked upon as an average over two equally probable puckered conformations. For one of these, ⁴J_{Pt-H} (equa-

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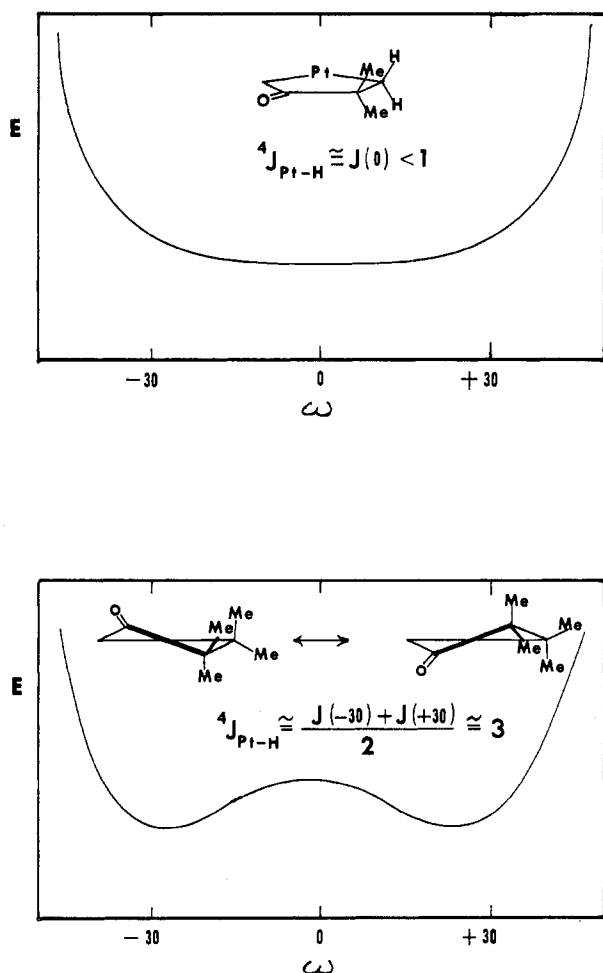


Figure 7. Effect of methyl substitution on conformational energy profile of $\text{Pt}(\text{aba})\text{Cl}_2^-$ and on ${}^4J_{\text{Pt-H}}$.

torial) $\cong 6$ Hz and ${}^4J_{\text{Pt-H}}(\text{obsd}) \cong \frac{1}{2}(6 + 0) = 3$ Hz. This is shown schematically in Figure 7.

The comparative effects of replacement of *N*-H protons by CH_3 groups on ${}^3J_{\text{Pt-H}}$ of CH_2 protons of glycine and ethylenediamine complexes can also be understood in terms of this model. The smaller relative decrease in ${}^3J_{\text{Pt-H}}$ resulting from methyl substitution on $\text{Pt}(\text{gly})\text{Cl}_2^-$ reflects a greater contribution from puckered species for which $J_{\text{obsd}} = \frac{1}{2}(J_{\text{ax}} + J_{\text{eq}})$. Since this average value is greater than that

expected for the eclipsed conformation, which is no doubt more important for $\text{Pt}(\text{gly})\text{Cl}_2^-$, the decrease in ${}^3J_{\text{Pt-H}}$ with methyl substitution on N is somewhat less than for comparable *en* complexes (39 to 33 Hz vs. 40 to 30 Hz).

Clearly it would be desirable to test the conclusions regarding the conformational situation in these complexes by energy minimization calculations. Such calculations are in progress and will be reported when they are completed. We have also begun to investigate effects of methyl substitution of *N*-H protons of chelated 1,2-propanediamine (*pn*) and 2,3-butanediamine (*bn*) on ${}^4J_{\text{Pt-N}}$ of C-CH_3 protons. If, as our data indicate, ${}^4J_{\text{Pt-H}}$ of C-CH_3 protons is a sensitive indicator of the conformational situation of the Pt-N-C-CH_3 moiety, we might expect to observe sizable coupling in *N*-substituted *pn* and *bn*, where conformational energy barriers might be expected to be higher than they are in *pn* complexes.²² The failure to observe long-range coupling between ${}^{195}\text{Pt}$ and C-CH_3 in *pn* complexes may indicate that the preference for pseudoequatorial orientation for the CH_3 group and the energy barrier to ring inversion may be much smaller than generally assumed.²³ Again the lack of axial groups in square-planar complexes may be an important factor.

Registry No. $\text{Pt}(\text{gly})\text{Cl}_2^-$, 17567-43-0; $\text{Pt}(\text{sarc})\text{Cl}_2^-$, 21791-00-4; $\text{Pt}(\text{dmgly})\text{Cl}_2^-$, 21791-01-5; $\text{Pt}(\text{ala})\text{Cl}_2^-$, 20332-84-7; *cis*- $\text{Pt}(\text{meala})\text{Cl}_2^-$, 37047-41-9; *trans*- $\text{Pt}(\text{meala})\text{Cl}_2^-$, 37047-42-0; $\text{Pt}(\text{dmala})\text{Cl}_2^-$, 37047-43-1; $\text{Pt}(\text{aba})\text{Cl}_2^-$, 21791-02-6; $\text{Pt}(\text{meaba})\text{Cl}_2^-$, 37047-45-3; $\text{Pt}(\text{dmaba})\text{Cl}_2^-$, 37047-46-4; $\text{Pt}(\text{gly})(\text{NH}_3)_3^+$, 37047-47-5; $\text{Pt}(\text{sarc})(\text{NH}_3)_3^+$, 37047-48-6; $\text{Pt}(\text{ala})(\text{NH}_3)_3^+$, 37047-49-7; (R,R)- $\text{Pt}(\text{meala})(\text{NH}_3)_3^+$, 37047-50-0; (S,R)- $\text{Pt}(\text{meala})(\text{NH}_3)_3^+$, 37047-34-0; $\text{Pt}(\text{aba})(\text{NH}_3)_3^+$, 37047-35-1; $\text{Pt}(\text{meaba})(\text{NH}_3)_3^+$, 37047-36-2.

Acknowledgments. Support for this research was provided by the National Science Foundation research (GP-19229) and undergraduate research participation (GY-8833) grants and by the Sloan Foundation through a grant to Grinnell College. The assistance of Dr. J. Philip Bays (Argonne National Laboratory) and Dr. Paul Gilles (University of Kansas) in obtaining 100-MHz nmr spectra of some samples is gratefully acknowledged.

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