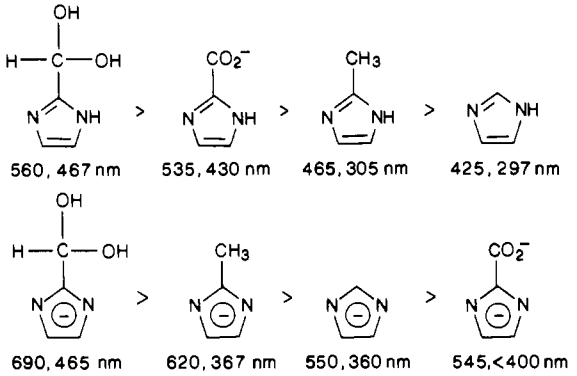
data is compatible with the following π-donor order for both the neutral ligand and the imidazolato form of the ligand for these rings (LMCT band positions are listed below each ring for the $(NH_3)_5Ru^{III}L$ complex):



It appears that the extra ionic charge of $2CO_2imH^-$ is an advantage in its role of π-donation for the parent imidazole series, but loses importance relative to a full anion charge localized on the five-membered ring. Therefore its position in the π-donor series shifts below im^- and above $2CH_3imH$; the other neutral R substituents remain in their logical electron-releasing order: $CH(OH)_2 \geq CH_3 > H$. Once the imidazolato form is created by deprotonation of the neutral parent ring structure, less assistance is provided by the 2-substituent in lowering the $d\pi \leftarrow (\pi_1)_L$ transition energy. The additional shifts on the π_1-based transition are calculated to be 3364 cm^{-1}, R = $-CH(OH)_2$; 4737 cm^{-1}, R = $-CH_2^-$; 5376 cm^{-1}, R = $-CH_3$; and 5347 cm^{-1}, R = H. Therefore $-CH_3$ is actually the better releasing group toward the anionic ring, compared to R = $-CH(OH)_2$.

Acknowledgment. We gratefully acknowledge the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Contribution from the Department of Chemistry and Ames Laboratory of the U.S. Department of Energy, Iowa State University, Ames, Iowa 50011

Study of Stereodynamics by Variable-Temperature ^{195}Pt NMR Spectroscopy. Diastereomerism in Platinum(II) Thioether Complexes and Solvent Effects

John A. Galbraith, Kent A. Menzel, Eva Marie A. Ratilla, and Nenad M. Kostić*

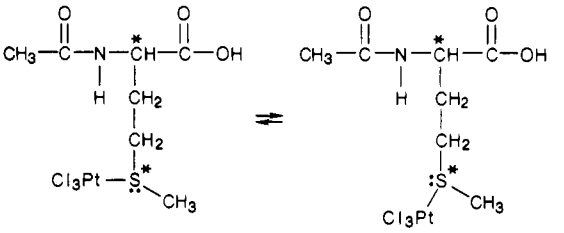
Received December 23, 1986

We have synthesized and characterized new $[PtCl_3(thioether)]^-$ complexes with the following thioethers as unidentate ligands: *N*-formyl-DL-homomethionine (FHMetH), *N*-acetyl-L-methionine (AcMetH), *N*-acetyl-*S*-methyl-DL-cysteine (AcMeCysH), DL-3-(methylthio)-1,2-propanediol (MTPD), and DL-3-(methylthio)-2-butanone (MTB). These complexes constitute a series in which the length of the $(CH_2)_x$ chain connecting the chiral carbon and sulfur atoms is varied systematically: x = 3, 2, 1, 1, and 0, respectively. Each of the complexes exists in two diastereomeric forms, which are related by intramolecular inversion of configuration at the coordinated sulfur atom. The diastereomers are clearly evident in the ^{195}Pt NMR spectra, whose dependence on temperature yields the ΔG^* values for inversion. Stereodynamic processes involving all but the simplest thioether ligands and processes resulting in subtle changes in molecular structure proved intractable by the common ^1H and ^{13}C NMR methods. The barrier to inversion depends on the solvating ability of the medium in an interesting way. Small amounts of diglyme in aqueous solution reduce the difference in chemical shifts between the ^{195}Pt NMR peaks of the diastereomers and thus lower the coalescence temperature, but they do not affect the barrier significantly. Large amounts of diglyme, however, lessen the stabilizing effect of hydration upon the thioether complex and lower the barrier. In unidentate complexes, which have flexible structures, the chiral C atom provides virtually no discrimination between the two configurations of the chiral S atom irrespective of the length of the $(CH_2)_x$ chain between the two atoms. Significant discrimination is evident, however, in the bidentate complex *cis*-$[PtCl_2(MeCysH)]$. Steric constraint, such as that provided by chelation, seems to be a prerequisite for chiral discrimination.

Introduction

Inversion of the pyramidal configuration at coordinated chalcogen atoms (S, Se, and Te) has been observed in various metal complexes.[1] Virtually all of these studies are based on the principle that inversion causes an interchange of diastereotopic H atoms in the prochiral CH_2 group and consequently gives rise to the collapse of an AB quartet into a singlet in the ^1H NMR spectrum. Although elegant experiments have been based on this stereochemical principle, reliance on it, and on the corresponding ^1H NMR techniques, has restricted previous studies to complexes containing relatively simple ligands of the $(RCH_2)_2S$ and RCH_2SCH_2R' types and to the corresponding bidentates, for which the collapse of the methylene quartet upon heating is easily discernible.

Stereodynamic studies of metal complexes with biological ligands and, ultimately, with proteins clearly demand a different experimental method. In a previous publication[2] we reported on sulfur inversion in the complex $[PtCl_3(AcMetH)]^-$, the process shown in eq 1. With *N*-acetyl-L-methionine acting as a unidentate


(1)

thioether ligand, this complex is a realistic model for the binding of $PtCl_3^-$ label to the side chain of a methionine residue in proteins. The inversion process even in this relatively simple compound proved intractable by the common methods of ^1H and ^{13}C NMR spectroscopy. The corresponding ^1H and ^{13}C signals of the diastereomers were already coalesced at 278 K. In other words, the ^1H and ^{13}C nuclei proved insufficiently sensitive to the minor structural changes caused by inversion at the sulfur atom.

Owing to the great dependence of the ^{195}Pt chemical shift on the ligand atoms and on the more distant environment,[3-7] ^{195}Pt

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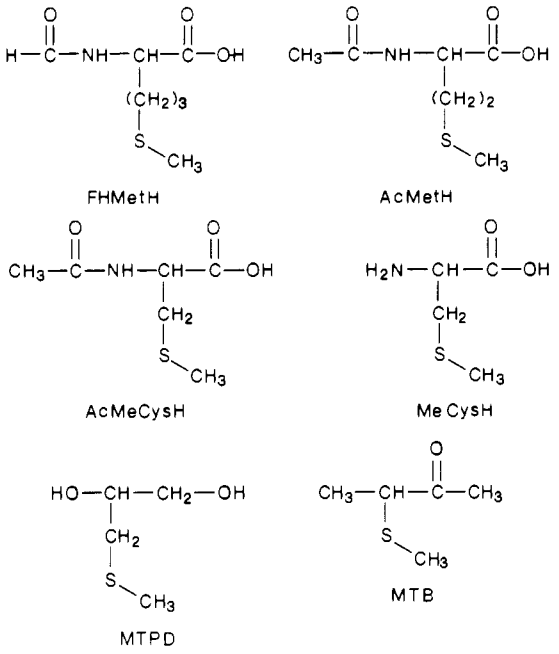
NMR spectroscopy proved uniquely suited to the task. The spectrum of the two diastereomers, consisting of two clearly resolved signals, is as simple as it can be. Its variation with temperature yielded $\Delta G^{\ddagger} = 63.7$ kJ mol^{-1} at 335 K.[2] This study demonstrated the great potential of variable-temperature ^{195}Pt NMR spectroscopy as a method for the study of stereodynamics.

The ^{195}Pt NMR signals due to the two diastereomers of $[PtCl_3(AcMetH)]^-$ have virtually equal intensities. The chiral carbon atom evidently does not discriminate between the two configurations at the chiral sulfur atom, presumably because the $(CH_2)_2$ chain precludes any appreciable interaction between them. To examine the factors governing chiral discrimination and stereodynamics in metal complexes with thioether ligands, we varied systematically the separation between the carbon and sulfur atoms in the following unidentate ligands: *N*-formyl-DL-homomethionine (FHMetH), *N*-acetyl-*S*-methyl-DL-cysteine (AcMeCysH), DL-3-(methylthio)-1,2-propanediol (MTPD), and DL-3-(methylthio)-2-butanone (MTB). A chelate complex of *S*-methyl-L-cysteine (MeCysH) was included for comparison.



Materials and Methods

Chemicals. The ligands MTPD and MTB and deuteriated solvents were obtained from Aldrich Chemical Co. and the ligand MeCysH was purchased from Sigma Chemical Co. K_2PtCl_4 was obtained from Aldrich Chemical Co. and borrowed from Johnson Matthey, Inc.

NMR Measurements. The ^{1}H (at 300 MHz) and ^{13}C (at 74.5 MHz) NMR spectra were recorded with a Nicolet NT 300 spectrometer, using residual H_2O, acetone, and dioxane as internal standards. The ^{195}Pt NMR spectra of unenriched samples were recorded with a Bruker WM 300 spectrometer at 64.4 MHz, using 10- and 20-mm probes. Solvents contained ca. 25% of the deuterio isotopomer for lock and were made 0.5 M in HCl in order to prevent decomposition of the complexes. Each spectrum was acquired in 8K data points, with two sets of parameters, corresponding respectively to the spectral width, pulse duration, tilt angle, and delay time. With the 10-mm probe, they were as follows: 100 kHz, 10 μs, 13°, 200 ms; 20 kHz, 65 μs, 90°, 3300 ms. With the 20-mm probe, they were as follows: 20 kHz, 100 μs, 90°, 500 ms; 50 kHz, 50 μs, 45°, 200 ms. The sample temperature was maintained within ±0.5 K with the Bruker variable-temperature controller. A solution of K_2PtCl_4 in aqueous NaCl, kept in a coaxial inset tube, was used as an external reference at room temperature. The ^{195}Pt chemical shift at 294 K with respect to the $PtCl_6^{2-}$ standard can be obtained by subtracting 1614 ppm from the corresponding value with respect to the $PtCl_4^{2-}$ reference.[3] Signals occurring at stronger fields than the reference signal have negative chemical shifts. The chemical shifts of $PtCl_4^{2-}$ and $PtCl_6^{2-}$, ions with similar compositions and identical charges, depend similarly on temperature.[3,8] Since these temperature effects are small and the range of ^{195}Pt shifts is extremely wide, the use of the same correction factor at other temperatures would have little, if any, effect on the discussion and conclusions.

Synthesis of the Ligands. *N*-Formyl-DL-homomethionine (FHMetH) was prepared according to the published procedure[9] and its purity proved on the basis of its melting point (397 K) and of its ^{1}H NMR spectrum (δ values) in CD_3OD: 1.52–1.82, m, $^{\beta}CH_2{}^{\gamma}CH_2$; 1.94, s, CH_3S; 2.39, t, CH_2S; 4.37, t, $^{\alpha}CH$; 7.98, s, C(O)H. *N*-Acetyl-*S*-methyl-DL-cysteine (AcMeCysH) was prepared by acetylation of *S*-methyl-DL-cysteine according to the procedure developed for methionine.[10] The purity of the ligand was proved by its sharp melting point (426 K) and by its ^{1}H NMR spectrum (δ values) in 0.5 M DCl: 1.81, s, $CH_3C(O)$; 1.88, s, CH_3S; 2.73, m, CH_2S; and 4.35, q, $^{\alpha}CH$.

Synthesis of $AsPh_4[PtCl_3(FHMetH)]\cdot H_2O$. A solution of 30 mg (0.16 mmol) of the ligand FHMetH in 0.75 mL of methanol was added dropwise, with stirring, to a solution of 65 mg (0.16 mmol) of K_2PtCl_4 in 1.25 mL of 0.5 M HCl. Both solutions were shielded from light. The color changed from red to yellow during the mixing. The reaction mixture was stirred, in the dark, for 30 min at room temperature and then centrifuged. A solution of 70 mg (0.17 mmol) of $AsPh_4Cl$ in 1.25 mL of water was added to it dropwise, with stirring. The mixture was centrifuged and the clear, nearly colorless, supernatant removed with a pipet. The sticky residue was washed, by stirring, with several 3-mL portions of cold water. The residue, still a gum, was dried in vacuo, dissolved in 2 mL of methanol, and centrifuged. The clear solution was evaporated to dryness to yield 56 mg or 40% of orange microcrystals, whose melting point was ca. 353 K. Anal. Found (calcd): C, 41.55 (41.65); H, 4.39 (3.93); N, 1.40 (1.57); S, 3.80 (3.59). Proton NMR spectrum (δ values) in CD_3OD: 1.88–1.99, br, $^{\alpha}CH_2{}^{\beta}CH_2$; 2.26, t, ^3J(Pt–H) = 45.9 Hz, CH_3S; 2.93, br, CH_2S; 4.46, br s, $^{\alpha}CH$; 8.07, s, C(O)H.

Synthesis of $AsPh_4[PtCl_3(MTPD)]\cdot H_2O$. The reaction between a solution of 21 μL (0.20 mmol) of MTPD in 1 mL of water and a solution of 83 mg (0.20 mmol) of K_2PtCl_4 in 1.5 mL of water was carried out as described above for the FHMetH complex. The precipitate was obtained with a solution of 90 mg (0.215 mmol) of $AsPh_4Cl$ in 1.5 mL of water. Since the resulting salt is slightly soluble in water, the supernatant remained pale yellow. The washed and dried residue was dissolved in 2 mL of acetone and ca. 6 mg of an insoluble material removed by centrifugation. Acetone was removed by distillation and the residue dried in an evacuated, desiccated Abderhalden apparatus in refluxing dichloromethane: yield 96 mg, 50%; mp ca. 325 K. Anal. Found (calcd): C, 40.60 (40.77); H, 3.71 (3.91). Proton NMR spectrum (δ values) in acetone-d_6: 2.29, t, ^3J(Pt–H) = 46.2 Hz, CH_3S; 3.10, br, CH_2S; 3.59, br, CH_2O; 3.76, t, CH; 4.18, br, 2 OH; 7.88, m, 4 Ph.

Synthesis of $K[PtCl_3(AcMeCysH)]$. The reaction between 88.6 mg (0.50 mmol) of AcMeCysH and 208 mg (0.5 mmol) of K_2PtCl_4 was carried out as described for the analogous complex of *N*-acetyl-L-methionine.[2]

Synthesis of $AsPh_4[PtCl_3(MTB)]\cdot H_2O$. A solution of 24 μL (0.20 mmol) of MTB in 0.2 mL of acetone was added, in the dark, to a stirred solution of 83.1 mg (0.20 mmol) of K_2PtCl_4 in 1.5 mL of 0.5 M HCl. After brief heating in a water bath and standing at room temperature overnight, the reaction mixture was centrifuged and the clear, golden yellow supernatant removed with a pipet. A solution of 90 mg (0.22 mmol) of $AsPh_4Cl$ in 1.5 mL of water was added, dropwise, to the stirred supernatant. The precipitate was sticky at first but became dispersed after thorough stirring. The salt was removed by centrifugation, washed with 3-mL portions of cold water as described for the FHMetH complex, and dried in vacuo. The dry solid was dissolved in 2 mL of methanol and left in the dark for 1 week. A small amount of solid material was removed by centrifugation and methanol removed by vacuum distillation. The yield of the orange microcrystalline powder was 110 mg or 70%; the melting point was ca. 405 K. Anal. Found (calcd): C, 42.27 (42.42); H, 3.81 (3.93); S, 3.98 (3.91); Cl, 13.0 (13.0). Proton NMR spectrum (δ values) in acetone-d_6: 1.50, d, J = 6.9 Hz, CH_3CH; 2.10, t, ^3J(Pt–H) = 45.6 Hz, CH_3S; 2.4, br, $CH_3C(O)$; 4.27, br, CH; 7.88, m, 4 Ph.

Synthesis of $NBu_4[PtCl_3(MTB)]$. This salt was obtained by the procedure described above for the $AsPh_4$ salt, except that precipitation was effected with 63 mg (0.22 mmol) of NBu_4Cl. Proton NMR spectrum (δ values) in acetone-d_6: 0.98, t, CH_3 in Bu; 1.46, sextet, J = 6.9 Hz, CH_3CH_2 in Bu; 1.54, d, J = 6.9 Hz, CH_3CH; 1.82, m, NCH_2CH_2 in Bu; 2.16, t, ^3J(Pt–H) = 45.2 Hz, CH_3S; 2.4, br, $CH_3C(O)$; 3.47, m, NCH_2 in Bu; 4.31, br, CH.

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Scheme I

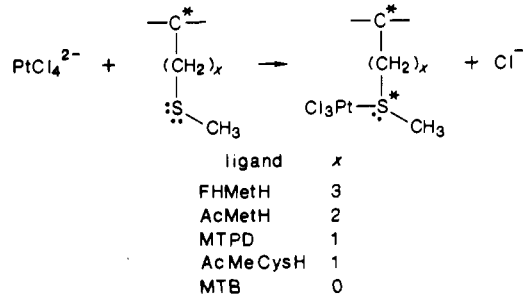


Table I. Principal ^1H NMR Spectroscopic Data for Unidentate $PtCl_3$(thioether)$^-$ Complexes

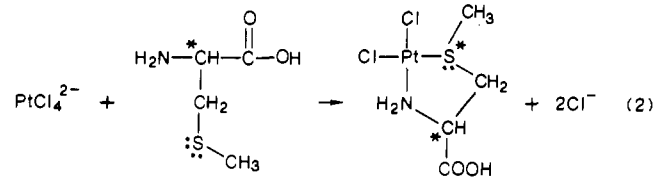
thioether ligand	downfield shift of CH_3S res upon coord, ppm	$^3J(^{195}Pt-^1H)$ in $PtSCH_3$, Hz
FHMetH	0.32	45.9
AcMetH[a]	0.31	49.6
MTPD	0.34	46.2
AcMeCysH	0.34	47.4
MTB	0.24	45.2

[a] Reference 2.

Synthesis of *cis*-[$PtCl_2$(MeCysH)]. This complex was prepared according to published procedures.[11,12]

Formation of Complexes and Their Characterization

FHMetH, AcMetH, MTPD, AcMeCysH, and MTB displace one Cl^- ligand and coordinate to the Pt(II) atom as monodentate thioethers, as shown in Scheme I. The AcMetH complex was a subject of our previous publication.[2] MeCysH forms a chelate complex,[11,12] as shown in eq 2. All the complexes are stable in



(2)

solution and as solid salts.

Comparisons between the ^1H NMR spectra of the complexes and those of the free ligands reveal the expected effects of coordination—movement of the ligand resonances downfield owing to the deshielding effect of the Pt(II) atom. Particularly informative is the triplet with relative intensities 1:4:1, arising from the three-bond coupling $^{195}Pt-^1H$ in $PtSCH_3$, the fragment present in all of the complexes. The spectroscopic data in Table I agree fully with the corresponding values for simpler complexes containing the *trans*-$ClPt^{II}S(CH_3)_2$ fragment.[13-15]

Inversion of Configuration at the Sulfur Atom

Since the chiral carbon atom in each of the ligands is stable toward racemization under the conditions of our experiments, the chirality of the sulfur atom gives rise to two diastereomers, shown in Scheme II. (The same consideration applies to complexes synthesized from optically active and from racemic ligands.) Owing to the rather narrow ranges of chemical shifts that they span, the ^1H and ^{13}C nuclei are insufficiently sensitive to the small differences in the molecular environment, such as those existing between the two diastereomers. Moreover, the ^1H NMR spectra of all the ligands for which $x > 0$ proved too complex to permit

Scheme II

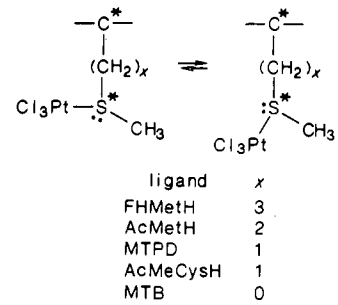


Table II. Barriers to Inversion of Sulfur Configuration in Unidentate [$PtCl_3$(thioether)]$^-$ Complexes, As Determined by Variable-Temperature ^{195}Pt NMR Spectroscopy

thioether ligand	x in $C^*(CH_2)_xS^*$	solvent 0.5 M HCl: diglyme	coalescence temp, T_c, K	ΔG^* at T_c, kJ mol^{-1}
FHMetH	3	*a*	~250	
AcMetH[b]	2	6:1	335	66.7
MTPD	1	1:0	>376	
		1:2	353	66.4
AcMeCysH	1	1:0	>376	
		4:1	>376	
		2:1	>376	
		1:1	>376	
		1:2	>376	
MTB	0	1:0	370	70.6
		6:1	367	70.1
		4:1	363	69.3
		1:1	338	64.5
		2:3	300	57.3
		1:2	<290	

[a] The solvent is acetone for the FHMetH complex. [b] Reference 2.

a reliable identification of the corresponding resonances of the two diastereomers. The superposed effects of $^{195}Pt-^1H$ coupling, $^1H-^1H$ coupling, and diastereomerism obfuscate the spectroscopic information regarding the third of these phenomena. Although the ^1H and ^{13}C spectra proved somewhat useful in the case of the MTB complex (for which $x = 0$), the NMR methods based on these two nuclei are neither generally applicable nor convenient.

Barriers to Inversion. The larger the frequency difference between the NMR signals of the isomers, the higher the temperature (designated T_c) at which the signals will coalesce as the isomers interconvert.[16-19] Unlike those of ^1H and ^{13}C, the known chemical shifts of the ^{195}Pt nucleus span a range of some 15 000 ppm.[5] Unlike the ^1H or ^{13}C resonances of the two diastereomers, which are already coalesced below 273 K, the ^{195}Pt resonances are well-separated (by 6–35 ppm, i.e., by 386–2250 Hz, depending on the thioether ligand) at room temperature. In all the unidentate complexes except that of AcMeCysH, the resonances coalesce in the accessible temperature region, as Table II shows.

The ^{195}Pt chemical shifts of all the unidentate complexes, listed in Table III, fall near the value of −1143 ppm (vs. $PtCl_4^{2-}$), found for the simple thioether complex [$PtCl_3(SMe_2)$]$^-$.[3,8] This agreement indicates again that all the ligands shown in Schemes I and II are coordinated to Pt(II) as unidentate thioethers. The small and uniform movement of the signals downfield (toward less negative values) upon heating agrees with the known temperature dependence of the ^{195}Pt chemical shift in anionic complexes.[3,8] All the temperature-related changes are reversible. The barriers to inversion, i.e., the ΔG^* values at the respective coalescence temperatures, were determined as explained in our previous report.[2,16-19] The results are presented in Table II, and a typical set of spectra is shown in Figure 1.

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Table III. Platinum-195 NMR Spectra of Unidentate $[PtCl_3(thioether)]^-$ Complexes and of the Bidentate *cis*-$[PtCl_2(MeCysH)]$ Complex

thioether ligand	x in $C^*(CH_2)_xS^*$	solvent	chem shifts, ν, ppm[c]	$\Delta\nu$, ppm (temp, K)	intens ratio
FHMetH	3	acetone	−1147, −1152	5 (200)	1.0:1.0
AcMetH[a]	2	6:1 0.5 M HCl: diglyme	−1168, −1174	6 (278)	1.0:1.0
MTPD	1	0.5 M HCl	−1152, −1171	19 (294)	1.0:1.2
AcMeCysH	1	0.5 M HCl	−1145, −1179	34 (294)	1.0:1.2
MTB	0	0.5 M HCl	−1124, −1138	14 (294)	1.0:1.0
MeCysH[b]	1	DMF	−1381, −1414	33 (294)	2.6:1.0

[a] Reference 2. [b] Coordinated as S,N-bidentate ligand. [c] Referenced to $PtCl_4^{2-}$.

The coalescence of ^{195}Pt peaks may, in principle, be explained in terms of several mechanisms. (1) Since the values of ΔG^* are relatively large, the substituents on the S atom rather heavy, and species in Scheme II diastereomers, nuclear tunneling can be ruled out.[1] (2) Dissociation of one of these substituents and subsequent recombination can also be ruled out. This mechanism would require an activation energy far in excess of the values obtained and would not permit the sharpening of the ^{195}Pt NMR signal above the coalescence temperature, a phenomenon we observed in several cases. Other Pt(II)–thioether complexes were shown to maintain the ^1H–^{195}Pt coupling above the coalescence temperature[1,20a] and not to exchange the thioether ligands.[1,20b] (3) Since the T_c and ΔG^* values proved to be independent of the concentration of the complex in several experiments, bimolecular exchange can also be ruled out.[1] (4) We conclude that the temperature dependence of the ^{195}Pt NMR patterns is caused by intramolecular inversion of configuration at the chiral S atom. Indeed, the values of ΔG^* fall in the middle of the rather narrow range of such data obtained for Pt(II) complexes with common thioether ligands.[1]

Although the ^{195}Pt chemical shifts of the two diastereomers depend on temperature, the coalescence of the corresponding NMR signals is not due simply to their merger upon heating. The temperature coefficients of both signals in Figure 1 at lower temperatures, while they are still separate, is 0.4 ppm K^{-1}, consistent with the known values for similar complexes.[3a,8,21] Since the temperature coefficient depends mainly on charge[8] and is insensitive even to the geometric isomerism,[21] it is understandable that the two diastereomers, which have the same composition and charge, should have the same temperature coefficient of the ^{195}Pt chemical shift. In the absence of the inversion, therefore, the separation between the two peaks, $\Delta\nu$, should remain constant upon heating.

The spectra in Figure 1 clearly demonstrate the broadening of the signals around the coalescence temperature and sharpening of the signal above this temperature. The line widths (in Hz) of the five spectra, in order of increasing temperature, are as follows: 123 and 113, 225 and 266, 256 and 276, 429, and 272. This pattern of line widths is fully consistent with intramolecular inversion as the cause of the coalescence. The spectra of the $[PtCl_3(MTPD)]^-$ complex, shown in Figure 2, exhibit even larger broadening near T_c because the $\Delta\nu$ value for this complex is greater than that for the MTB complex.

The FHMetH complex, which has the longest side chain (x = 3), already exhibits a single ^{195}Pt NMR signal at 294 and 273 K. Upon cooling, however, this signal splits into two, which move apart as the temperature decreases; their separation is 2 ppm at 235 K and 5 ppm at 200 K, the lowest temperature accessible. Since the process of interchange could not be frozen to obtain the limiting value of $\Delta\nu$, which is necessary for calculation of the ΔG^* barrier, there was no need for an accurate value of the coalescence temperature, either.

The ^{195}Pt signals due to the diastereomers of the AcMeCysH complex were 34 ppm apart when pure aqueous solvent was used and 27 ppm apart when the solvent was two–thirds diglyme;

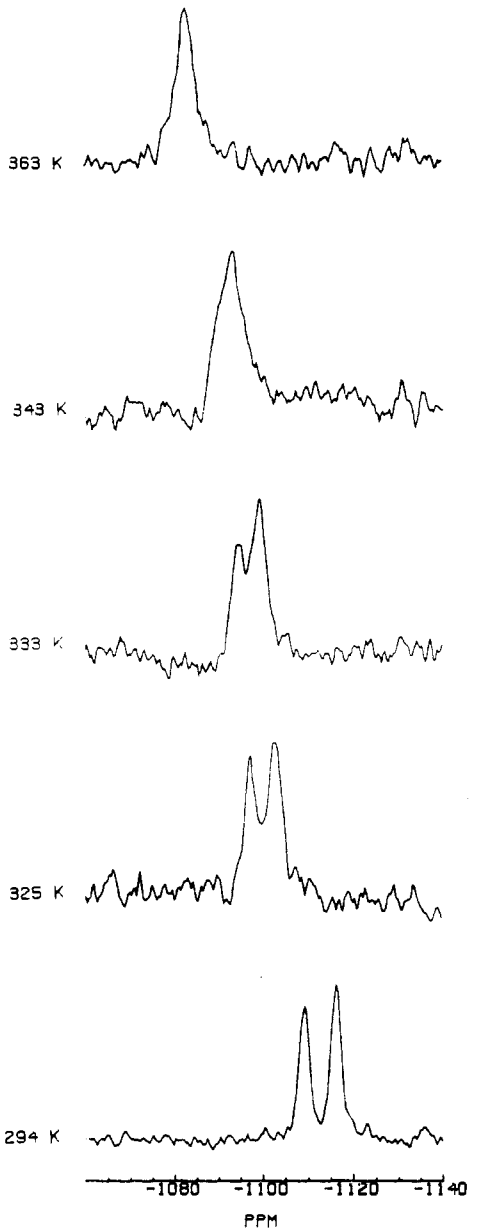

Figure 1. Variable-temperature ^{195}Pt NMR spectra of $[PtCl_3(MTB)]^-$ in a solution containing 0.5 M DCl and diglyme in the ratio of 1:1. MTB stands for DL-3-(methylthio)-2-butanone. The chemical shifts are referenced to $PtCl_4^{2-}$ ion at 294 K.

intermediate separations were obtained with solvents of intermediate compositions. In no case were the signals close enough to permit coalescence in the accessible range of temperatures.

Dependence of Inversion Barrier on Solvent. In order to extend the temperature range in which ^{195}Pt NMR spectra could be measured, we added diglyme, which has a high boiling point and low freezing point, to the solutions of complexes in 0.5 M HCl. The temperature range did expand, as expected, but some unexpected phenomena occurred as well. These interesting ad-

(20) (a) Cross, R. J.; Green, T. H.; Keat, R. *J. Chem. Soc., Dalton Trans.* **1976**, 1150. (b) Cross, R. J.; Green, T. H.; Keat, R.; Patterson, J. F. *J. Chem. Soc., Dalton Trans.* **1976**, 1486.
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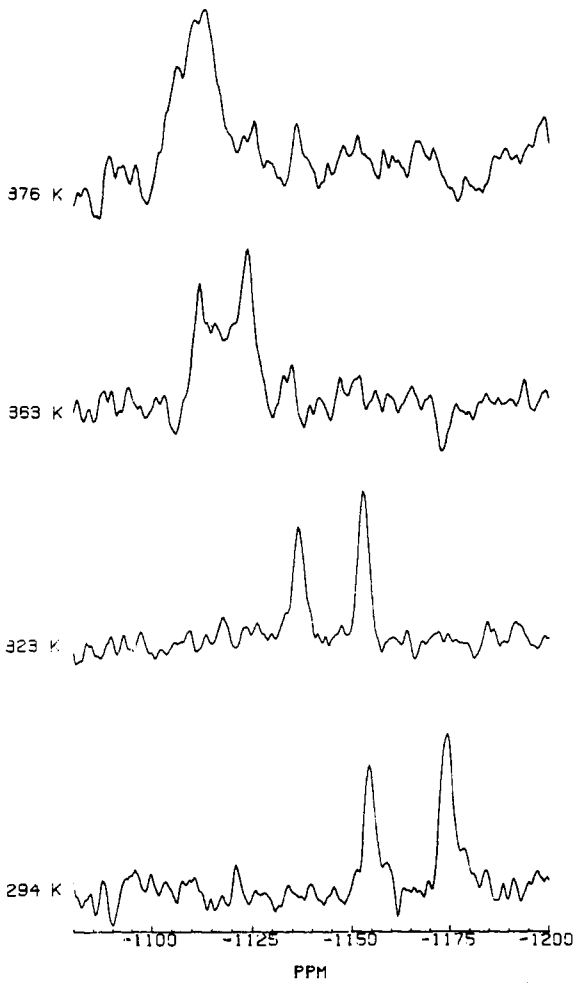


Figure 2. Variable-temperature ^{195}Pt NMR spectra of $[PtCl_3(MTPD)]^-$ dissolved in 0.5 M DCl. MTPD stands for DL-3-(methylthio)-1,2-propanediol. The chemical shifts are referenced to $PtCl_4^{2-}$ ion at 294 K.

Table IV. Effect of Solvent Composition on the ^{195}Pt NMR Spectrum of $[PtCl_3(MTB)]^-$ at 294 K

0.5 M HCl: diglyme	chem shift, ν, ppm[a]	$\Delta\nu$, ppm
1:0	−1123, −1138	15
6:1	−1126, −1140	14
4:1	−1119, −1132	13
2:1	−1111, −1120	9
1:1	−1109, −1116	7
2:3	−1107, −1109	2
1:2	−1110	0

[a] Referenced to $PtCl_4^{2-}$.

ditional effects are best examined in the case of the MTB complex, on the basis of the data in Tables II and IV.

Addition of diglyme causes small changes in the signal positions, an effect not unusual in view of the general dependence of ^{195}Pt chemical shift on solvent properties. As long as diglyme remains the minor constituent (less than ca. 10%) of the solvent, it merely raises the boiling point, the original purpose for its use. When more abundant, but still the minor constituent (up to ca. 20%), it reduces the separation between the diastereomer signals and thus lowers the coalescence temperature; the inversion process itself appears to remain virtually unaffected, however, because the ΔG^* value changes only slightly. Further increase in the fraction of diglyme brings about a significant decrease in the barrier to inversion, an indication that the process itself has been affected. When the excess of diglyme over the aqueous component becomes approximately twofold, the signals of the two diastereomers already become coalesced below room temperature. All the solvent-related changes are reversed when the solvent is restored to its original composition.

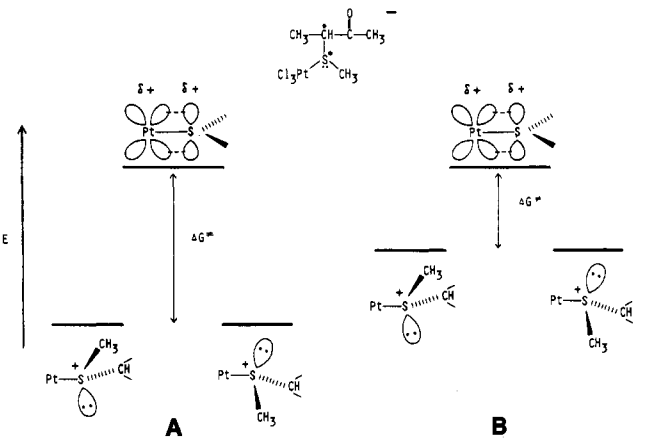


Figure 3. Dependence of the barrier to sulfur inversion in $[PtCl_3(MTB)]^-$ on the solvent composition: (A) aqueous solvent; (B) solvent richer in diglyme than in water. MTB stands for DL-3-(methylthio)-2-butanone.

The first effect of diglyme—lowering of the coalescence temperature for the given stereodynamic process—would otherwise require use of an NMR spectrometer with a weaker magnet. Our findings indicate that the same can perhaps be accomplished simply by a judicious choice of the solvent. In the MTB case the decrease in $\Delta\nu$ is large (see Table IV) and T_c is accessible. In the MTPD case the decrease in $\Delta\nu$ is small (see above) and the corresponding lowering of T_c is insufficient to render it accessible in the strong magnetic field (64.4 MHz for ^{195}Pt). The solvent effect is evident in both cases. The difference in degree between the MTB and MTPD complexes may be related to the difference between the ligands: whereas the former is hydrophobic, the latter contains two OH groups and is hydrophilic. The exact cause of the difference is not clear.

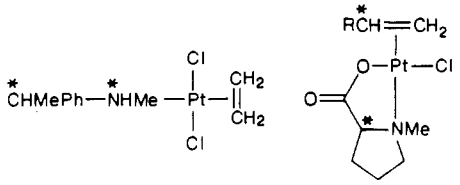
This interesting solvent effect is not limited to diglyme; acetone and perhaps *N*,*N*-dimethylformamide (DMF) behave similarly. Since the MTB complex, the simplest one used in this study, gives rise to a tractable ^1H spectrum, we compared ^1H NMR spectra of $[PtCl_3(MTB)]^-$ in solutions in which the ratio D_2O:acetone-d_6 was 1:0, 2:1, 1:2, and 0:1. Addition of acetone caused the CH_3S and the CH_3CH peaks of the two diastereomers, which were distinct in the D_2O solution, to gradually merge and coalesce at room temperature. Although DMF reduces $\Delta\nu$ in a desired way, the coordinating ability of this solvent, albeit weak, limits its applicability.

Future studies will tell whether solvent effects can be used profitably in stereodynamic studies. A suitable liquid must be miscible with the principal solvent (usually water) and compatible with the solute and should raise the boiling point, lower the freezing point, or both. A simple method for lowering the coalescence temperature would be highly desirable in the work with biomolecules, many of which have limited thermal stability.

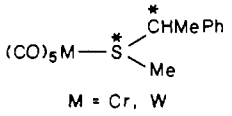
The second effect of diglyme—gradual lowering of the barrier to inversion—can perhaps be explained with reference to Figure 3. In a simple view, a thioether complex is akin to a sulfonium ion: the pyramidal, trivalent S atom bears a positive formal charge. In the transition state, π back-donation of the p → d type between the planar S atom and the Pt atom, an interaction allowed by symmetry, would cause partial dispersal of the positive charge. Although both the pyramidal and the planar structure are solvated by water, this stabilizing effect probably is greater for the pyramidal structure because the charge in it is more localized. As diglyme is added and water excluded from the solute, the differential stabilization of the pyramidal form relative to the planar one decreases and the barrier to inversion is lowered.

Chiral Discrimination

Stereoselectivity in chemical reactions often results from small details of molecular structure, which the ^{195}Pt nucleus evidently can sense. The potential of ^{195}Pt NMR spectroscopy in the study of diastereomerism went virtually unrecognized prior to our work. For only two compounds



has the ^{195}Pt chemical shift beeen shown to depend on diastereomerism.[22,23] The chromium and tungsten carbonyl complexes[24]



M = Cr, W

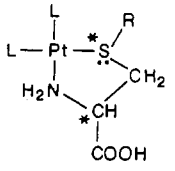
are related to our platinum complexes, for they contain a chiral, unidentate thioether ligand. The present study seems to be the first one devoted to a systematic examination of chiral (in)discrimination in a series of homologous Pt complexes by means of ^{195}Pt NMR spectroscopy.

Unidentate Complexes. The relative intensities of the resonances, presented in Table III, indicate that in each of the unidentate thioether complexes the diastereomers, shown in Scheme II, have nearly equal abundance. In other words, the chiral carbon atom provides virtually no discrimination between the two configurations of the chiral sulfur atom irrespective of the length of the methylene chain between these two atoms. The difference between the ^{195}Pt chemical shifts of the two diastereomers probably is a consequence of long-range, noncovalent interactions of the Pt atom with the different substituents at the chiral carbon atom.[2] Since the difference evidently is small, these interactions probably are weak or similar in the diastereomers, or both. Since the diastereomers evidently are very similar in properties and in stability, an attempt to assign the ^{195}Pt NMR peaks to them, i.e., to assign absolute configurations, would be unwarranted.

Salts of the $[PtCl_3(MTB)]^-$ complex with the cations K^+ and $AsPh_4$ give virtually identical ^{195}Pt NMR spectra. Properties of the counterion evidently have no significant effect on the relative abundance of the two diastereomers.

The findings regarding the platinum thioether complexes agree with those regarding the $Cr(CO)_5(SMe(CHMePh))$ complex, shown above, for which the diastereomeric ratio is 6:4.[24] To our knowledge, this chromium complex and the platinum complexes reported herein are the only examples of diastereomerism due to the unidentate thioether ligand.

Chelate Complexes. In search of the thioether complex that would exhibit chiral discrimination, we examined the compound *cis*-$[PtCl_2(MeCysH)]$, in which *S*-methyl-L-cysteine acts as a bidentate ligand, as shown in eq 2. The general formula of several known *S*-alkylcysteine chelates is



In the complex under consideration L is Cl and R is CH_3. Previous studies of diastereomerism in these complexes[25-28] and in related α-amino acid chelates[25,29-31] were impeded by the complexity of the ^1H NMR patterns due to the superposed effects of ^1H–^1H coupling, ^{195}Pt–^1H coupling, and diastereomerism. Although ^{13}C NMR spectra of the chelates can be assigned with more certainty, their acquisition requires concentrated solutions and relatively long time.

As in the studies of the unidentate complexes (see above), ^{195}Pt NMR spectroscopy proved to be well-suited to the task: the spectrum is extremely simple and is easily recorded. The complex *cis*-$[PtCl_2(MeCysH)]$ in DMF-d_6 solution at 294 K gives rise to just two ^{195}Pt NMR signals, at −1381 and −1414 ppm relative to the $PtCl_4^{2-}$ standard. These peaks occur at higher magnetic field than those of the unidentate complexes (see Table III) mainly because of the ring effect and partly because the donor set $SNCl_2$ creates a stronger ligand field than the set SCl_3.[3]

The intensity ratio of the two signals is 2.6:1.0. The chelate complex evidently exhibits greater chiral discrimination than do the unidentate complexes. The difference between the ^{195}Pt chemical shifts of the diastereomer resonances reflects the dissimilarity between the Pt environments, but this difference alone cannot be taken as a measure of chiral discrimination. Although the shift difference in the unidentate AcMeCysH complex (34 ppm) is virtually the same as that in the chelate MeCysH complex (33 ppm), the intensity ratio is 1.0:1.2 in the former complex and 2.6:1.0 in the latter one. Chiral discrimination evidently is absent from the former complex and present in the latter one.

Molecular structures are known for two chelate complexes homologous to the one under consideration: *cis*-$[PtCl_2(EtCysH)]$[27] and *cis*-$[PdCl_2(MeCysH)]$.[32] Both diastereomers are present in the crystal of each complex. In each case, the chelate ring of the L-amino acid adopts the λ conformation with an equatorial COOH group and axial alkyl (Et or Me) group. The opposite configurations at the sulfur atom keep the alkyl group on the different sides of the average ring plane, trans or cis with respect to the α-H atom. Although the environments of the metal atom in the diastereomers are only slightly different, the corresponding ^{195}Pt NMR signals are far apart.

Comparison between the unidentate and chelate complexes reveals the structural characteristics associated with the occurrence of chiral discrimination. Unidentate thioethers do not exhibit it probably because they are too flexible. A greater constraint, such as that provided by bidentate coordination, seems to be a prerequisite for chiral discrimination.

Prospects for ^{195}Pt NMR Spectroscopy in Studies of Stereodynamics

Our previous report[2] demonstrated the applicability of variable-temperature ^{195}Pt NMR spectroscopy to the study of stereodynamics; the present report extends its use. The new method is well-suited to monitoring of exchange processes that cause only small structural changes and of those involving relatively complex molecules. Such processes, one of which is examined in this report, are not easily tractable by the common ^1H and ^{13}C NMR methods. Although the ^{195}Pt nucleus is less receptive than ^1H, it is 19.1 times more receptive than the routinely used ^{13}C. Spectra of good quality can be obtained with a 20-mm probe from ca. 15 mM solutions in ca. 15 min. We believe that metal nuclei are certain to find use in dynamic NMR spectroscopy.

Acknowledgment. This work was financed by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-ENG-82. K_2PtCl_4 was borrowed from Johnson Matthey, Inc. We thank the sponsors for their generous support.

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