peak arises from the bonding of Pt(II) to a quadrupole nucleus, nitrogen.[31,32] The resonance observed here is comparable to that observed for Pt(4-EtPy)Cl_3 (δ = -2772 in CH_2Cl_2).[33]

None of the ^1H NMR shifts observed here agree with those reported by Theophanides[6] for Pt(thiamin)Cl_3. The chemical shifts cited by these authors for H(6') and H(41') are shifted from those we have observed by 0.2 ppm upfield and 0.6 ppm downfield, respectively. All other thiamin resonances differ by less than 0.1 ppm. However, none are identical. It is possible that the NMR spectrum reported by Theophanides was not acquired on a freshly prepared sample and is, therefore, that of a reaction product of Pt(thiamin)Cl_3 and the solvent. Our ^1H NMR results also differ from those reported by Adeyemo[34] for this complex. In fact, Adeyemo's results are more consistent with those we observe for the first main decomposition product resulting from the reaction of Pt(thiamin)Cl_3 with DMSO (see Figure 1b).

The spectrum shown in Figure 1b is that of Pt(thiamin)Cl_3 after it was allowed to stand in DMSO for 15 min. It shows the proton resonances of the complex and another component in solution, indicative of a possible reaction between the complex and DMSO. The nature of this reaction was elucidated with the acquisition of ^{195}Pt and ^1H NMR data along with conductance measurements.

Conductance results in DMSO which show that Pt(thiamin)Cl_3 is a nonconductor are indicative of a nondissociated complex. With time the conductance increases and after several hours, a comparison to other thiamin salts (Table II) shows that a 1:1 electrolyte is present in solution. Two possible reactions, a and b, will produce compounds that are consistent with these conductance findings.

$$\text{Pt(thiamin)Cl}_3 + \text{DMSO} \rightarrow \text{(Pt(thiamin)(DMSO)Cl}_2)^+ + \text{Cl}^- \quad \text{(a)}$$

$$\text{Pt(thiamin)Cl}_3 + \text{DMSO} \rightarrow \text{(thiamin)}^+ + \text{(Pt(DMSO)Cl}_3)^- \quad \text{(b)}$$

On the basis only of conductivity data, Theophanides[6] postulated the reaction a takes place. However, our ^{195}Pt NMR data provide strong evidence that reaction b, where thiamin has been displaced by DMSO, has occurred. Figure 2 shows two ^{195}Pt resonances observed for a DMSO solution of Pt(thiamin)Cl_3 1 h after mixing: one at δ = -2896, attributed to Pt(thiamin)Cl_3 and another at δ = -2965. This latter resonance, identical with the ^{195}Pt signal we have observed for K[Pt(DMSO)Cl_3],[12] confirms the presence of the complex anion (Pt(DMSO)Cl_3)$^-$ in solution. We do not detect the presence of Pt(DMSO)$_2Cl_2$ δ (^{195}Pt) = -3455)[12] in solutions of Pt(thiamin)Cl_3.

Due to the large trans effect of DMSO and its negative charge, (Pt(DMSO)Cl_3)$^-$ is very reactive toward the positively charged thiamin molecule. The course of this subsequent reaction is currently under study.

Registry No. I, 111290-95-0; II, 111290-96-1; III, 111290-97-2; K_2PtCl_4, 10025-99-7; Pt(DMSO)Cl_3^-, 31203-96-0; (Hthiamin)Cl_2, 67-03-8; (thiamin)NO_3, 532-43-4; ^{195}Pt, 14191-88-9.

Supplementary Material Available: Listings of hydrogen atom parameters for Pt(thiamin)$Cl_3 \cdot H_2O$ (Table XIII) and anisotropic temperature factors (Tables XIV-XVI) and best weighted least-squares planes (Tables XVII-XIX) for (Hthiamin)$PtCl_4$, (Hthiamin)$_2(PtCl_4)Cl_2 \cdot 2H_2O$, and Pt(thiamin)$Cl_3 \cdot H_2O$ and two ORTEP diagrams of stacking and interbase interactions in Pt(thiamin)$Cl_3 \cdot H_2O$ (Figures 7 and 8) (9 pages); listings of observed and calculated structure factor amplitudes for all three compounds (48 pages). Ordering information is given on any current masthead page.

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S,O- versus S,N-Chelation in the Reactions of the *cis*-Diamminediaquaplatinum(II) Cation with Methionine and *S*-Methylcysteine[1]

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The reactions of *cis*-Pt$(NH_3)_2(H_2O)_2^{2+}$ with *S*-methyl-L-cysteine (mecysH) and L-methionine (metH) have been followed by ^1H, ^{13}C, ^{15}N, and ^{195}Pt NMR (the last two with ammine ligands substituted with ^{15}N). With a small excess of platinum, and with pH maintained near 5, the chelate products Pt$(NH_3)_2$(mecys-*S*,*N*)$^+$ and Pt$(NH_3)_2$(met-*S*,*N*)$^+$ are formed. In each case, the different configurations about sulfur give two slowly interconverting diastereomers. In strongly acidic solution (pH $\leq$0.5), the initial product in the reaction with mecysH is Pt$(NH_3)_2$(mecysH-*S*,*O*)$^{2+}$ (two diastereomers), which slowly converts to the S,N-chelate. A similar reaction sequence occurs with methionine, but *cis*-Pt$(NH_3)_2$(metH-*S*)$_2^{2+}$ is also formed, in competition with Pt$(NH_3)_2$(metH-*S*,*O*)$^{2+}$. All of these complexes slowly lose ammonia on standing.

Introduction

The best characterized complexes of platinum and palladium with the sulfur-containing amino acid methionine and its analogues are the dichloro complexes M(LH)Cl_2. X-ray crystal structure determinations have been carried out, inter alia, for the complexes with M = Pt, LH = L-methionine (metH),[2] *S*-ethyl-L-cysteine[3] and M = Pd, LH = *S*-methyl-L-cysteine (mecysH).[4] In each of these, there is a S,N-chelate ring. In the unit cell, there is one molecule of each of the two diastereomers arising from the different configurations of the S-alkyl group and the nonbonding electron pair on sulfur. After some initial confusion,[5,6] the ^1H NMR spectra of M(mecys)Cl_2^- (M = Pd, Pt) have been interpreted as showing unequivocally that S,N-chelate rings are present

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Table I. ^{195}Pt and ^{15}N NMR Data[a]

compd	struct	pH	isomer	δ_{Pt}[b]	^{15}N (ammine) δ_N[c]	J(Pt–N)[d]	donor atom trans
$Pt(NH_3)_2$(mecys-*S*,*N*)$^{+}$[f]	**2**	5	a	*e*	−47.6	255.6	S
					−67.4	279.8	N
			b		−47.2	255.4	S
					−67.4	279.8	N
$Pt(NH_3)_2$(mecysH-*S*,*N*)$^{2+}$[f]	**3**	0.5	a	−3218 (b)	−47.6	257.3	S
					−67.7	286.2	N
			b		−47.4	257.3	S
					−67.5	286.2	N
$Pt(NH_3)_2$(met-*S*,*N*)$^{+}$	**4**	7	major (b?)	*e*	−42.2	252.9	S
					−61.9	279.8	N
			minor (a?)		−42.2	259.2	S
					−62.1	279.8	N
$Pt(NH_3)_2$(metH-*S*,*N*)$^{2+}$[g]	**5**	0.5		−3136 (b)	−42.4	252.9	S
					−62.3	285.2	N
$Pt(NH_3)_2$(mecysH-*S*,*O*)$^{2+}$	**6**	0.5	*h*	−2686 (dd)	−37.6	283.7	S
					−39.7	280.2	
					−82.5	347.6	O
					−84.5	348.6	
$Pt(NH_3)_2$(metH-*S*,*O*)$^{2+}$	**7**	0.5	major	−2652 (dd)	−40.1	270.0	S
					−82.5	368.1	O
			minor	−2618 (dd)	−43.3	264.0	S
					−82.5	348.6	O
$Pt(NH_3)_2$(metH-*S*)$_2^{2+}$	**8**	0.5	major	−3639 (t)	−42.4	264	S
			minor	−3685 (t)			

[a] All ammine ligands ^{15}N substituted and cis. Chemical shifts are shown to lower shielding. [b] Relative to Na_2PtCl_6 (±5 ppm). Abbreviations: b, broad; dd, doublet of doublets; t, 1:2:1 triplet. [c] Relative to $^{15}NH_4^+$ (±0.05 ppm). [d] Measured from ^{15}N spectrum, ±1 Hz. [e] Not measured. [f] See text for assignment of peaks to particular isomers. [g] Peaks due to different diastereomers not resolved. [h] Assignment of peaks to particular isomers not attempted.

in solution, with two diastereomers interconverting slowly enough to allow separate sets of signals to be observed for them both.[7]

Diammine complexes $[Pt(NH_3)_2(L)]Cl$ have been obtained by reaction of $Pt(LH)Cl_2$ with excess ammonia.[8-11] Spectroscopic and chemical data have usually been interpreted in terms of S,N-chelation, although Shanjin et al.[11] have suggested S,O-chelation on the basis of a value for $\nu_{asym}(CO_2)$ higher than expected for deprotonated carboxylate. It has been noted[8,9] that ammonia coordinated trans to sulfur in $Pt(NH_3)_2(met)^+$ is labilized and that reaction of *cis*-$Pt(NH_3)_2Cl_2$ with methionine gives a mixture of products, with liberation of some ammonia.[12]

We have recently used multinuclear NMR to study the reactions in solution between *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ (**1**) and amino acids $^+NH_3(CH_2)_nCO_2^-$ (n = 1–3).[13,14] Coordination to platinum is initially through carboxylate oxygen, with the rate of subsequent formation of a N,O-chelate ring very dependent on the chain length, n. More complex amino poly(carboxylate)[13] and amino poly(phosphonate)[15] ligands were also shown by these methods to coordinate initially through a single oxygen atom, with subsequent formation of chelate rings.

In this paper, we describe the use of multinuclear NMR in characterizing the products of reactions in solution between **1** and the amino acids L-methionine and *S*-methyl-L-cysteine. Ismail and Sadler have reported briefly[16] that *cis*-$Pt(^{15}NH_3)_2Cl_2$ with *N*-acetylmethionine (acmetH) (1:2) at pH 2.2 after 3.5 h at 298 K gave ^{15}N peaks due to *cis*-$Pt(NH_3)_2$(acmetH-*S*)Cl^+, *cis*-$Pt(NH_3)$(acmet-*S*)Cl_2, and a large peak from $^{15}NH_4^+$. Kostic et al.[17,18] have measured the variable-temperature ^{195}Pt NMR spectra of K[$PtCl_3$(acmet-*S*)] and the *N*-acetyl-*S*-methylcysteine analogue and shown that two platinum signals observed at low temperatures coalesce at higher temperatures as the rate of inversion at sulfur increases.

Experimental Section

Starting Materials. $(^{15}NH_4)_2SO_4$ (99% ^{15}N, Stohler) was supplied by Novachem (Melbourne). L-Methionine (Hopkins and Williams) and *S*-methyl-L-cysteine (Sigma) were used as supplied. *cis*-$Pt(NH_3)_2(ONO_2)_2$ (with either ^{14}N or ^{15}N in the ammine ligands) was prepared as previously described.[19,20] Samples of *cis*-$Pt(ND_3)_2(ONO_2)_2$ were prepared by allowing a solution of *cis*-$Pt(NH_3)_2(ONO_2)_2$ in D_2O to stand for several days, followed by evaporation over silica gel in a vacuum desiccator.

Instrumentation. The 10.1-MHz ^{15}N, 21.4-MHz ^{195}Pt, 25.05-MHz ^{13}C, and 100-MHz ^1H NMR spectra were run as previously described[13,14,20] on a JEOL FX-100 instrument with a 10-mm tunable probe (a 5-mm tube was used for ^1H spectra). An internal lock on deuterium of the solvent D_2O was used for ^{13}C and ^1H spectra. Other spectra were run with a ^7Li external lock. The 400-MHz ^1H and 100.4-MHz ^{13}C spectra were run with an internal deuterium lock on a JEOL GX-400 instrument. The ^1H spectra were run with either a 5-mm ^1H or a 5-mm $^{13}C/^1H$ probe. A total of 32K data points were used, with spectrum width 4 KHz, 16 scans, 45° tilt of magnetization vector, and 3-s delay between pulses. The ^{13}C spectra were run with a 10-mm tunable probe. A total of 64K data points were used, with spectrum width 21 kHz, 1000–3000 scans, 45° tilt, and 3-s delay.

Unless otherwise noted, spectra of all nuclei other than ^1H were ^1H-decoupled. Chemical shifts are positive to lower shielding. ^{15}N chemical shifts (±0.1 ppm) are relative to $^{15}NH_4^+$ in a coaxial capillary containing 5 M $^{15}NH_4{}^{15}NO_3$ in 2 M HNO_3. ^{195}Pt–^{15}N coupling constants were measured, whenever possible, from the ^{15}N spectra, which, because of narrower line widths, gave more accurate values (±1 Hz) than ^{195}Pt spectra. ^{195}Pt shifts (±5 ppm) were measured relative to a separate sample of Na_2PtCl_6 in aqueous solution (0.5 g/mL). ^{13}C shifts (±0.01

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Table II. ^{1}H NMR Data[a]

compd	struct	pH	isomer	S–CH$_3$ δ_{CH_3}	S–CH$_3$ ^3J(Pt–H)	CH$_X$[b] δ_{H_X}	CH$_X$[b] J_{AX}	CH$_X$[b] J_{BX}	CH$_2$[c] δ_{H_A}	CH$_2$[c] δ_{H_B}	CH$_2$[c] J_{AB}
Pt(ND$_3$)$_2$(mecys-*S*,*N*)$^+$	**2**	5.5	major (a)	2.63	50.3	3.83	11.3	4.1	3.06	3.04	13.9
			minor (b)	2.57	51.2	3.59	6.0	5.6	3.12	3.23	13.7
Pt(ND$_3$)$_2$(mecysD-*S*,*N*)$^{2+}$	**3**	0.5	major (a)	2.66	49.8	4.15	11.9	4.8	3.11	3.22	14.2
			minor (b)	2.63	50.8	3.91	8.3	5.2	3.13	3.41	13.3
Pt(ND$_3$)$_2$(met-*S*,*N*)$^+$	**4**	5	major (b?)	2.53	48.9	3.50	(10.1)	(2.5)			
			minor (a?)	2.52	49.8	3.65	(5.1)	(5.1)			
Pt(ND$_3$)$_2$(metD-*S*,*N*)$^{2+}$	**5**	0.5	major (b?)	2.54	*d*	3.75	(10.6)	(2.3)			
			minor (a?)	2.53	*d*	3.91	(5.6)	(4.4)			
Pt(ND$_3$)$_2$(mecysD-*S*,*O*)$^{2+}$	**6**	0.5	*f*	2.73[e]	45.8	4.66	12.9	4.9	2.97	3.61	13.0
			f	2.57[e]	46.0	4.62	12.0	2.4	3.32	3.20	14.5
Pt(ND$_3$)$_2$(metD-*S*,*O*)$^{2+}$	7	0.5	major	2.47	*d*	5.33	(10.7)	(5.2)			
			minor	2.45	*d*	5.58	(9.5)	(6.4)			
Pt(ND$_3$)$_2$(metD-*S*)$_2^{2+}$	**8**	0.5		2.64	44.5						

[a] In D_2O; shifts to lower shielding from TSS. *J* values are in Hz. All values were measured from 400-MHz spectra, except for Pt–S–CH$_3$ coupling constants, which were measured from 100-MHz spectra. [b] For *S*-methylcysteine complexes, for which J_{AX} and J_{BX} were determined. Spectra of methionine complexes were not fully analyzed, and the values given in parentheses are the "apparent values" from splitting of the H_X signal. [c] For *S*-methylcysteine complexes only; the methylene region is complex for methionine compounds. [d] Only 400-MHz spectra were run. Pt–S–CH$_3$ coupling constants were not measured. [e] *S*-methyl peaks cannot be associated with particular ABX peaks. [f] Not possible to assign peaks to particular isomers.

Table III. ^{13}C NMR Data[a]

compd	struct	pD	isomer	S–CH$_3$ δ_C	S–CH$_3$ *J*(Pt–C)	CH δ_C	CH *J*(Pt–C)	S–CH$_2$ δ_C	S–CH$_2$ *J*(Pt–C)	C–CH$_2$–C[b] δ_C	C–CH$_2$–C[b] *J*(Pt–C)	–COO δ_C	–COO *J*(Pt–C)
mecysD		5.3		15.72		54.32		35.53				174.21	
Pt(ND$_3$)$_2$(mecys-*S*,*N*)$^+$	2	5.7	major (a)	21.28	20.5	62.70	13.9	42.25	≤7			174.20	47.6
			minor (b)	22.45	17.6	63.23	11.8	42.40	≤7			174.73	55.6
Pt(ND$_3$)$_2$(mecysD-*S*,*N*)$^{2+}$[c]	3	0.5	major (a)	21.27		61.12		40.54				171.54	
			minor (b)	22.91		61.95		41.43				171.94	
Pt(ND$_3$)$_2$(mecysD-*S*,*O*)$^{2+}$[c]	6	0.5	*e*	24.63		52.48		34.03				173.68	
				21.33		50.96		33.02				173.14	
metD		6		15.14		55.18		31.25		30.08		176.10	
Pt(ND$_3$)$_2$(met-*S*,*N*)$^+$	4	6	major (b?)	20.11	≤5	58.15	17.6	33.72	24.4	28.88	39.0	177.10	*d*
			minor (a?)	20.47	≤5	56.09	20.5	31.26	22.5	28.27	43.0	176.45	*d*

[a] In D_2O. Shifts to lower shielding are from external Me_4Si. Coupling constants are in Hz. [b] Methionine complexes only. Assignment with S–CH$_2$ could be reversed. [c] 100.4-MHz spectrum; platinum couplings not observed. [d] Satellite signals too weak to be observed. [e] Peaks cannot be assigned to a particular isomer, and it is not possible to determine which ^{13}C peaks come from the same isomer.

ppm) are reported relative to external tetramethylsilane (Me_4Si) with dioxane (δ_C 67.73) as internal reference. Proton chemical shifts are relative to the methyl signal of sodium 3-(trimethylsilyl)propanesulfonate (TSS).

Typical NMR Experiment. The following procedure was used to prepare a solution containing Pt(^{15}NH$_3$)$_2$(mecysH-*S*,*O*)$^{2+}$. *cis*-Pt(^{15}NH$_3$)$_2$(ONO$_2$)$_2$ (0.15 g, 0.42 mmol) was dissolved in 2 mL of water. The pH of the solution was monitored by using Merck Acilit narrow-range indicator strips. A 1 M HNO_3 solution was used to adjust the pH to ≤0.5. The solution was filtered through a cotton-wool plug into a 10 mm diameter NMR tube. The ^{15}N NMR spectrum was then run to check that the solution did contain only the expected *cis*-[Pt(^{15}NH$_3$)$_2$(H$_2$O)$_2$](NO$_3$)$_2$, with traces of [Pt(^{15}NH$_3$)$_2$(ONO$_2$)(H$_2$O)](NO$_3$).[20] Solid *S*-methyl-L-cysteine (0.049 g, 0.36 mmol) was added and the tube shaken briefly to dissolve the solid. The pH remained below 0.5. Within 3 min, scans for ^{15}N or ^{195}Pt NMR commenced.

For ^{13}C experiments, *cis*-Pt(^{14}NH$_3$)$_2$(ONO$_2$)$_2$ was used, with D_2O as the solvent, and 3 M D_2SO_4 used to acidify the solution. For ^{1}H spectra, solutions were prepared on one-third of the above scale, and Pt(^{14}ND$_3$)$_2$(ONO$_2$)$_2$ was used. For solutions at pH 5–6, a 1 M solution of NaOH in H_2O (or D_2O) was used, as appropriate, to adjust the pH (or pD).

Results and Discussion

^{15}N and ^{195}Pt NMR data are summarized in Table I, ^{1}H data in Table II, and ^{13}C data in Table III.

Pt(NH$_3$)$_2$(mecys-*S*,*N*)$^+$. The pH of a solution of *S*-methyl-L-cysteine in H_2O was adjusted to 5 with 1 M NaOH solution. This solution was added to a solution of *cis*-[Pt(^{15}NH$_3$)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ and the pH again adjusted to 5. Proportions of the reagents were such that a small excess of *cis*-Pt(^{15}NH$_3$)$_2$(H$_2$O)$_2^{2+}$ (**1**) was present. Formation of hydroxo-bridged dimers at this pH is slow and does not interfere with the reactions studied. The 10.1-MHz ^{15}N spectrum of the resultant solution is shown in Figure 1a. Along with the singlet with "satellites" (from coupling to ^{195}Pt, $I = {}^1/_2$, 33.6% abundance) from unreacted **1** (δ_N −84.9, $^1J(^{195}Pt-^{15}N)$ = 390 Hz[20]), the spectrum showed two barely resolved peaks (with satellites) near −48 ppm and a singlet with satellites at −67.5 ppm. The low shielding of the former peaks

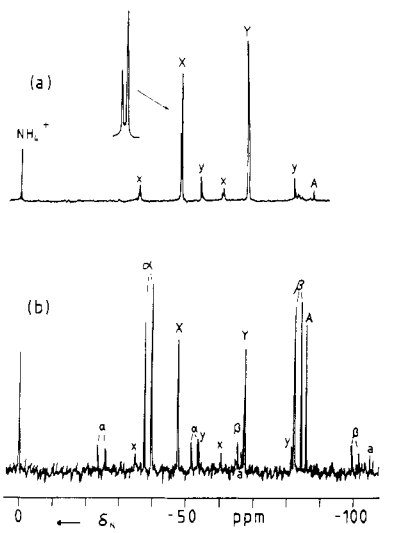


Figure 1. 10.1-MHz ^{15}N NMR spectra of solutions obtained by mixing aqueous solutions of *cis*-[Pt(^{15}NH$_3$)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ and *S*-methylcysteine: (a) with pH maintained near 5 (inset is a fourfold frequency expansion); (b) with pH ≤0.5, spectrum scanned 3–25 min after mixing. Peaks are labeled as follows: (A, a) *cis*-Pt(^{15}NH$_3$)$_2$(H$_2$O)$_2^{2+}$ (**1**); (X, x) S,N-chelate complex (**2** or **3**), ammine trans to S; (Y, y) **2** or **3**, ammine trans to N; (α, α) S,O-chelate complex (**6**), ammine trans to S; (β, β) S,O-chelate complex (**6**), ammine trans to O.

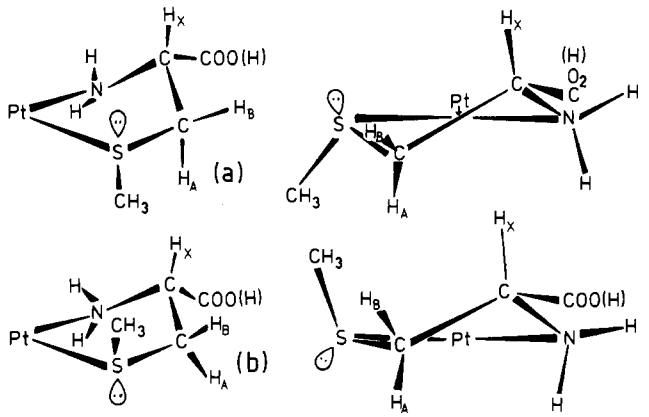


Figure 2. Diastereomers of the *S*-methylcysteine S,N-chelate ring. (a) is considered to be the preferred isomer (see text).

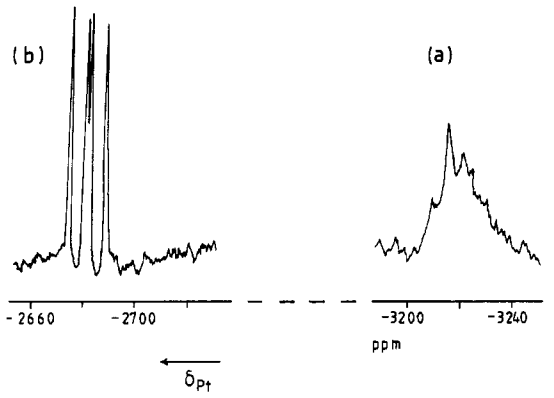
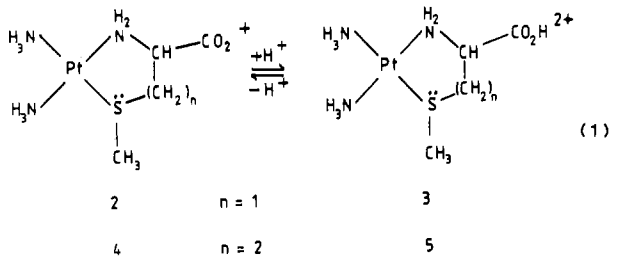


Figure 3. 21.4-MHz ^{195}Pt spectra of solutions of (a) $Pt(^{15}NH_3)_2$(mecys-*S*,*N*)$^+$ (**2**) (pH 5.5) and (b) $Pt(^{15}NH_3)_2$(mecysH-*S*,*O*)$^{2+}$ (**6**) (pH 0.5).

and the small Pt–N coupling constant (256 Hz) correspond to ammine trans to sulfur.[21,22] The spectrum therefore shows that a S,N-chelate ring was formed (**2**). The two different peaks from ammine trans to sulfur would then correspond to the two diastereomers arising from different configurations about sulfur, shown in Figure 2. Their intensity ratio is near 2:1.

Slight changes occurred if acid was added to this solution (Table I), corresponding to protonation of the uncoordinated carboxyl group (eq 1). At low pH, separate peaks were resolved for



(1)

2 n = 1 3

4 n = 2 5

ammine nitrogen trans to the amino acid nitrogen in the two diastereomers, as well as for ammine trans to sulfur.

The ^{195}Pt NMR spectrum of this solution is shown in Figure 3b: a broad peak with some structure. The broadness is expected if ^{14}N of mecysH coordinates to platinum, owing to interaction between ^{195}Pt and the quadrupolar ^{14}N nucleus.[13,23] The platinum chemical shift depends primarily on the set of donor atoms bound to platinum.[16,21] δ_{Pt}, at −3218, lies in the region expected for a PtN_3S complex (cf. $Pt(^{15}NH_3)_3S(O)(CH_3)_2)^{2+}$. −3213 ppm[21]). Signals due to the two diastereomers apparently overlap.

Although no excess ligand was present in these solutions, ^{15}N NMR spectra showed that ammonia was lost slowly from the

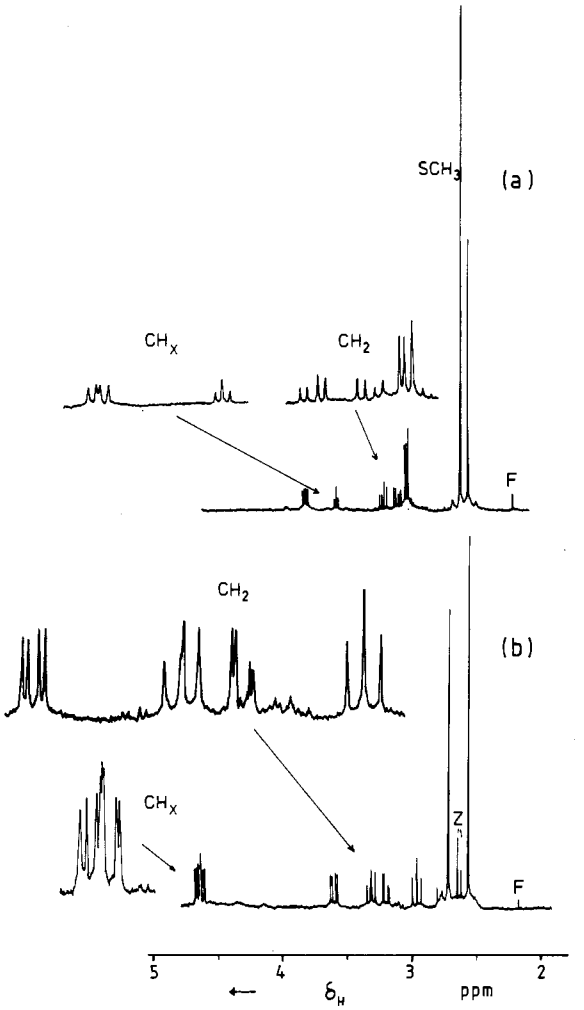


Figure 4. 400-MHz ^1H NMR spectra in D_2O: (a) $Pt(ND_3)_2$(mecys-*S*,*N*)$^+$ (**2**) (pD 5.5); (b) *cis*-$Pt(ND_3)_2(D_2O)_2^{2+}$ (**1**) with mecysD run within 5 min of mixing (pD 0.5). Inset portions are fourfold frequency expansions. Labeled peaks represent the following: (F) *S*-methyl peak of free ligand; (Z) *S*-methyl peak of the S,N-chelate (**3**) (small chemical shift differences from corresponding peaks in the two spectra arise from the difference in pD between the solutions).

complex. When the reference capillary containing $^{15}NH_4{}^{15}NO_3$ was removed, ammonia loss from the complex was evidenced by the appearance and growth of a sharp singlet from $^{15}NH_4{}^+$. This loss of ammonia was faster in acid solution than in solutions with pH 5 or above. At pH ~0.5, ammonia loss was detected within 2 h. Even at pH 5, after several days, most of the ^{15}N NMR intensity was in the $^{15}NH_4{}^+$ peak, with a weak, complex pattern observed from ammine ligands still coordinated.

The 100-MHz ^1H NMR spectrum of a similar solution in D_2O[24] showed two singlets with satellites from the *S*-methyl groups (intensity ratio 2:1). The remainder of the spectrum was relatively complex and was not easily interpreted. The spectrum resembled the 60-MHz ^1H spectrum for $Pt(ND_3)_2$(mecys-*S*,*N*)$^+$ depicted by Erickson et al.[10] The 400-MHz ^1H NMR spectrum of a similar solution is shown in Figure 4a. At this higher field, chemical shift anisotropy relaxation of the ^{195}Pt nucleus in the square-planar complex becomes much faster,[25] and satellites from coupling to ^{195}Pt have almost totally disappeared from the spectrum. Apart from the *S*-methyl peaks, the spectrum showed two ABX patterns, from the methylene (AB) and methine (X) protons in the two diastereomers.

(21) Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Inorg. Chem.* **1985**, *24*, 3514.
(22) Kerrison, S. J. S.; Sadler, P. J. *J. Chem. Soc., Chem. Commun.* **1977**, 861.
(23) Ismail, I. M.; Kerrison, S. J. S.; Sadler, P. J. *Polyhedron* **1982**, *1*, 57.

(24) In D_2O, the amine protons of the amino acid ligand will be replaced by deuterium. In figures and schemes, "H" will be used to indicate either ^1H or ^2H (D).

(25) Lallemand, J.-Y.; Soulie, J.; Chottard, J.-C. *J. Chem. Soc., Chem. Commun.* **1980**, 436.

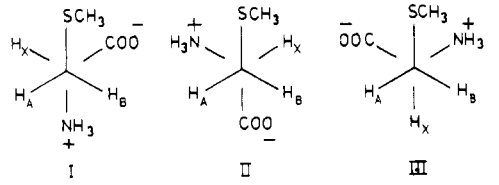


Figure 5. Rotamers of *S*-methyl-L-cysteine.

Significant changes occurred in the spectrum as the pD was changed. Spectra were fully analyzed at pD 0.5 and 5.5, to give the shifts and coupling constants listed in Table II.

In their discussion of the ^1H NMR spectra of M(mecys)Cl_2^- (M = Pd, Pt), Kozlowski et al.[5-7] assumed that the proton–proton coupling constants were determined solely by the relative populations of the three rotamers I–III shown in Figure 5. On this basis, they postulated that for the major diastereomer of Pd(mecys)Cl_2^- the rotamer populations were 0.21, 0.61, and 0.18, respectively, and for the minor diastereomer 0.18, 0.60, and 0.22. Since rotamer II would correspond to a S,N-chelate ring with carboxyl equatorial, these results were interpreted as indicating that a S,N-chelate structure is present in solution, as in solid Pd(mecysH)Cl_2. However, once the S,N-chelate structure has been established, it does not appear to us to be useful to continue to discuss the spectra in terms of variations in the populations of the three rotamers. Rotamer I could not be present at all in a S,N-chelate; the assumption is made that coordination to a metal ion would not affect the values of the coupling constants for a rotamer; and it is assumed that in the chelate ring conformation the dihedral angles between the HCC planes must remain at either 60 or 180°. It is more realistic to interpret the spectra in terms of the conformations of the chelate rings. As mentioned above, the two diastereomers of Pd(mecysH-*S*,*N*)Cl_2 are present in the unit cell of the crystal lattice.[4] For each diastereomer, the carboxyl group is equatorial, but there are significant differences in detail between the two conformations, which we have attempted to illustrate in Figure 2. For the diastereomer labeled b (**2b**), there appears to be significant steric interaction between the *S*-methyl group and H_X, which is relieved to some extent if the ring becomes less puckered. For the diastereomer labeled a (**2a**), there are no comparable interactions, and a greater puckering of the ring is evident than in **2b**. There will be differences in detail when the other ligands present are changed from chloride to ammine, and in solution, the observed NMR spectrum will be the population-weighted average of spectra corresponding to each of the different conformations that contribute to the overall equilibrium. However, the following observations can be made: (i) The preferred conformation for each diastereomer has the carboxyl group equatorial. (ii) Diastereomer **2b**, with the *S*-methyl group trans to carboxyl, will be less favored thermodynamically than the diastereomer **2a**, because of the steric interactions mentioned above. (III) In the conformation with the carboxyl group equatorial, the ring will be less puckered for diastereomer **2b** than for diastereomer **2a**, so that the ring substituents can be less accurately described as "axial" or "equatorial". There may also be a greater relative population of the conformation with carboxyl axial for **2b** than for **2a**.

The major diastereomer, which gives the more intense set of peaks, is therefore assigned as **2a**. The peak due to the methine proton, H_X, is easily assigned for each diastereomer, as these multiplets occur at lowest shielding. For diastereomer **2a**, one of the methylene protons has a large coupling with H_X (11.3 Hz), typical of a H_{ax}–H_{ax} coupling. This proton is therefore assigned as H_A (as labeled in Figure 2a) and the other methylene proton as H_B. As expected for an equatorial–axial coupling constant, $J(H_B–H_X)$ is much smaller (4.1 Hz). When this complex is protonated to Pt$(ND_3)_2$(mecysD-*S*,*N*)$^{2+}$ (**3a**), H_X shifts to lower shielding by 0.32 ppm. H_B, which is equatorial and adjacent to the equatorial carboxyl group, shifts in the same direction 0.18 ppm, but H_A, which is axial, is shifted only slightly (0.05 ppm). All of the proton–proton coupling constants increase slightly on protonation. For the other diastereomer, **3b**, the coupling constants

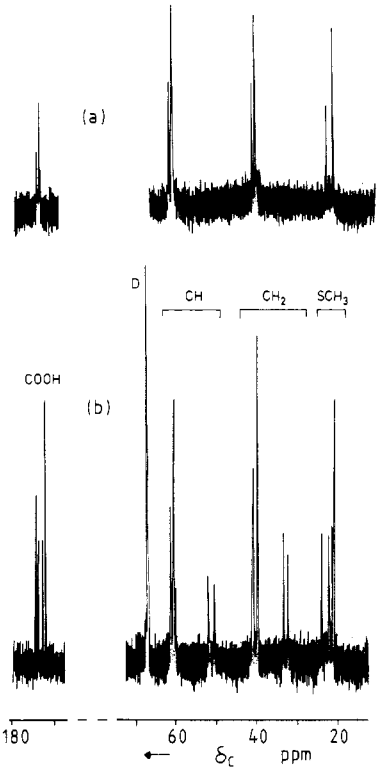


Figure 6. 100-MHz ^{13}C NMR spectra of D_2O solutions at pD 0.5: (a) Pt$(ND_3)_2$(mecysD-*S*,*N*)$^{2+}$ (**3**); (b) *cis*-Pt$(ND_3)_2(D_2O)_2^{2+}$ (**1**) with mecysD, scanned 0–3 h after mixing. (the peak labeled "D" is from dioxane internal reference).

between H_X and the two different methylene protons are much less differentiated (8.3 and 5.2 Hz), but $J(H_A–H_X)$ may still be assigned as the larger of the two. This is consistent with a distortion of the chelate ring conformation for diastereomer **3b**, which makes the protons H_A and H_X less "axial" in character, perhaps coupled with an increased population of the conformation with the carboxyl group axial. In the deprotonated form, **2b**, the two coupling constants involving H_X are almost the same (6.0, 5.6 Hz), consistent with a still greater distortion of the conformation with carboxyl "equatorial", or a decreased preference for this conformation. Again, the chemical shifts of H_X and H_B are sensitive to the protonation state of the carboxyl group but not the shift of H_A.

A solution of Pt$(ND_3)_2$(mecys-*S*,*N*)$^+$ (**2**) at pD 5 was sufficiently stable to allow a 25.05-MHz ^{13}C NMR spectrum to be obtained overnight, although weak peaks were observed from the products of the deammination reactions. Apart from these, the spectrum showed two sets of resonances, corresponding to the two diastereomers, with satellites from platinum coupling observable about some of the peaks, as indicated in Table III. The spectrum was qualitatively similar to that described for Pt(mecys-*S*,*N*)Cl_2^- by Jezowska-Trzebiatowska et al.,[6] except that these authors did not mention the presence of platinum coupling. Comparison with the spectrum of the free ligand at pD 5.3 (Table III) shows that all of the carbon nuclei resonate significantly to lower shielding in the complex, except the carboxyl carbon, which scarcely shifts. The peaks from the minor diastereomer, **2b**, occur to lower shielding than those from the major diastereomer, **2a**.

In more strongly acidic solution, ammonia loss occurred too rapidly to allow an overnight run, which would have been required to obtain a 25.05-MHz ^{13}C spectrum on our instrument. The greater sensitivity of our higher field spectrometer allowed a 100.1-MHz spectrum to be obtained within 2 h, before extensive decomposition occurred. The spectrum is shown in Figure 6a. As usual at higher fields, no peaks due to platinum coupling were observed. Except for the *S*-methyl peaks, all of the resonances occurred to higher shielding in the protonated form of the complex, **3**, compared with the resonances for **2**.

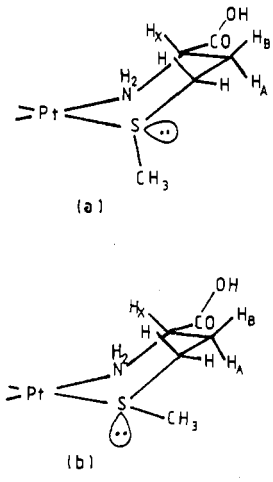


Figure 7. Diastereomers of the L-methionine S,N-chelate ring.

$Pt(NH_3)_2$(met-*S*,*N*)$^+$. Reaction of **1** with L-methionine, with pH maintained near 5, gave a solution containing $Pt(NH_3)_2$(met-*S*,*N*)$^+$ (**4**), which could be protonated to $Pt(NH_3)_2$(metH-*S*,*N*)$^{2+}$ (**5**) (eq 1). These species were characterized by NMR data summarized in Tables I–III.

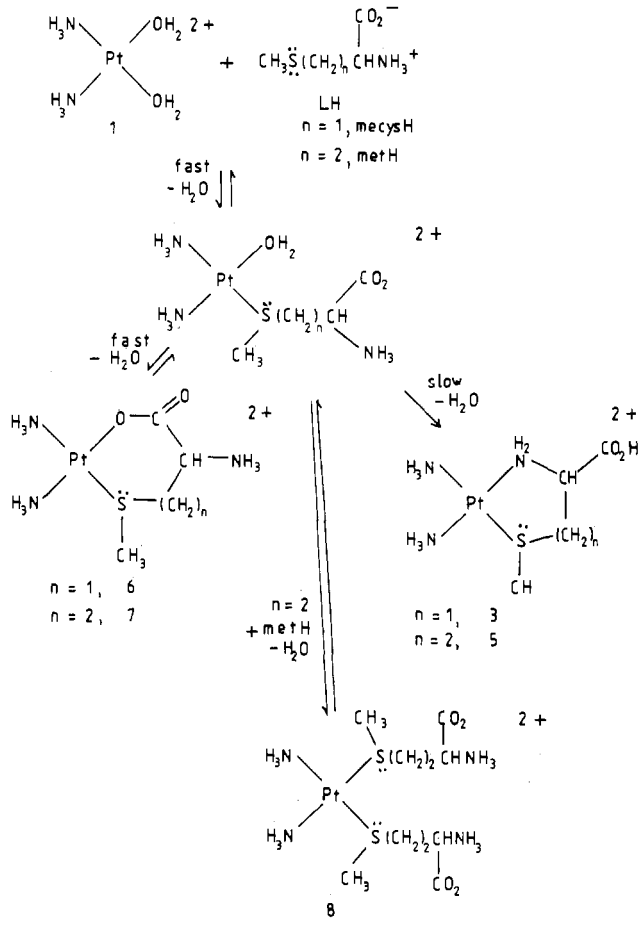
In the ^{15}N spectra, peaks due to the different diastereomers were resolved. They occurred slightly to lower shielding than the corresponding peaks in the mecys analogues, and Pt–N coupling constants were slightly smaller. Loss of ammonia from the complex was faster than for the mecys analogue under comparable conditions.

In the ^1H spectra, two *S*-methyl peaks were resolved, with an intensity ratio approximately 5:3, corresponding to the two diastereomers. The crystal structures of M(metH-*S*,*N*)Cl_2 (M = Pt,[1] Pd[26]) show a flattened-chair conformation, with the carboxyl group equatorial, for each diastereomer (Figure 7). There is only a slight preference for one diastereomer over the other. Perhaps the diastereomer labeled b (**5b**) would be expected to be slightly preferred, as the *S*-methyl group would then be equatorial in the conformation that had the carboxyl group equatorial. The five nonequivalent methine and methylene protons for each diastereomer gave a complex spectrum, even at 400 MHz. No attempt was made to analyze the spectrum in detail. However, the signals from the methine proton (H_X) are well-separated and could be easily assigned. The splittings in these H_X multiplets are given in Table II, but it should be remembered that these do not necessarily correspond to the values of the proton–proton coupling constants involving H_X, which could be obtained only if a full analysis of the spectrum were possible. However, it is noteworthy that the larger difference between the splittings in the H_X multiplet is observed for the major diastereomer, which tends to confirm its assignment as **5b**, in which both the *S*-methyl and carboxyl groups can be equatorial. For each diastereomer, the H_X multiplet shifts to lower shielding when the uncoordinated carboxyl group of **4** is protonated to give **5**.

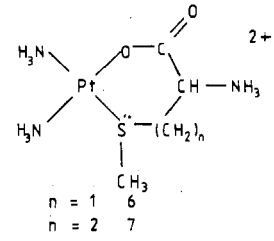
The ^{13}C NMR spectrum of **4** showed two sets of signals, corresponding to the two diastereomers. Peaks near 20 ppm were assigned to the *S*-methyl groups on the basis of a quartet splitting in the ^1H-coupled spectrum. No coupling to platinum was observed in the 25.05-MHz spectrum for these peaks, although quite large coupling constants were observed for the methine and methylene carbon atoms in the chelate ring. There is no clear basis on which to differentiate between the signals due to the two methylene groups, which have similar chemical shifts in both the free ligand and the complex, and the assignments given in Table III for these groups could be reversed.

Volshtein et al.[8,9] have reported that the pink tetrachloroplatinate salt $[Pt(NH_3)_2(metH)][PtCl_4]$ precipitates when K_2PtCl_4 solution is added to a solution containing $Pt(NH_3)_2(metH)^{2+}$. In our hands, addition of K_2PtCl_4 solution to concentrated aqueous solutions of $[Pt(NH_3)_2(metH)](NO_3)_2$ or $[Pt(NH_3)_2(mecysH)](NO_3)_2$ did not produce an immediate precipitate of a pink solid. Instead, a yellow (probably polymeric) solid, in relatively small quantities, slowly deposited.

Scheme I



Reactions between *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ (1) and the Ligands in Strongly Acidic Solution. The pH of a solution of **1** was decreased below 0.5 by addition of 1 M HNO_3. Slightly less than 1 mol equiv of mecysH was added, and scanning of the ^{15}N spectrum commenced immediately. The spectrum after 5 min of scanning was very noisy, and satellite peaks could not be observed, but it showed, in addition to peaks from **1**, four singlets not previously observed, of approximately equal intensity. Two, near −38 ppm, must be due to ammine trans to sulfur[21] and two, near −83 ppm, to ammine trans to oxygen.[13,20,21] The spectrum showed no peaks from the S,N-chelate complex **3**. With continued accumulation, the satellites became visible, and peaks due to **3** appeared and grew. The spectrum run from 3 to 25 min after mixing is shown in Figure 1b. The Pt–N coupling constant for ammine trans to oxygen in the new species was near 348 Hz, too small for ammine trans to water[19–21] but consistent with ammine trans to carboxylate oxygen (cf. ammine trans to acetate in Pt-$(^{15}NH_3)_3(O_2CCH_3)^+$, δ_N −84.8, J(Pt–N) = 332 Hz[14]). The complex initially formed in this solution was therefore formulated as $Pt(^{15}NH_3)_2$(mecysH-*S*,*O*)$^{2+}$ (**6**) (Scheme I), for which two



diastereomers are again possible (Figure 8). Because all four

(26) Warren, R. C.; McConnell, J. F.; Stephenson, N. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 1402.

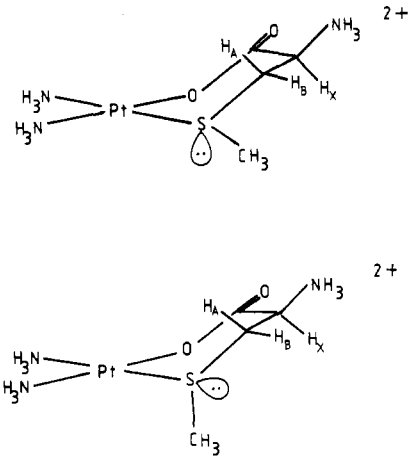


Figure 8. Diastereomers of $Pt(NH_3)_2(mecysH\text{-}S,N)^{2+}$ (**6**).

signals observed for **6** have similar intensities, there is no basis for pairing one peak for ammine trans to sulfur with a particular peak for ammine trans to oxygen or for assigning individual peaks to one diastereomer or the other. Peaks due to the S,N-chelate **3** continued to grow with time, until, after 1 h, these were dominant in the spectrum, with those from **6** very weak.

The ^{195}Pt NMR spectrum of a solution prepared similarly was run as soon as possible after the reagents were mixed. Along with a triplet from **1** and a growing broad peak from the S,N-chelate **3**, the spectrum showed a doublet of doublets at −2684 ppm, with peak separations corresponding to the Pt–N coupling constants measured from the ^{15}N NMR spectrum of **6** (Figure 3b). This chemical shift is in the region expected for a PtN_2OS complex (cf. −2813 ppm for *cis*-$Pt(^{15}NH_3)_2\{S(O)(CH_3)_2\}(H_2O)^{2+}$ [21]). With time, these peaks became weaker as the broad peak from **3** grew.

Strongly acidic D_2O solutions of **1** and mecysH were mixed with similar conditions, and the 400-MHz ^1H NMR spectrum was run immediately. This spectrum (Figure 4b) was quite different from that of the S,N-chelate complex **3** (Figure 4a). The spectrum showed two *S*-methyl peaks with similar intensities and two ABX patterns from the methylene and methine protons of two diastereomers. Connectivity within an ABX pattern was confirmed by homonuclear decoupling experiments, but there was no way to connect one methyl resonance with a particular ABX pattern. The ABX spectra were analyzed to give the chemical shifts and coupling constants listed in Table II. These values are consistent with a preference for a chair conformation in solution, with the protonated amine group equatorial, for each diastereomer. With the ring protons labeled as in Figure 8, the methine proton, H_X, and H_A are axial and $J(H_A\text{–}H_X)$ is large, while H_B is equatorial, with a much smaller coupling constant to H_X. As expected, peaks from **3** grew with time, while those from **6** diminished. The 100-MHz ^1H spectrum of a similar solution allowed the Pt–S–CH_3 coupling constants to be determined.

Attempts to obtain a 25.05-MHz ^{13}C spectrum of **6** were unsuccessful, as this required an overnight run with most of the desired compound disappearing within the first few hours of accumulation. No Pt–C coupling constants could therefore be measured. With the greater sensitivity of our high-field instrument, a satisfactory ^{13}C NMR spectrum could be obtained by scanning for 3 h after the reagents were mixed in strongly acidic solution. Although peaks from the S,N-chelate are stronger in the resultant spectrum than those due to **6** (Figure 6b), there was no difficulty in observing two sets of resonances from the diastereomers of the S,O-chelate **6**.

From all of these results, it is clear that the reaction of **1** with mecysH in acid produces initially the S,O-chelate complex **6**, which subsequently isomerizes to the S,N-chelate **3** (Scheme I). Addition of more acid to the solution slows this rearrangement, while addition of base to increase the pH to 5–6 causes it to occur instantaneously. It is very likely that, when mecysH reacts with **1**, the sulfur atom coordinates to the metal ion first, to form *cis*-$Pt(NH_3)_2(mecysH\text{-}S)(H_2O)^+$ (Scheme I), as the thioether sulfur would be expected to be very reactive toward platinum and would not be affected by the pH of the solution. Since the acid dissociation constant for the carboxyl group is much higher than for the protonated amine group, there will be a much higher concentration of deprotonated carboxyl than deprotonated amine groups in acid solution. It is, therefore, the carboxyl oxygen that displaces the second water molecule under these conditions, to form a S,O-chelate, although a S,N-chelate is undoubtedly more stable thermodynamically. It is evident from molecular models that the amine nitrogen atom in **6** cannot approach the metal ion while the chelate ring remains intact. The isomerization therefore occurs through cleavage of the Pt–O bond, to form *cis*-$Pt(NH_3)_2(mecysH\text{-}S)(H_2O)^{2+}$ in equilibrium with **6**. It is most likely that the platinum–carboxylate bond will re-form, but this produces no net change. The much less probable formation of a Pt–N bond to form a S,N-chelate ring is irreversible. Since protons are released in the last reaction, it is strongly inhibited kinetically in strongly acidic solution and is self-inhibiting in the absence of added acid.

When mecysH was simply added to a solution of **1**, without addition of any other acid or base, ^1H NMR spectra run soon after mixing showed that a mixture of **3** and **6** was obtained. Their relative proportions depended on concentration and details of the mixing procedure. The pH at this stage was near 1.5. The first portion of mecysH to react with **1** forms the S,N-chelate **3** quickly, but the acid liberated by this reaction then inhibits further formation of this compound as more mecysH reacts. The last portion of the ligand to react therefore forms the S,O-chelate **6**, which converts to **3** only slowly.

Preliminary examination of the reaction between **1** and methionine in strongly acidic solutions showed that it was more complicated than with mecysH. In particular, there was some evidence for the formation of *cis*-$Pt(NH_3)_2(metH\text{-}S)_2^{2+}$ (**8**), in which methionine is bound to the metal only through sulfur. The reactions of **1** with 3 mol equiv of metH at pH <0.5 were therefore monitored. With ^{15}N-substituted ammine, the most striking observation from the ^{15}N NMR spectrum was the rapid appearance and growth of a peak due to free $^{15}NH_4^+$, which accounted for almost all of the ^{15}N NMR intensity by $^1/_2$ h after mixing. The major peaks due to coordinated ammine were a singlet with satellites centered at −42.4 ppm, assigned to **8**. Peaks due to $Pt(^{15}NH_3)_2(metH\text{-}S,N)^{2+}$ (**5**) were also observed (the central peak corresponding to ammine trans to S in **5** coincided with that of **8**). The ^1H NMR spectrum of a solution in D_2O prepared in a similar way showed a sharp signal at 2.64 ppm from the two *S*-methyl groups. At 100 MHz, satellites were observed ($^3J(Pt\text{–}S\text{–}CH_3) = 44.5$ Hz). The signals from other ligand protons were quite broad at both 100 and 400 MHz. This is probably due to a rate of inversion at sulfur that is intermediate on the NMR time scale: fast enough to cause the *S*-methyl groups to give just one sharp resonance, if the chemical shifts of the methyl protons in the different environments are not very different, but not fast enough to simplify fully the spectrum of the methine and methylene protons. The ^{195}Pt spectrum of a solution of *cis*-$Pt(^{15}NH_3)_2(metH\text{-}S)_2^{2+}$ (**8**) showed two broad triplets, the stronger at −3639 ppm and the weaker at −3685 ppm. The high shielding indicates that two sulfur atoms are bound to platinum. The two broad triplets probably arise from the different diastereomers possible from *S*-methyl configurations, R,R and S,S (distinguished from each other chemically only because of the enantiomeric center on carbon, and unlikely to be resolved) and R,S. Kostic et al.[17] observed for the *N*-acetylmethionine complex $PtCl_3(acmetH\text{-}S)^-$ two separate ^{195}Pt signals, which coalesced at higher temperatures. Because of the rapid loss of ammonia from our complexes, even at room temperature, no attempt was made to observe coalescence of these peaks by heating the solution.

Peaks due to **8** were always observed when methionine was added to **1** in strongly acidic solution, even when **1** was in considerable excess. Peaks from the S,N-chelate **5** were initially weak but grew over a period of 2 h to become the only significant species in solution. In addition, peaks were observed in the spectra that could be assigned to $Pt(NH_3)_2(metH\text{-}S,O)^{2+}$ (**7**). These peaks,

listed in tables, were initially strong but decreased in intensity with time (more rapidly than peaks from **8**). These peaks were all sharp, in keeping with the general observation throughout this work that rates of inversion at sulfur are relatively slow on the NMR time scale when the sulfur atom is incorporated in a chelate ring. Again, peaks due to two diastereomers are resolved (intensity ratio approximately 3:1), including two distinct doublets of doublets in the ^{195}Pt spectrum (Table I). One unusual aspect of the ^1H spectrum is the very low shielding of the resonances due to the methine proton in **7**, near 5.4 ppm (Table II). Because of the complexity of the methylene region of this spectrum, no attempt was made to analyze it in detail. A clear assignment of peaks due to **7** was not possible in the ^{13}C spectrum, because this species disappeared too rapidly from the solution.

Some of the spectra from solutions containing **7** and **8** also showed a number of weaker peaks (e.g., in the ^{15}N spectrum and in the *S*-methyl region of the ^1H spectrum). No attempt was made to assign these in detail. It is possible that some of these peaks were due to *cis*-$Pt(NH_3)_2$(metH-*S*)$(H_2O)^{2+}$.

Since the S,O-chelate ring in $Pt(NH_3)_2$(metH-*S*,*O*)$^{2+}$ (**7**) is seven-membered, it might be expected to be less stable thermodynamically and kinetically than the corresponding six-membered ring in $Pt(NH_3)_2$(mecysH-*S*,*O*)$^{2+}$ (**6**). This probably accounts for the greater complexity of the reactions involving methionine. There would be a higher proportion of the aqua complex *cis*-$Pt(NH_3)_2$(metH-*S*)$(H_2O)^{2+}$ in equilibrium with the chelate, and the rate of ring closure to the S,O-chelate is probably slower than in the mecys analogue. This allows some *cis*-$Pt(NH_3)_2$(metH-*S*)$_2^{2+}$ (**8**) to form in the course of the reaction between **1** and methionine. It might also be expected that this factor would allow much faster isomerization from the S,O- to the S,N-chelate. In fact, from our qualitative observations, the rates of isomerization are comparable for mecys and methionine complexes. The balancing factor is probably a slower rate of formation of the six-membered chelate ring in $Pt(NH_3)_2$(metH-*S*,*N*)$^{2+}$ (**5**) from *cis*-$Pt(NH_3)_2$(metH-*S*)$(H_2O)^{2+}$ than in the corresponding formation of the five-membered ring in $Pt(NH_3)_2$(mecysH-*S*,*N*)$^{2+}$ (**3**). We have previously shown that formation of a Pt-N bond to produce a chelate ring is much slower when the ring to be formed is six- rather than five-membered, in amino acid[14] and (aminoalkyl)-phosphonate[27] complexes of platinum.

Conclusion. We have now demonstrated that "metastable" complexes play an important role in the solution chemistry of these complexes with relatively complex ligands, as well as those with simpler amino acids and analogues.[13,14,27] As has been previously noted,[16] the facile loss of coordinated ammonia from diammineplatinum(II) complexes with sulfur donors has some implications when the ultimate fate of ammine-platinum complexes in vivo is under consideration.

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Registry No. **1**, 52241-26-6; **2a**, 111349-55-4; **2b**, 111465-01-1; **3a**, 111349-56-5; **3b**, 111465-02-2; **4** (a?), 111465-03-3; **4** (b?), 111464-97-2; **5**, 111349-57-6; **6**, 111464-98-3; **7** (isomer 1), 111464-99-4; **7** (isomer 2), 111465-04-4; **8**, 111465-00-0; *cis*-$Pt(NH_3)_2(ONO_2)_2$, 41575-87-5; D_2, 7782-39-0.

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Reduction of n-$C_5H_{11}N_3$ Catalyzed by Single Cubane Clusters with Mo-Fe-S and Fe-S Cores, Mediated with Methyl Viologen in Aqueous Micellar Solutions

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The Mo-Fe-S double cubane cluster $[Mo_2Fe_6S_8(SC_6H_4$-*p*-*n*-$C_8H_{17})_6(O_2C_6Cl_4)_2]^{4-}$ bridged by two SC_6H_4-*p*-*n*-$C_8H_{17}^-$ anions is dissociated into two $[MoFe_3S_4(SC_6H_4$-*p*-*n*-$C_8H_{17})_3(O_2C_6Cl_4)L]^{2-}$ (**1**; L = DMF, Me_2CO) single cubane clusters in polar organic solvents, such as DMF and Me_2CO. The solvent molecule coordinated to the molybdenum of the $MoFe_3S_4$ core is easily substituted by n-$C_5H_{11}N_3$. In the corresponding single cubane cluster with the Fe_4S_4 core, $[Fe_4S_4(SC_6H_4$-*p*-*n*-$C_8H_{17})_4]^{2-}$ (**2**), however, the thiolate ligand is substituted by n-$C_5H_{11}N_3$ only in the reduced 3- state. Both **1** and **2** function as catalysts for the reduction of n-$C_5H_{11}N_3$ by $Na_2S_2O_4$ in aqueous Triton X-100 micellar solutions, giving an equal amount of n-$C_5H_{11}NH_2$ and N_2. The reduction is enhanced efficiently by the addition of methyl viologen dication (MV^{2+}). The $MV^{\bullet+}$ radical cation formed by the reduction of MV^{2+} with $Na_2S_2O_4$ effectively transfers electrons to **1** to reduce n-$C_5H_{11}N_3$ not only with two electrons but also with six and eight electrons, affording N_2H_4 and NH_3 as well as n-$C_5H_{11}NH_2$ and N_2. On the other hand, **2** catalyzes only the two-electron reduction even in the presence of MV^{2+} to give n-$C_5H_{11}NH_2$ and N_2, suggesting that **1** is superior to **2** as a catalyst for the multielectron reduction of n-$C_5H_{11}N_3$.

Introduction

Nitrogenase is composed of iron-sulfur and molybdenum-iron-sulfur proteins, the former protein of which functions as an electron-transfer catalyst from a reduced species of ferredoxin to the latter protein involving molybdenum-iron cofactors (MoFe-co) and Fe_4S_4 clusters.[1] The MoFe-co may be an active center for the reduction of dinitrogen to ammonia and is believed to involve novel molybdenum-iron-sulfur clusters;[2] the most probable atomic ratios of Mo:Fe:S in the MoFe-co have been reported as 1:6-8:8-9.[3] The spectroscopic study on the MoFe-co suggests that both molybdenum and iron atoms are placed in a sulfide-rich coordination spheres.[4] Along this line, various Mo-Fe-S clusters have been prepared as models of the MoFe-co.[5] Among those,

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