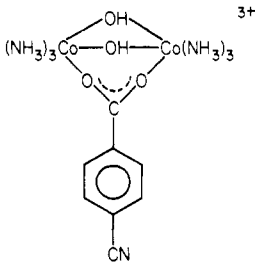
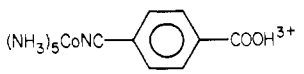


(1) the "nonreducible" nature of the ligand (deprotonated) and (2) relatively unstable precursor complex formation at the nitrile nitrogen.

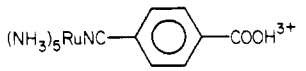
An intramolecular rate of electron transfer with the 4-cyanobenzoic acid complex can be estimated. A value of approximately 10 $Lmol^{-1}$ is available for the complexing of Cr(II) with carboxylates,[21] but in this case a somewhat lower value would be appropriate. If we use this value, an intramolecular rate constant for electron transfer $<0.028\ s^{-1}$ is obtained for 4-cyanobenzoic acid coordinated to cobalt(III).

One other possibility should be mentioned—a bridged outer-sphere mechanism where the bridging ligand serves only to hold the reductant in close proximity to the oxidant and thus facilitate outer-sphere electron transfer. Examples of this pathway involve oxidants with flexible saturated groups in the bridging ligands.[16,22] In the present case, the separation between Cr(II) and Co(III) is large with a rigid bridging ligand maintaining this separation, and this pathway does not appear likely.

The question of detailed mechanism for the reaction of



with Cr(II) can only be partly answered. Generally, reactions with Co(III) complexes involving remote attack have been assigned a radical-ion mechanism.[2,3] In terms of orbital symmetry, the donor–mediator–acceptor interaction, $\sigma-\pi-\sigma$, involves a mismatch in orbital symmetry and makes a resonance mechanism unfavorable. Analogous Ru(III) complexes are reduced by Cr(II) about 10^5 times faster than their Co(III) counterparts, and this is explained in terms of a change in mechanism to resonance transfer for Ru(III). In the latter case, resonance transfer is expected to provide a lower energy path than radical ion since the acceptor–mediator match is now $\pi-\pi$.[23] We have also studied the reaction of the



complex with Cr(II) and determined a rate constant of 2.8×10^4 L mol^{-1} s^{-1}. Thus, it appears that despite the "nonreducibility" of 4-cyanobenzoic acid it may react by a radical-ion mechanism when coordinated to cobalt(III) via the nitrile nitrogen. Similar arguments favor a resonance-transfer mechanism for the vanadium(II) reduction of the 4-cyanobenzoic acid complex. In this case the donor–mediator–acceptor interaction is $\pi-\pi-\sigma$, and the V(II) reduction proceeds more rapidly than the Cr(II) reduction even though V(II) is a weaker reductant. This change in detailed mechanism, resonance transfer for V(II) and radical ion for Cr(II), may explain the "anomalous" rate ratio referred to earlier.

Acknowledgment. The authors wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support of this research.

Registry No. Cr, 7440-47-3; $[(NH_3)_5Co(NCC_6H_4\text{-}4\text{-}CO_2H)]^{3+}$, 41759-02-8; $[(NH_3)_5Co(NCC_6H_4\text{-}3\text{-}CO_2H)]^{3+}$, 85135-60-0; V, 7440-62-2; $[(NH_3)_5Co(O_2CC_6H_4\text{-}4\text{-}CN)]^{2+}$, 40544-46-5; $[(NH_3)_5Cr(O_2CC_6H_4\text{-}4\text{-}CN)]^{2+}$, 85135-61-1.

(21) Cannon, R. D. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1222.
(22) Kupferschmidt, W.; Jordan, R. *Inorg. Chem.* **1981**, *20*, 3469.
(23) Norris, C.; Nordmeyer, F. *Inorg. Chem.* **1971**, *10*, 1235.
(24) Balahura, R.; Wright, G.; Jordan, R. *J. Am. Chem. Soc.* **1973**, *95*, 1137.
(25) Balahura, R.; Purcell, W. *Inorg. Chem.* **1975**, *14*, 1469.
(26) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162.
(27) Nordmeyer, F.; Department of Chemistry, Brigham Young University, Provo, UT, personal communication (acid independent path only).
(28) $k^{25°C} = 0.18$ L mol^{-1} s^{-1} has been reported by: Fraser, R. In "Advances in the Chemistry of the Coordination Compounds"; Kirschner, S. Ed.; Macmillan: New York, 1961; p 287.

Contribution from the Department of Chemistry, Grinnell College, Grinnell, Iowa 50112

Kinetics and Mechanisms of Ligand Exchange, Substitution, and Isomerization of Me_2SO–Amino Acid Complexes of Platinum(II): Evidence for a Pseudorotation Mechanism

LUTHER E. ERICKSON,* T. A. FERRETT,[1a] and L. F. BUHSE[1b]

Received July 30, 1982

Kinetic data are reported for the reversible, second-order substitution of Cl^- of Pt(amino acid)(Me_2SO)Cl (amino acid = glycine, sarcosine, *N,N*-dimethylglycine, proline) by Me_2SO in aqueous solution at 35 °C to form *cis*(*N,S*)- and *trans*(*N,S*)-Pt(amino acid)(Me_2SO)Cl and for the reversible, second-order chloride- and Me_2SO-catalyzed isomerization of these isomers. In addition, second-order rate constants are reported for chloride and Me_2SO exchange of cis and trans isomers in D_2O and of Me_2SO-catalyzed isomerization of Pt(*N,N*-Me_2gly)(Me_2SO)Cl in D_2O, methanol-d_3, and $CDCl_3$. The rate data, derived from NMR and radioisotope techniques, show clearly that a pseudorotation (turnstile) mechanism (presumably involving five-coordinate Pt(amino acid)(Me_2SO)Cl_2^-) predominates by a factor of 4–20 over the consecutive displacement mechanism for chloride-catalyzed isomerization. By contrast, the effect of solvent composition on the Me_2SO-catalyzed isomerization and the rate of reaction of chloride ion with Pt(gly)$(Me_2SO)_2^+$ suggest that the Me_2SO-catalyzed isomerization occurs via a consecutive displacement reaction mechanism, with intermediate formation of Pt(amino acid)$(Me_2SO)_2^+$. A general mechanism involving Pt(amino acid)Cl_2^-, cis and trans isomers of Pt(amino acid)(Me_2SO)Cl, Pt(amino acid)$(Me_2SO)_2^+$, and eight distinct trigonal-bipyramidal, five-coordinate intermediates is proposed to account for the data.

In 1976 we reported that dimethyl sulfoxide (Me_2SO) reacts with anionic amino acid complexes of platinum(II) of general formula Pt(amino acid)Cl_2^- to form both *trans*(*N,S*)- and *cis*(*N,S*)-Pt(amino acid)(Me_2SO)Cl, with the Me_2SO coor-

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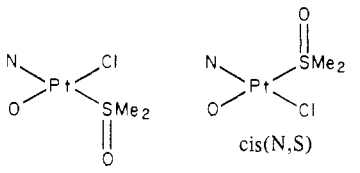
dinated through the sulfur atom.[2] We further concluded that



the cis(N,S) isomer was favored for amino acids that lacked nitrogen substitution.[3] Kinetic data were reported for the pseudo-first-order displacement of chloride by solvent Me_2SO and subsequent Me_2SO-catalyzed isomerization. More recently we have also established that several simple olefin–amino acid complexes of platinum(II) also prefer cis(N,olefin) coordination.[4]

The present study was undertaken to establish the mechanism of the isomerization reaction for these Me_2SO and olefin complexes in aqueous solution. Recent work has shown that the commonly cited generalization that isomerization reactions of platinum(II) complexes usually occur by consecutive displacement of ligands[5] is often not consistent with experimental observations, which suggests a mechanism involving pseudorotation of a CN = 5 intermediate.[6] These Me_2SO and olefin systems are particularly attractive to study because the equilibrium isomer distribution is known and the intermediate required in the consecutive displacement mechanism with Cl^- catalysis, Pt(amino acid)Cl_2^-, can be readily distinguished from the cis and trans isomers of Pt(amino acid)(Me_2SO)Cl. More importantly, investigation of the competitive formation of cis and trans isomers from Pt(amino acid)Cl_2^-, in conjunction with the isomerization reactions, provides a more stringent test of proposed mechanisms than is possible if only the isomerization of one isomer is studied. Details of the study of Me_2SO complexes and the general scheme are presented in this paper. More limited data for some olefin complexes will be described in a subsequent report.[7]

In order to provide a more complete picture of the isomerization reactions, the kinetics of ligand exchange of both cis and trans isomers was also investigated. Chloride ion exchange was studied by standard radioisotope techniques with ^{36}Cl-labeled KCl, and Me_2SO exchange was measured by NMR techniques with Me_2SO-d_6. In the course of investigating the Me_2SO exchange, we noted that Me_2SO also catalyzes the isomerization reaction and this observation was also incorporated into the complete kinetic scheme.

Experimental Section

Reagents. K_2PtCl_4 (Alfa, Inc.), amino acids (Sigma Chemical), and dimethyl sulfoxide (Baker) used to prepare the compounds involved in this work were used without further purification. D_2O (99.7% D) and Me_2SO-d_6 were obtained from Norrell, Inc.

NMR Spectra. NMR spectra were obtained with a Perkin-Elmer R-600 Fourier transform proton spectrometer with deuterium lock. For the dilute solutions 50–100 scans were routinely averaged to obtain the spectra. Chemical shifts and proton–platinum spin coupling constants of protons that were used to determine solution compositions are summarized in Table I.

Table I. Proton Chemical Shifts, δ ($^3J_{Pt-H}$), for Ligand Protons of Me_2SO Complexes and Related Species[a]

amino acid (AA)	group	species: Pt(AA)Cl_2^-	*trans*-Pt(AA)-(Me_2SO)Cl	*cis*-Pt(AA)-(Me_2SO)Cl
glycine	$S(CH_3)_2$		3.43 (20)	3.57 (26)
	CH_2	3.52 (37)	3.70 (30)	3.68 (41)
sarcosine	$S(CH_3)_2$		3.43 (20)	3.58 (25)
	NCH_3	2.68 (43)	2.68 (32)	2.88 (48)
N,N-dimethyl-glycine	$S(CH_3)_2$		3.45 (20)	3.60 (25)
	CH_2	3.65 (33)	3.79 (24)	3.84 (37)
	$N(CH_3)_2$	2.85 (35)	2.85 (27)	3.09 (39)
proline	$S(CH_3)_2$		3.43 (19)	3.57 (26)

[a] Chemical shifts are reported downfield from internal DSS and spin coupling constants in Hz.

Computer. Data analysis and computer simulation were done with a DEC-11/70 time-sharing system by using standard least-squares routines and the MIDAS program[8] for obtaining numerical solutions and graphical display for differential equations.

Synthesis of *cis*(*N,S*)- and *trans*(*N,S*)-Pt(amino acid)LCl. Trans isomers of the mixed amino acid–Me_2SO complexes were prepared by reaction of equimolar K[Pt(Me_2SO)Cl_3] and amino acid anion. The former was used in situ after its formation from equimolar aqueous K_2PtCl_4 and Me_2SO. Twenty milliliters of a solution containing five millimoles of K[Pt(Me_2SO)Cl_3] was added to five millimoles of the solid amino acid salt. After rapid (<5 min) formation of the trans complex, stoichiometric $AgNO_3$ (3 mmol/mmol of Pt) was added (as a concentrated solution) and the solution was centrifuged promptly to remove AgCl precipitate. Rotary evaporation of this solution to 5–10 mL and refrigeration overnight produced high yields (80–90%) of the yellow trans isomers.

Cis isomers of the same amino acids were prepared by heating the $KPtCl_4$–Me_2SO–amino acid reaction mixture for 1 h at 60–70 °C to achieve isomerization, catalyzed by the Cl^- still present, to the thermodynamically favored cis isomer. Silver nitrate was then added to precipitate the excess chloride (3 mmol of Ag/mmol of Pt), and the reaction mixture was centrifuged, concentrated, and refrigerated to obtain the cis isomer as a white (or very pale yellow) solid.

The structures were confirmed by analysis of the proton NMR spectra of D_2O solutions. Chemical shifts and $^3J_{Pt-H}$ coupling constants for Me_2SO ligands gave the clearest indication of isomer assignment with $\nu_{cis} - \nu_{trans} \simeq 10$ Hz (cis downfield) at 60 MHz and $^3J_{Pt-H}$ = 20 (trans) and 26 Hz (cis). Elemental analyses were also satisfactory.

Kinetic Runs. The kinetic data were obtained by following the changes in NMR spectra of reaction mixtures with time. In typical runs 0.05–0.10 mmol of solid K[Pt(amino acid)Cl_2] was added to 1.00 mL of a known concentration of Me_2SO in D_2O. Spectrra were run at frequent intervals while the sample tube was kept at probe temperature (35 °C). Similarly, solid trans isomer was dissolved in a D_2O solution of known KCl or Me_2SO concentration.

Regardless of the starting materials, the concentration of free Me_2SO and the coordinated Me_2SO of the cis and trans isomers could be monitored to follow the course of the reaction. Relative concentrations of the three species, Pt(amino acid)Cl_2^- and the cis and trans isomers, were obtained directly from the relative areas of corresponding NMR peaks. Although some overlap of peaks of ^{195}Pt satellites and other ligand protons sometimes complicated the analysis, inclusion of a carefully measured reference peak of DSS permitted complete assessment of the relative concentrations of all three species in the early stages of the reaction. Use of this internal standard also made it possible to determine relative concentrations at later stages of the equilibration for reactions in which the less soluble cis isomer precipitated.

Exchange Kinetics. The rates of exchange between cis and trans isomers and free Me_2SO were determined by dissolving the solid complexes in 1.00 mL of a solution containing a substantial excess of Me_2SO-d_6 and following the appearance of free Me_2SO in the NMR

(1) National Science Foundation Undergraduate Research Participant: (a) 1980; (b) 1981.
(2) Erickson, L. E.; Hahne, W. F. *Inorg. Chem.* **1976**, *15*, 2941. Erickson, L. E.; Albrecht, N. G.; Cartmell, J. W. *J. Coord. Chem.* **1976**, *5*, 135.
(3) This conclusion was at odds with the initial assignment of the stereochemistry; see: Kukushkin, Y. N.; Gurganova, G. P. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1970**, *15*, 2761.
(4) Erickson, L. E.; Brower, D. C. *Inorg. Chem.* **1982**, *21*, 838.
(5) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; Chapter 5.
(6) The relative importance of pseudorotation and consecutive displacement mechanisms has been thoroughly reviewed recently. See: Anderson, G. V.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *19*, 185.
(7) Erickson, L. E.; Estal, J. M.; Ferrett, T. A., manuscript in preparation.
(8) Available from Scientific Programmers, Bethlehem, PA 18018.

spectrum. Experiments were typically repeated at other Me_2SO-d_6 concentrations to establish the rate law.

Rates of exchange between cis and trans isomers and Cl^- were determined by dissolving 0.03 mmol of each complex in 1.0 mL of 0.1 M ^{36}Cl-enriched aqueous KCl. At regular intervals after the solution was mixed, 100-μL aliquots of this reaction mixture were passed through a Baker Analyzed GCA 540 anion-exchange resin in the nitrate form to remove Cl^- ion and the Pt(amino acid)-(Me_2SO)Cl containing solution was collected on steel planchets, evaporated to dryness, and counted with a Geiger counter. As the exchange reaction occurred, the counting rate of the platinum complex fraction increased to a limiting value determined by the specific activity of the Cl^- solution and the relative concentrations of Cl^- and complex. For each 100-μL aliquote, fractions were collected from the column until the activity, usually found in the third to seventh planchets, had returned to background level. The background count was subtracted from the count of each planchet. The subsequent net counts were added to obtain a total radiation count for each aliquot.

Preparation and Reactions of Pt(amino acid)(Me_2SO)$_2^+$. To investigate the possible involvement of the (Me_2SO)$_2$ complex [Pt(amino acid)(Me_2SO)$_2^+$] in the Me_2SO-catalyzed isomerization, *cis*(*N*,*S*)-Pt(gly)(Me_2SO)Cl was converted to the aquo complex by treatment with stoichiometric $AgNO_3$ in D_2O and the conversion of the cis isomer to *cis*-Pt(gly)(Me_2SO)(OH_2)$^+$ was monitored by observing the changes of the coordinated Me_2SO peak δ 3.52; $^3J_{Pt-H}$ = 23 Hz in the proton NMR spectrum. The solution was centrifuged between traces to remove AgCl formed by displacement of Cl^- by H_2O. Surprisingly, the rate of this reaction depends on Ag^+ concentration and appears to follow the second-order rate law $-d[cis]/dt = k_2[Ag^+][cis]$. The details of this process, which may involve a chloride-bridged binuclear complex Pt(amino acid)(Me_2SO)Cl–Ag,[9] are being investigated further at this time.

Conversion of the aquo complex to Pt(amino acid)(Me_2SO)$_2^+$ was accomplished by addition of Me_2SO to the reaction mixture containing the aquo complex. The relatively slow conversion of aquo complex to an equilibrium mixture of aquo and (Me_2SO)$_2$ complexes was again followed by changes in the NMR spectra. The two nonequivalent Me_2SO groups showing equal intensities and the relative shifts (3.67 and 3.58 ppm) and $^3J_{Pt-H}$ values (26 and 20.6 Hz) are typical of the cis(N,S)- and trans(N,S)-Me_2SO moieties of the individual cis and trans isomers of Pt(gly)(Me_2SO)Cl. With a twofold excess of Me_2SO initially, the conversion to Pt(gly)(Me_2SO)$_2^+$ is >80%.

The addition of stoichiometric chloride as 1 M KCl/D_2O produced almost immediate conversion to the thermodynamically favored *cis*(*N*,*S*)-Pt(gly)(Me_2SO)Cl, as revealed by NMR spectral changes. The reaction was essentially complete within 2 min. Thus, the (Me_2SO)$_2$ species is not stable in the presence of 1 equiv of Cl^- ion.

Results

Kinetic Data: Ligand Substitution and Isomerization. The kinetic data for isomerization and for substitution of Me_2SO by Cl^- obtained for several Me_2SO complexes are all adequately represented by Scheme I, where L = Me_2SO. The second-order rate constants are defined by eq 1–3, where [A],

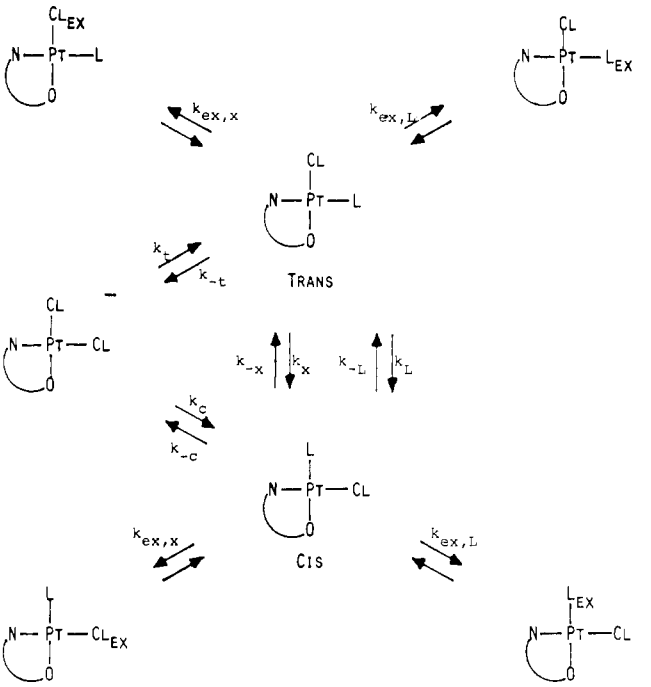
$$d[trans]/dt = k_t[A][L] + (k_{-x}[Cl^-] + k_{-L}[L])[cis] - (k_{-t} + k_x)[trans][Cl^-] - k_L[trans][L] \quad (1)$$

$$d[A]/dt = k_{-t}[trans][Cl^-] + k_{-c}[cis][Cl^-](k_t + k_c)[A][L] \quad (2)$$

$$d[cis]/dt = k_c[A][L] + (k_x[Cl^-] + k_L[L])[trans] - (k_{-c} + k_{-x})[cis][Cl^-] - k_{-L}[cis][L] \quad (3)$$

[trans], and [cis] are the concentrations of Pt(amino acid)Cl_2^-, *trans*(*N*,*L*)-Pt(amino acid)LCl, and *cis*(*N*,*L*)-Pt(amino acid)LC, respectively. The rate constants k_t, k_c, k_{-t}, and k_{-c}

Scheme I



are for ligand substitution, while k_x, k_{-x}, k_L, and k_{-L} are for the direct isomerization between trans and cis isomers with Cl^- or L catalysis.

The complete scheme evolved from a series of separate experiments. First, kinetic data for the conversion of Pt(amino acid)Cl_2^- to cis and trans isomers and their subsequent conversion to an equilibrium mixture of cis and trans isomers was treated as a system of competing reversible second-order reactions with the four rate constants k_c, k_{-c}, k_t, and k_{-t}. Isomerization occurs in this scheme only through consecutive displacement of ligands. For complexes for which the cis isomer predominates greatly at equilibrium, k_{-c} can be ignored and only three rate constants are required to characterize the system. Estimates of k_c and k_t were obtained from initial rates of appearance of cis and trans isomers. A computer simulation was then used to determine the value of k_{-t} that best reproduced the concentration–time data. The time at which the trans isomer concentration reached a maximum and the trans concentration at that time were the most important quantities employed to judge the quality of the fit. Reasonably good fits of the data for 2–3 half-lives of the dichloro complex (A) were obtained for the reaction of Pt(glycine)Cl_2^- with Me_2SO. The inadequacy of the consecutive displacement scheme was revealed when we compared a computer simulation to observed centration–time data for the isomerization reaction beginning with the trans isomer and Cl^-. The simulation was generated by using the rate constants obtained from experiments starting with the dichloro complex (A) and Me_2SO. The cis isomer concentration grew at a rate comparable to the rate of appearance of Pt(gly)(Me_2SO)Cl, whereas the consecutive displacement mechanism required that there be a substantial induction period while Pt(gly)Cl_2^- builds up, before a significant amount of cis isomer is formed. Thus a direct chloride-catalyzed path for isomerization was added to the initial scheme. The complete scheme also includes a pathway for catalysis of the isomerization by L = Me_2SO, consistent with the observation that the isomerization occurs at a significant rate when free Me_2SO is present, even in the absence of Cl^-.

The rate constants for substitution and exchange given in Table II for each amino acid and Me_2SO are average best fit values obtained from at least three sets of experiments. First k_L and k_{-L} were obtained by monitoring the Me_2SO-catalyzed

(9) Several such Ag^+-assisted aquation reactions of chloro complexes are listed by: Jones, M. M. Clark, H. R. *J. Inorg. Nucl. Chem.* **1971**, *33*, 413. However, no Pt(II) complexes are included, in spite of the fact that silver salts are commonly used to convert halo to corresponding aquo complexes.

Table II. Rate and Equilibrium Constants for Pt(amino acid)(Me_2SO)Cl Reactions at 35 °C

rate[a] or equil const	glycine	sarcosine	*N,N*-dimethylglycine	proline
$K = [cis]_{eq}/[trans]_{eq}$	45	6.9	1.2	
k_t	18	33	42	190
k_{-t}	1.3	0.83	1.1	1.0
k_c	17	27	17	<2
k_{-c}	0.025	0.10	0.33	
k_x	5.5	7.5	20	1.0
k_{-x}	0.13	1.1	17	
k_L	5.7	5.5	1.8	0.5
k_{-L}	0.13	0.80	1.6	
$k_{ex,L}$(trans)	4.0	9.0	10	
$k_{ex,L}$(cis)	600	27	5.0	
$k_{ex,x}$(trans)	>2400	2400	170	
$k_{ex,x}$(cis)	95	160		

[a] Second-order rate constants are all in L mol^{-1} s^{-1} as defined by Scheme I. Values given are 10^5k.

isomerization of the trans to cis isomers with the assumption of the rate law

$$-d[trans]/dt = k_L[L][trans] - k_{-L}[L][cis] = k_L'[trans] - k_{-L}'[cis] \quad (4)$$

where k_L' and k_{-L}' are pseudo-first-order rate constants for the isomerization. Plots of ln ($[trans]_t - [trans]_\infty$) vs. time were linear with slopes = $k_L' + k_{-L}'$. Separate values for k_L' and k_{-L}' were obtained from the equilibrium constant $K = [cis]/[trans] = k_L'/k_{-L}'$. The second-order rate constants k_L and k_{-L} were obtained by dividing k_L' and k_{-L}' by the Me_2SO concentration.

The remaining rate constants were then obtained from concentration–time plots for reactions of the dichloro complex with Me_2SO and of the trans isomer with Cl^-. Initial slopes of plots for the former permitted initial estimates of k_t and k_c; the reaction of the trans isomer with Cl^- yielded k_{-t} and k_x. For glycine, sarcosine, and proline complexes the reverse reactions (with rate constants k_{-c}, k_{-x}, and k_{-L}) were too slow to have significant effects on the concentration–time plots. The rate constant k_L were available from the Me_2SO catalysis experiments. The effects of small changes in rate constants on computer-simulated plots of concentration vs. time were then examined by systematically varying k values beginning with initial estimates based on initial slopes. We determined a set of best values for k_t, k_{-t}, k_c, and k_x from comparison of simulated and observed plots, noting particularly times at which concentrations reached (a) 1 half-life or (b) a maximum value and (c) crossover points where two concentrations are equal and the concentrations at these points. By requiring that the calculated data match experimental data for at least two (and usually three to four) different experiments within narrow limits, the uniqueness of the set of values for the rate constants is assured, within ±25%. Finally the much smaller k_{-x} and k_{-c} values were estimated from the trans to cis equilibrium constant, since

$$K_{eq} = k_x/k_{-x} = k_L/k_{-L} = k_tk_{-c}/k_{-t}k_c \quad (5)$$

For the glycine system K_{eq} was determined from the equilibrium constant $K = k_c/k_{-c}$ for the cis + Cl^- → $Pt(gly)Cl_2^-$ + Me_2SO reaction and the k_c value determined from kinetic data. The low solubility of the cis isomer precluded a determination of K_{eq} and k_{-c}, k_{-x}, and k_{-L} for the proline system.

For the *N,N*-dimethylglycine complexes, the reverse reactions cannot be ignored since the equilibrium constant for trans → cis is 1.2. However, the Me_2SO-catalyzed isomerization is slower than the Cl^--catalyzed isomerization so the system can be described quite accurately by the six rate constants k_c, k_{-c}, k_t, k_{-t}, and k_x, and k_{-x}. Of these, k_{-t} and k_{-c} are much smaller than the rest, which is reflected (a) in the essentially complete reaction of $Pt(dmg)Cl_2^-$ with Me_2SO to form nearly equimolar cis and trans isomers and (b) in the failure of the $Pt(dmg)Cl_2^-$ concentration to build up past 5% of the initial trans concentration when 0.13 M Cl^- is added to 0.05 M *trans*-Pt(dmg)(Me_2SO)Cl.

Kinetic Data: Ligand-Exchange Reactions. Ligand-exchange reactions of cis and trans isomers were treated as reversible second-order reactions as represented by eq 6

$$Pt(amino\ acid)LCl + L^* \rightarrow Pt(amino\ acid)L^*Cl + L \quad (6)$$

for which

$$-d[Pt-L]/dt = k_{ex,L}([Pt-L][L^*] - [Pt-L^*][L]) \quad (7)$$

where $L^* = Me_2SO$-d_6. With a large excess of L^*, the second term can be dropped and the disappearance of coordinated Me_2SO becomes a first-order process with a rate constant $k_1 = k_{ex,L}[L^*]$. The $k_{ex,L}$ values listed in Table II were obtained from first-order plots of ln [Pt–L] vs. time, where [Pt–L] is the relative concentration of the unsubstituted isomer.

When the exchange reaction and the isomerization reaction have comparable rates, the disappearance of Pt–L and appearance of free L may be complicated by the isomerization reaction. For the thermodynamically favored cis isomers of glycine or sarcosine, the rate of exchange is much greater than the rate of isomerization, so this complication does not present a problem. For the trans isomer of glycine or sarcosine Pt–L disappears and L appears by both pathways so the observed rate of disappearance of Pt–L is an upper limit on the actual exchange rate. The $k_{ex,L}$ values given in Table II for the trans isomers of glycine and sarcosine are the differences between the observed rate constants based on the appearance of free Me_2SO and k_L, the independently determined rate constant for Me_2SO-catalyzed isomerization.

For the *N,N*-dimethylglycine complex, the rate of Me_2SO exchange of the trans isomer is greater than the isomerization rate so that it can be determined from the disappearance of the *trans*-Pt–L Me_2SO peak. Relative rates of exchange of cis and trans isomers were then determined by first chemically equilibrating a cis–trans mixture and then adding excess Me_2SO-d_6 and measuring the relative rates of decrease of coordinated Me_2SO peaks of both isomers in the NMR spectrum.

The rate of chloride exchange was determined by measuring the activity of ^{36}Cl incorporated into the platinum complex after it was separated from a solution containing labeled Cl^-. The data were fit by assuming that the reaction

$$Pt-Cl + {}^{36}Cl^- \rightarrow Pt-{}^{36}Cl + Cl^- \quad (8)$$

is described by eq 9:

$$d[Pt-Cl]/dt = k_{ex,Cl}[Pt-Cl][{}^{36}Cl] - k_{ex,Cl}[Pt-{}^{36}Cl][Cl^-] \quad (9)$$

Equation 9 can be integrated to yield

$$\ln \{[Pt-Cl]_0[{}^{36}Cl^-]_0 + ([Pt-Cl]_0 + [{}^{36}Cl^-]_0)[Pt-{}^{36}Cl]\} = \ln [Pt-Cl]_0[{}^{36}Cl]_0 + k_{ex,Cl}\{[Pt-Cl]_0 + [{}^{36}Cl^-]_0\}t \quad (10)$$

which was used to obtain $k_{ex,Cl}$ from linear plots of the left-hand side vs. t and the known initial concentrations of Pt–Cl and $^{36}Cl^-$.

Isomer Ratio at Equilibrium. For the Me_2SO complexes the equilibrium ratio of cis to trans isomers decreases with *N*-methyl substitution from 45 to 6.9 to 1.2 in the series glycine, sarcosine, and *N,N*-dimethylglycine. The ratio could not be determined readily for proline because of the very low solubility of the cis isomer (<0.003M, estimated). This trend is reflected in the rate constants k_t, k_{-t}, and k_{-c}. Most of the variation

Table III. Effects of Solvent on Rate[a] and Equilibrium Constants for Isomerization of *trans*-Pt(*N*,*N*-Me_2gly)(Me_2SO)Cl at 55 °C

solvent	$10^5 k_L$	$10^5 k_{-L}$	$K = k_L/k_{-L}$
D_2O	4.2	3.9	1.08
methanol-d_3	1.12	1.16	0.97
$CDCl_3$	0.93	2.40	0.39

[a] See footnote *a* of Table II.

can be attributed to the effect of substitution on k_{-c}, the rate constant for displacement of Me_2SO of the cis isomer by Cl^-, which decreases by an order of magnitude in going from glycine to *N*,*N*-dimethylglycine. This cis isomer preference for the glycine complex is somewhat greater in D_2O than in Me_2SO.[2]

Solvent Effects on Isomerization Rates. The effect of solvent composition on the rate of the isomerization of *trans*-Pt(*N*,*N*-dimethylglycine)(Me_2SO)Cl in 0.50 M Me_2SO at 55 °C is summarized in Table III. This complex was used in the study because it was the only one that is sufficiently soluble (0.50 M) in all three solvents. The rates of both forward and reverse reactions are substantially less in the less polar methanol and chloroform than they are in water. In addition to influencing the rate of reaction, the solvent also influences the equilibrium constant for the reaction. Whereas the cis isomer is slightly favored over the trans in D_2O, the trans isomer is slightly favored over the cis in methanol-d_3 and is favored by about a 3/1 ratio in $CDCl_3$. Thus, the rate of the forward reaction is more sensitive to the solvent composition than that of the reverse reaction.

Discussion

Chloride-Involved Isomerization Pathways. The ability to monitor simultaneously concentrations of both cis and trans isomers and the dichloro species enabled us to assess the relative importance of the consecutive displacement and chloride-catalyzed mechanisms for the isomerization reaction of trans isomers. Consecutive displacement of Me_2SO by Cl^- followed by displacement of Cl^- by Me_2SO is associated with k_{-t} and k_c and chloride catalysis with k_x. A rough measure of the relative importance of the chloride-catalyzed isomerization and the consecutive displacement pathways is given by the ratio $k_x/(k_x + k_{-t})$, which varies from 0.80 for the glycine complex to 0.95 for dimethylglycine. This fraction is a *lower limit* for the fraction of initial trans molecules that isomerizes without conversion to Pt(amino acid)Cl_2^- since k_t is typically larger than k_c and a substantial fraction of Pt(amino acid)Cl_2^- formed is converted back to the trans isomer, from whence it again has an 80–95% chance of direct conversion to the cis isomer. In any case, the consecutive displacement route for isomerization is definitely a minor route for these complexes.

The insignificance of the consecutive displacement pathway for chloride-involved isomerization is particularly striking for the proline complex. The reaction of Pt(pro)Cl_2^- with Me_2SO yields essentially exclusively *trans*-Pt(pro)(Me_2SO)Cl at a rate which is greater than the combined rates of formation of cis and trans isomers for the other amino acids. The subsequent isomerization of the trans isomer to the insoluble cis isomer follows a simple second-order rate law for both Cl^- and Me_2SO catalysis, and both rates are an order of magnitude slower than those of any of the other three systems. The low solubility of the cis isomer makes it impossible to obtain a reliable equilibrium constant for the reaction so that k_{-c}, k_{-x}, and k_{-L} could not be estimated, but they are probably less than 10^{-6} L mol^{-1} s^{-1}.

Me_2SO-Catalyzed Isomerization Pathways. For the chloride-involved isomerization the relative importance of the consecutive displacement pathway and Cl^--catalyzed pathway can be assessed because the concentrations of cis and trans isomers and dichloro species can be followed independently.

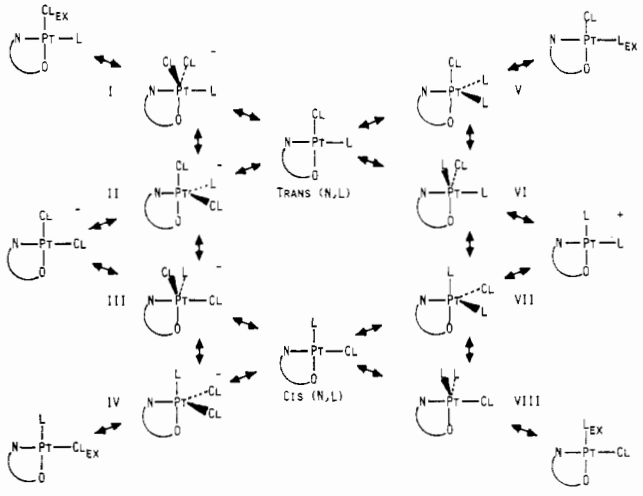


Figure 1. Proposed general mechanism for ligand substitution, isomerization, and exchange of Pt(amino acid) LCl species.

However, no direct evidence for existence of species Pt(amino acid)$(Me_2SO)_2^+$, the analogous ionic intermediate in the Me_2SO-catalyzed isomerization, could be found in the NMR spectrum. Even in pure Me_2SO, only the trans and cis species are evident in the spectrum.[2]

Although Pt(amino acid)$(Me_2SO)_2^+$ cannot be observed directly, two observations suggest that the Me_2SO-catalyzed isomerization proceeds mainly by a consecutive displacement mechanism involving such an intermediate. First of all, Pt(gly)$(Me_2SO)_2^+$ reacts rapidly ($t_{1/2} < 1$ min) with stoichiometric Cl^- to form essentially all *cis*-Pt(gly)(Me_2SO)Cl, so that very little $(Me_2SO)_2$ species would ever build up in any reaction mixture containing stoichiometric Cl^-. Roulet and Barbey used a similar argument in concluding that the alkyl sulfide catalysis of cis–trans isomerization of bis(dialkyl sulfide)dihaloplatinum(II) occurs via the four-coordinate species Pt(dialkyl sulfide)$_3Cl^-$.[10] Furthermore, the effect of solvent polarity on k_L and k_{-L}, the rate constants for Me_2SO catalysis of the isomerization reactions, argues for involvement of a polar intermediate.[11] If Pt(amino acid)$(Me_2SO)_2^+$ were formed as in intermediate, the isomerization rates would be expected to decrease with decreased solvent polarity, since the cis and trans isomers are neutral species. On the other hand, if the neutral five-coordinate species Pt(amino acid)-$(Me_2SO)_2Cl$ were involved, the rate should be little affected by solvent polarity. As shown in Table III, the rates of isomerization of Pt(*N*,*N*-Me_2gly)(Me_2SO)Cl are substantially greater in D_2O than they are in less polar methanol-d_3 and $CDCl_3$. Thus we conclude that the Me_2SO-catalyzed isomerization may proceed by the usual consecutive displacement mechanism via Pt(amino acid)$(Me_2SO)_2^+$.

Me_2SO and Cl^- Exchange Rates. The Me_2SO-exchange rates are not significantly different for the trans isomers of glycine, sarcosine and *N*,*N*-dimethylglycine, but they decrease by an order of magnitude with methyl substitution for the cis isomers. By contrast, Cl^--exchange rates decrease sharply with methyl substitution for the corresponding trans isomers but are comparable, and much slower, for the cis isomers. Thus, the rate of exchange of the ligand cis to the nitrogen is most influenced by methyl substitution at the nitrogen. Chloride-exchange rates are faster than chloride-catalyzed isomerization so exchange rate data were not complicated by isomerization or substitution) reactions. For *cis*-Pt(gly)(Me_2SO)Cl, the chloride-exchange rate was too fast to measure reliably by our techniques.

(10) Roulet, R.; Barbey, C. *Helv. Chim. Acta* **1973**, *56*, 2179.
(11) Louw, W. J. *Inorg. Chem.* **1977**, *16*, 2147.

General Mechanism. A general mechanism that accounts for the observed kinetic data is shown in Figure 1. The mechanism shows the cis and trans isomers, the products of Cl^- and L (=Me_2SO in this case) exchange of these isomers, the anionic species Pt(amino acid)Cl_2^-, the cationic species Pt(amino acid)L_2^+, four postulated CN = 5 intermediates that could serve as intermediates for chloride exchange or displacement of L by Cl^-, and four parallel CN = 5 intermediates that could serve as intermediates for L exchange or displacement of Cl^- by L. The four intermediates I–IV provide simple routes for displacement of L by Cl^- and for Cl^- exchange of the cis and trans isomers of Pt(amino acid)LCl, but vertically adjacent pairs can also be interconverted by a pseudorotation process that is most clearly described as a 60° turnstile rotation of the $PtCl_2L$ moiety about the PtNO plane.[12] Similarly intermediates V–VIII provide simple routes to displacement of L by Cl^- and for L exchange; vertically adjacent pairs can be interconverted by a 60° turnstile rotation of the PtL_2Cl moiety about the PtNO plane.

This mechanism, in addition to appealing to a sense of symmetry and order, accounts for the observed rate data including (a) the fact that Cl^- can catalyze the isomerization without a consecutive displacement of ligands, (b) the fact that exchange of both Cl^- and L for both isomers can occur without isomerization, and (c) the fact that methyl substitution affects the relative rates of these processes. In terms of this mechanism, the chloride-catalyzed isomerization occurs via intermediate II, which undergoes a 60° turnstile rotation or pseudorotation to III, followed by loss of Cl^-. This process occurs in competition with the consecutive displacement pathway, which goes trans → II → Pt(amino acid)Cl_2^- → III → cis. Chloride-exchange reactions, by contrast, can occur via I or IV and do not require formation of II or III. Similarly, L exchange can occur via V and VIII and does not require formation of IV or VII. Thus exchange reactions are generally faster than isomerization or substitution reactions for a given isomer. It should be noted that exchange reactions could also go by turnstile rotation mechanisms involving, for example

$$\textit{trans}\text{-Pt–Cl} \rightarrow \text{II} \rightarrow \text{I} \rightarrow \textit{trans}\text{-Pt–Cl}_{ex}$$

but the kinetic data do not permit us to distinguish between these alternate pathways.

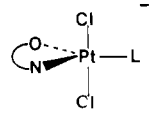
The effect of *N*-methyl substitution on the rate constants can be readily accounted for by the proposed general mechanism of Figure 1. The two rate constants that are most affected by *N*-methyl substitution are $k_{ex,Cl}$ for the trans isomers and $k_{ex,L}$ for the cis isomers. In each case the proposed intermeidate is a symmetric one with two Cl atoms or Me_2SO ligands eclipsing NH_2 protons of coordinated glycine. Thus Cl^- exchange for *trans*-Pt(gly)(Me_2SO)Cl via and I and Me_2SO exchange of *cis*-Pt(gly)(Me_2SO)Cl via VIII are orders of magnitude faster than any of the substitution or isomerization reactions, and the rates are reduced drastically by methyl substitution. This substituent effect can be attributed either to steric effects or to loss of intramolecular hydrogen bonding between NH_2 protons and Cl atoms or Me_2SO oxygen atoms on methyl substitution.[2]

Me_2SO exchange for trans isomers and Cl^- exchange of cis isomers, by contrast, are not much influenced by methyl substitution. Both $k_{ex,Cl}$(cis) and $k_{ex,L}$(trans) increase moderately with methyl substitution, which might be a reflection of small changes in the inductive effect of the NH_2 group with methyl substitution. However, the substituent effect is small, consistent with the small difference between trans isomers and V or cis isomers and IV, especially in the Pt–N–O– coordination plane.

Unlike the Cl^-- and Me_2SO-exchange reactions, which involve symmetric intermediates having identical ligands in the equatorial plane and reactants and products with identical energy, the substitution and isomerization reactions involve unsymmetric intermediates and reactants and products of unequal energy. The effect of substituents on the rates of substitution and isomerization is less easily accounted for by the proposed mechanism. Nevertheless, several features of the data fit the model well. In particular, the relatively small effect of methyl substitution on k_t and k_{-t} is consistent with involvement of II, in which the coordination around the nitrogen is similar to that of both Pt(amino acid)Cl_2^- and *trans*-Pt(amino acid)LCl. The ratio k_t/k_{-t}, which is the equilibrium constant for the Pt(amino acid)Cl_2^- → trans reaction, is also not much affected by methyl substitution.

The large change in the equilibrium constant for the trans → cis isomerization with methyl substitution is associated mainly with effects on k_{-c}, k_{-x}, and k_{-L}, with k_c, k_x, and k_L showing much smaller variation. Thus the decrease in preference for the cis isomer with methyl substitution is associated mainly with an *increase* with methyl substitution in the rate of reactions that convert the cis isomer back to the trans isomer or Pt(amino acid)Cl_2^-. This result is somewhat surprising. On the basis of the effects of substitution on exchange rates, rates of reactions going through III would be expected to be decreased by methyl substitution. Of course, the decrease would have to be greater in the forward (toward cis) than the reverse (away from cis) direction to also account for the substantial decrease in the relative stability of the cis isomer with substitution. In any case, isomerization and substitution reactions that go through III behave anomalously.

Five-Coordinate Species. The CN = 5 ionic intermediates that we suggest as the ones involved in chloride-catalyzed isomerization (II and III) are very similar to the one suggested by Louw for the iodide-catalyzed isomerization of PtL_2I_2 (where L = PMe_2Ph),[11] which Anderson and Cross identify as the only well-documented case of a likely pseudorotation mechanism catalyzed by an anion.[6] Perhaps proposed intermediates II and III might both be unstable with respect to the symmetric species IX.



IX

Several reports of the isolation of parallel neutral CN = 5 species with a diamine or diimine chelate ligand, an olefin ligand, and two Cl^- ligands have appeared.[13–16] In these species the two chlorides occupy equivalent axial positions. Parallel kinetic behavior is observed for Me_2SO complexes described in this paper and the olefin complex Pt(gly)(2-methyl-3-buten-2-ol)Cl.[7] Thus, a turnstile (pseudorotation) mechanism appears to be an important isomerization pathway for chloride-catalyzed isomerization of complexes of Pt(amino

(12) Several distinct topological changes can lead to interchange of ligands on five-coordinate species as summarized by: Muetterties, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 1636, 4115. The turnstile description seems most appropriate to describe the process when two adjacent sites are part of a chelate ring. See: Ugi, I.; Marguarding, D.; Klusacek, H.; Gillespie, P.; Ramirez, F. *Acc. Chem. Res.* **1971**, *4*, 288. The process can also be viewed as a Berry pseudorotation involving simultaneous opening of the O–Pt–Cl angle and closing of the N–Pt–L angle. See: Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

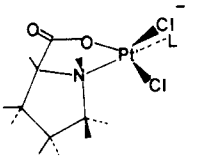
(13) Maresca, L.; Natile, G.; Cattalini, L. *Inorg. Chem.* **1975**, *14*, 79.
(14) Maresca, L.; Natile, G.; Calligaris, M.; Delise, P.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 2386.
(15) DeRenzi, A.; Panunzi, A.; Saporite, A.; Vitagliano, A. *Gazz. Chim. Ital.* **1977**, *107*, 549.
(16) Van der Poel, H.; Van Koten, G.; Kokkes, M.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 2941.

acid)LCl, where L = Me_2SO or an olefin. Along with our previously reported parallel isomer preference of mixed Me_2SO- or olefin–amino acid complexes of platinum(II),[4] these observations emphasize the similar coordinating properties of Me_2SO and olefins for Pt(II), which are revealed clearly by the similarities of $K[Pt(Me_2SO)Cl_3]$ and Zeise's salt, $K[Pt(ethylene)Cl_3]$.[17]

The isolation of five-coordinate neutral species of general formula $Pt(diamine)(Me_2SO)Cl_2$, parallel to the olefin complexes that have been reported, should be possible, and the mechanism of their conversion to four-coordinate species in polar solvents would help to clarify the role of such species in isomerization of the four-coordinate species. Such a study of L_2PtX_2 and the five-coordinate species L_3PtX_2, where L = phosphole, has recently been reported by MacDougall, Nelson, and Mathey.[18]

It is not clear why the turnstile (pseudorotation) mechanism should predominate for the chloride-catalyzed isomerization while the consecutive displacement mechanism appears to predominate for the Me_2SO-catalyzed reaction. Clearly, different intermediates are involved so there is no particular reason to expect similar behavior. Of course, without being able to observe the $Pt(amino\ acid)(Me_2SO)_2^+$ species, we are basing our conclusions about the mechanism of the Me_2SO-catalyzed isomerization on less direct evidence. It appears that the Me_2SO-catalyzed reaction simply conforms to the usual pattern in platinum(II) complexes; the chloride-catalyzed reaction is the unusual one.

Proline and Sarcosine Complexes. This discussion has focused primarily on the complexes of glycine and its methyl substituents, but the data for the proline complexes can also be understood in terms of the proposed mechanism. The presence of the proline ring introduces both asymmetry and additional steric effects that strongly influence the kinetics. First of all k_t is so much greater than k_c that $Pt(pro)Cl_2^-$ is converted completely to the trans isomer by Me_2SO before any cis complex is observed in solution. The rate constant k_t is also greater than any of the isomerization rate constants of the other substituted glycines. The trans isomer is converted essentially completely to the cis isomer at equilibrium, partly owing to the very low solubility of the cis isomer. However, the rates of both Cl^-- and Me_2SO-catalyzed isomerization are both much slower than corresponding reactions with the glycine complexes. In each case, the reaction would be required to go through an intermediate, II or VI, in which steric effects would be substantial as suggested by X.



X

It should be noted that, for both proline and sarcosine complexes, the asymmetry of the molecule requires that two nonequivalent sets of intermediates should be included in a complete mechanism. However, the broad features of the kinetic behavior can be accounted for without reference to this important distinction. For example, the two distinct forms of intermediate X for L-proline would both be expected to show large steric effects on the isomerization mechanism.

Acknowledgment. This research was supported by a Northwest Area Foundation Grant of Research Corp. and by the National Science Foundation through the Undergraduate Research Participation Program (1980, Grant No. SPI-7926580; 1981, Grant No. SPI-8025688) and an equipment grant (No. CDP-8007871) toward purchase of a Fourier transform NMR spectrometer. The able assistance of the Grinnell College physical chemistry class of 1981 in demonstrating the feasability of the Me_2SO exchange is also acknowledged with appreciation.

Registry No. $Pt(gly)Cl_2^-$, 24653-14-3; $Pt(N,N\text{-}Me_2gly)Cl_2^-$, 85152-54-1; $Pt(pro)Cl_2^-$, 45847-73-2; $Pt(AA)Cl_2^-$ (AA = sarcosine), 24653-15-4; *trans*-$Pt(gly)(Me_2SO)Cl$, 60338-47-8; *cis*-$Pt(gly)(Me_2SO)Cl$, 60383-64-4; *trans*-$Pt(N,N\text{-}Me_2gly)(Me_2SO)Cl$, 62929-50-4; *cis*-$Pt(N,N\text{-}Me_2gly)(Me_2SO)Cl$, 62870-11-5; *trans*-$Pt(pro)(Me_2SO)Cl$, 85152-56-3; *cis*-$Pt(pro)(Me_2SO)Cl$, 85201-30-5; *trans*-$Pt(AA)(Me_2SO)Cl$ (AA = sarcosine), 85201-82-7; *cis*-$Pt(AA)(Me_2SO)Cl$ (AA = sarcosine), 85152-55-2; Me_2SO, 67-68-5; Cl^-, 16887-00-6.

(17) Considerable evidence is summarized by: Davies, J. A. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 141.
(18) MacDougall, J. J.; Nelson, J. H.; Mathey, F. *Inorg. Chem.* **1982**, *21*, 2145.