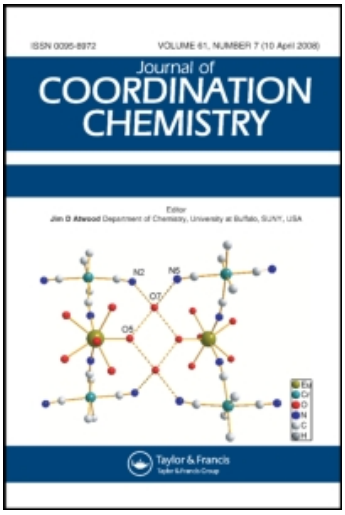

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A PROTON NMR STUDY OF THE STEREOCHEMISTRY AND KINETICS OF THE REACTIONS OF DIMETHYL SULFOXIDE WITH POTASSIUM DICLOROGLYCINATOPLATINATE(II) AND ITS METHYL DERIVATIVES

Luther E. Erickson[a]; James W. Cartmell[a]; Norman G. Albrecht[a]
[a] Department of Chemistry, Grinnell College, Grinnell, Ia., U.S.A.

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A PROTON NMR STUDY OF THE STEREOCHEMISTRY AND KINETICS OF THE REACTIONS OF DIMETHYL SULFOXIDE WITH POTASSIUM DICLOROGLYCINATOPLATINATE(II) AND ITS METHYL DERIVATIVES.

LUTHER E. ERICKSON, JAMES W. CARTMELL and NORMAN G. ALBRECHT

Department of Chemistry, Grinnell College, Grinnell, Ia., 50112, U.S.A.

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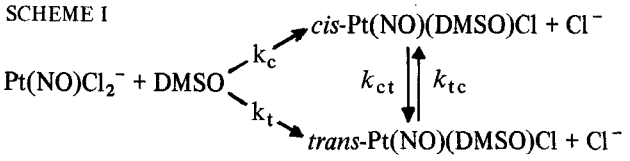
Amino acid complexes of general formula $K[Pt(NO)Cl_2]$, where NO denotes the metal bonded atoms of the amino acid, react completely with solvent DMSO to yield two products, *cis*- and *trans*-Pt(NO) (DMSO)Cl, where *cis* and *trans* refer to positions of DMSO relative to coordinated nitrogen. The products were identified and kinetic data were obtained from changes in the proton nmr spectra of the amino acid, when DMSO-d_6 was the solvent, or of both amino acid and coordinated DMSO, when ordinary DMSO was the solvent. For glycine and α-aminoisobutyric acid complexes, the rate of displacement of *trans* chloride exceeds that of *cis* chloride by a factor of 3. However, subsequent equilibration favors the *cis* isomer over the *trans* isomer by a factor of 10. By contrast, for the corresponding N,N-dimethyl derivatives, the rates of formation of the two isomers are more nearly the same and the equilibrium ratio does not differ from the kinetic ratio. In addition to providing a sensitive technique for evaluating small differences in kinetic *trans*-effects, these observations strongly suggest that the stereochemistry of Pt(NO) (DMSO)Cl for the corresponding alanine complex described by Kukushkin and Guryamava should be denoted *cis*, rather than the *trans* reported.

INTRODUCTION

In attempting to evaluate the effect of solvent on the conformation of glycinate chelate rings in platinum chelates of amino acids of general formula $K[Pt(NO)Cl_2]$,[1] where NO denotes the amino acid atoms which are coordinated to platinum, we noticed that the compounds react quite rapidly with dimethyl sulfoxide (DMSO) solvent. Such a reaction of DMSO with the alanine complex $K[Pt(ala)Cl_2]$, had been reported by Kukushkin and Guryamava, who isolated the same neutral complex, denoted Pt(NO) (DMSO)Cl, by five separate routes[2]. On the basis of some assumptions concerning the stereochemistry of intermediate reactions, they concluded (1) that the coordinated DMSO is linked to platinum at the sulfur, and (2) that the DMSO is *trans* to the nitrogen of the chelated alanine. The relatively complex changes we observed in the nmr spectra of freshly dissolved samples of two or three methyl substituted glycine complexes convinced us that more than one DMSO-containing product is usually produced.

A more thorough investigation has revealed that both *cis* and *trans* (where *cis* and *trans* here refer to the relation between coordinated DMSO and the amine nitrogen of the chelated amino acid) products are formed in the reaction with solvent DMSO (Scheme I). Furthermore, the kinetically favored product is often not the thermodynamically favored product is produced by subsequent equilibration of the *cis* and *trans* isomers. On the basis of the spectral changes and the kinetic data calculated from the spectral data, we conclude that the stereochemistry assigned by Kukushkin and Guryamava is not correct and that the thermodynamically preferred product of the reaction with the alanine complex is the *cis* isomer.

SCHEME I



Conclusions about the stereochemistry of the reaction were based on kinetic studies (monitered by following changes in the proton nmr spectrum) of the detailed course of the reaction of solvent DMSO with four amino acid complexes whose nmr spectra were somewhat simpler than that of alanine. The four were glycine (gly), N,N-dimethylglycine (dmg), α-aminoisobutyric acid (aba), and N,N-dimethyl-α-aminoisobutyric acid(dmaba). In every case, we

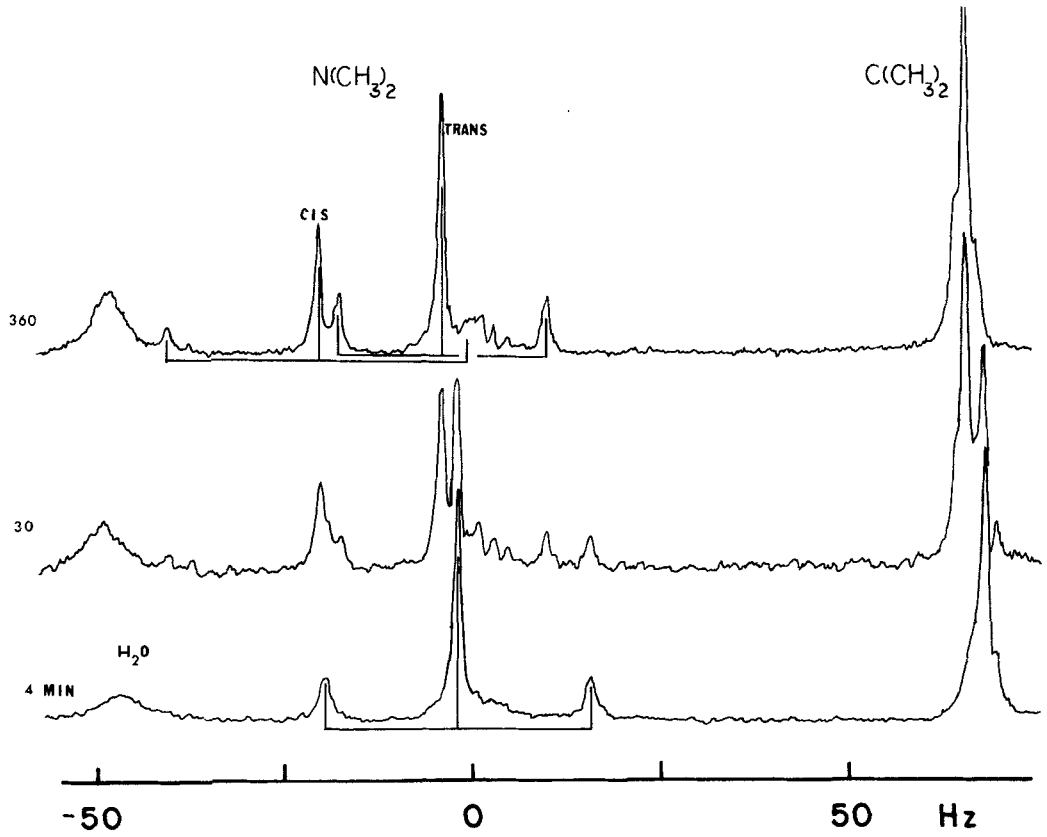


FIGURE 1. Proton nmr spectra of K[Pt(dmaba)Cl_2] in DMSO-d_6 showing the changes resulting from displacement of Cl^- by solvent at 41°.

found that both *cis* and *trans* isomers need to be considered. By following the disappearance of starting material, the simultaneous appearance of the two products and the subsequent changes in their relative concentrations, we were able to account for all data and to determine first-order rate constants, k_c, k_t, k_{ct}, and k_{tc}, for the four steps shown in Scheme I.

EXPERIMENTAL SECTION

Materials

Syntheses of amino acids and their dichloro complexes of platinum(II) were carried out as described earlier.[1] Reagent grade dimethyl sulfoxide (Baker) was used without further purification. Dimethyl sulfoxide-d_6 (99.5% deuterium) was obtained from Thompson-Packard, Inc.

Kinetic Runs

Kinetic runs were all made at the nmr spectrometer (Varian A-60) magnet temperature (41 ± 1°). Approximately 0.5 M solutions were prepared by adding 0.25 mmoles of complex to 0.50 ml DMSO or DMSO-d_6 in a dry centrifuge tube. In most cases, the material dissolved essentially completely with stirring in a few seconds. However, each sample was centrifuged before transfer to a dry nmr tube and insertion in the spectrometer probe. Traces were recorded at intervals frequent enough to follow the course of the reaction.

RESULTS

Spectral Assignments and Spectral Changes.

Two examples, Figures 1 and 2, are shown to

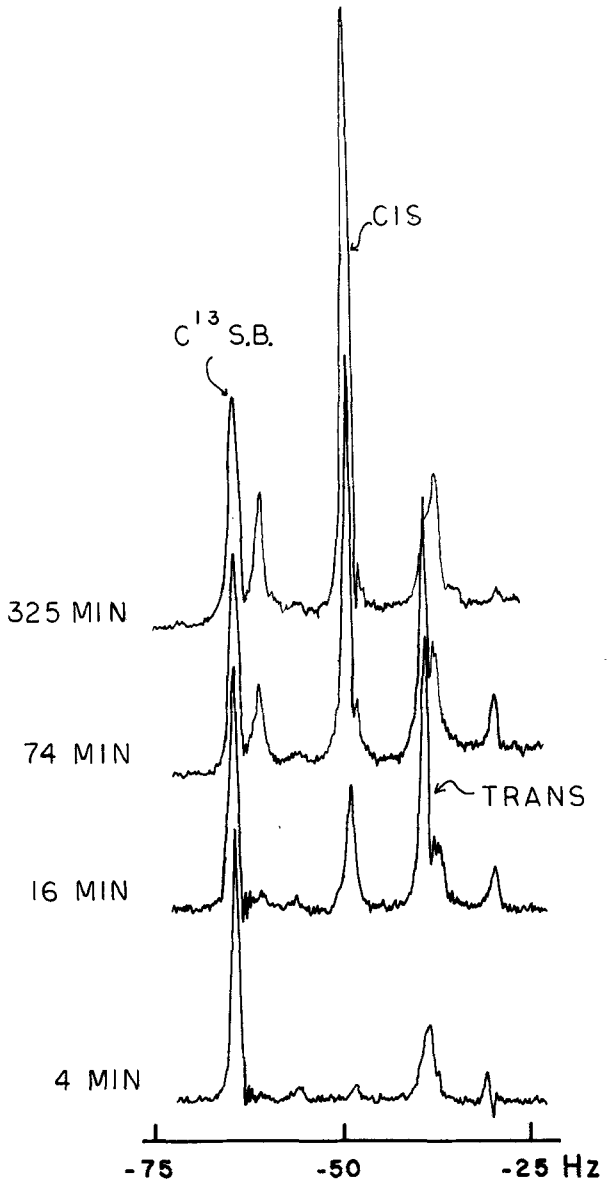


FIGURE 2. Proton nmr spectra of K[Pt(aba)Cl_2] in DMSO at 41° showing the appearance of peaks due to coordinated DMSO.

illustrate the complementary information available from spectra in DMSO and DMSO-d_6 and the contrasting kinetic behavior of unsubstituted and N,N-dimethyl amino acid complexes. Figure 1 depicts changes in the $C(CH_3)_2$ and $N(CH_3)_2$ regions of the spectrum of K[Pt(dmaba)Cl_2] dissolved in DMSO-d_6. Both the original $C(CH_3)_2$ and $N(CH_3)_2$ peaks, each surrounded by ^{195}Pt satellites to yield 1:4:1 triplets, disappear as the reaction proceeds. In the $N(CH_3)_2$ region, of the spectrum, two new peaks are evident after 30 minutes. At 360 minutes, the two new peaks with their ^{195}Pt-satellites have completely displaced the original 1:4:1 triplet. The two products have different coupling to ^{195}Pt. For the downfield triplet, $^3J_{Pt\text{-}NCH}$ = 39.2 Hz; for the upfield, 25.6 Hz. In the $C(CH_3)_2$ region of the spectrum, corresponding peaks for the two products are somewhat downfield from starting material, but are not resolved. It should be noted that a parallel study in ordinary DMSO yielded complementary information. In ordinary DMSO, (1) the $C(CH_3)_2$ region changes as shown in Figure 1, (2) the $N(CH_3)_2$ region is completely obscured by solvent DMSO, and (3) two new peaks and their ^{195}Pt-satellites appear well downfield from solvent DMSO. Their rates of growth and relative intensities parallel those of the $N(CH_3)_2$ 1:4:1 triplets in DMSO-d_6. For the glycine complex, only the growth of coordinated DMSO in ordinary DMSO could be used to obtain kinetic data since CH_2 peaks of the two products overlapped considerably.

Typical spectral changes associated with the appearance of coordinated DMSO are illustrated in Figure 2, which shows such changes for the reaction of K[Pt(aba)Cl_2] with DMSO. The strong peak that appears soon after mixing at −42.1 Hz (relative to solvent DMSO) reaches a maximum between 16 and 74 minutes and then decreases as the initially smaller peak at −52.4 Hz becomes more prominent. For all four complexes for which good kinetic data were obtained, separate peaks for two DMSO-containing products were observed in this part of the spectrum. The chemical shifts and $^3J_{Pt\text{-}SCH}$ values indicate S-coordinated DMSO[3,4]. In every case, the total area of peaks attributed to coordinated DMSO relative to the total area of amino acid proton peaks was consistent with single chloride substitution; i.e., there was no evidence for the presence of $Pt(NO)(DMSO)_2^+$. For example, for K[Pt(aba)Cl_2], after equilibration in DMSO, the total area of the two coordinated DMSO peaks and their ^{195}Pt-satellites equaled the total area of the aba-$C(CH_3)_2$ peaks, which are unresolved for the two species.

Spectral assignment for the four dichloro amino acid complexes and the *cis* and *trans*-DMSO containing products of each are summarized in Table I. Peak assignments were based on the following consistent patterns evident in the data: (1) Replacement of chloride by DMSO produces a substantial increase (about 5 Hz) in $^3J_{Pt\text{-}NCH}$ for

TABLE I
NMR Spectral Parameters for $K[Pt(NO)Cl_2]$ and DMSO Products

Species	Chemical Shifts[a]				$^3J_{Pt-H}$, Hz		
	CH_2	$C\text{-}(CH_3)_2$	$N(CH_3)_2$	$S(CH_3)_2$	CH_2	$N(CH_3)_2$	$S(CH_3)$
$Pt(gly)Cl_2^-$	−31.0	–	–	–	38	–	–
cis-Pt(gly)(DMSO)Cl	−47.0	–	–	−52.0	42.3	–	23.5
trans-Pt(gly)(DMSO)Cl	−47	–	–	−43.3	30	–	18.0
$Pt(dmg)Cl_2^-$	−51.5	–	−11.0	–	33.5	35.2	–
cis-Pt(dmg)(DMSO)Cl	−69.5	–	−29.2	−51.5	39.2	40.6	22.0
trans-Pt(dmg)(DMSO)Cl	−69.5	–	−14.3	−40.0	25.6	27.6	20.0
$Pt(aba)Cl_2^-$	–	75.4	–	–	–	–	–
cis-Pt(aba)(DMSO)Cl	–	72.5	–	−52.4	–	–	23.5
trans-Pt(aba)(DMSO)Cl	–	71.6	–	−42.1	–	–	18.6
$Pt(dmaba)Cl_2^-$	–	66.5	−2.0	–	–	35.5	–
cis-Pt(dmaba)(DMSO)Cl	–	64.5	−20.5	−57.8	–	40.2	22.8
trans-Pt(dmaba)DMSO)Cl	–	64.5	−5.0	−46.5	–	27.6	20.0

[a]In Hz at 60 MHz, relative to solvent DMSO methyl peak; positive shifts are upfield from DMSO

CH_2 or $N(CH_3)_2$ protons for one of the products and a similar decrease (about 8 Hz) for the other product. (2) For CH_2 and $C(CH_3)_2$ protons, the effect of chloride replacement by DMSO on chemical shifts is virtually the same for both products. (3) For $N(CH_3)_2$ protons, the effect of chloride replacement on the chemical shift is small (2-3 Hz) for one product and much larger (18 Hz) for the other. (4) The product which experienced the larger downfield $N(CH_3)_2$ shift has the larger coupling between $N(CH_3)_2$ and ^{195}Pt. (5) The difference in $S(CH_3)_2$ shifts of the two products is about 10 Hz for all four compounds. (6) $^3J_{Pt\text{-}H}$ values for $S(CH_3)_2$ protons of the two products are similar, but the value for the more downfield DMSO methyl resonance is somewhat larger. The difference in $^3J_{Pt\text{-}H}$ for $S(CH_3)_2$ protons between the two products is larger for $N(CH_3)_2$ species than for NH_2 species. (7) The downfield DMSO product $S(CH_3)_2$-peak is associated with the more downfield $N(CH_3)_2$ peak (the one which has larger coupling to ^{195}Pt) and also with the CH_2-peak which has the larger coupling to ^{195}Pt.

These facts are all consistent with the assignments given if we assume that $^3J_{Pt\text{-}H}$ increases with Pt–N or Pt–S bond strength and that replacement of chloride by DMSO weakens the Pt–N bond *trans* to the DMSO. Furthermore, this assignment is consistent with the expectation that the chemical shift of $N(CH_3)_2$ protons should be influenced more by replacement of the chloride *cis* to the nitrogen. The close parallel in the $S(CH_3)_2$ shifts and coupling constants of the 4 compounds then permits assignment of peaks for the two aba isomers on the basis of DMSO $S(CH_3)_2$ peaks alone. Correlation of kinetic and spectral data adds further weight to the correctness of the assignments given in Table I.

Kinetic Data

Kinetic data, obtained for reactions of the four dichloro complexes with solvent DMSO at 41°C, are summarized in Table II. For the NH_2 complexes, $Pt(gly)Cl_2^-$ and $Pt(aba)Cl_2^-$, data are reported for the reaction with ordinary DMSO as monitered by the

TABLE II
Rate Constants for Reactions of Solvent DMSO with $KPt(amino\ acid)Cl_2$ at 41°C.

Starting Complex	k_c, sec^{-1}	k_t, sec^{-1}	k_c/k_t	k_{ct}, sec^{-1}	k_{tc}, sec^{-1}	$k_{tc}/k_{ct} = \frac{\text{(cis) eq}}{\text{(trans) eq}}$
$K[Pt(gly)Cl_2]$	1.7×10^{-4}	5.0×10^{-4}	0.34	3×10^{-5}	3.3×10^{-4}	11 ± 3
$K[Pt(dmg)Cl_2]$	1.8×10^{-4}	1.5×10^{-4}	1.2	–	–	1.2
$K[Pt(aba)Cl_2]$	1.8×10^{-4}	5.0×10^{-4}	0.36	1.7×10^{-5}	1.7×10^{-4}	10 ± 2
$K[Pt(dmaba)Cl_2]$	1.8×10^{-4}	3.0×10^{-4}	0.6	–	–	0.6

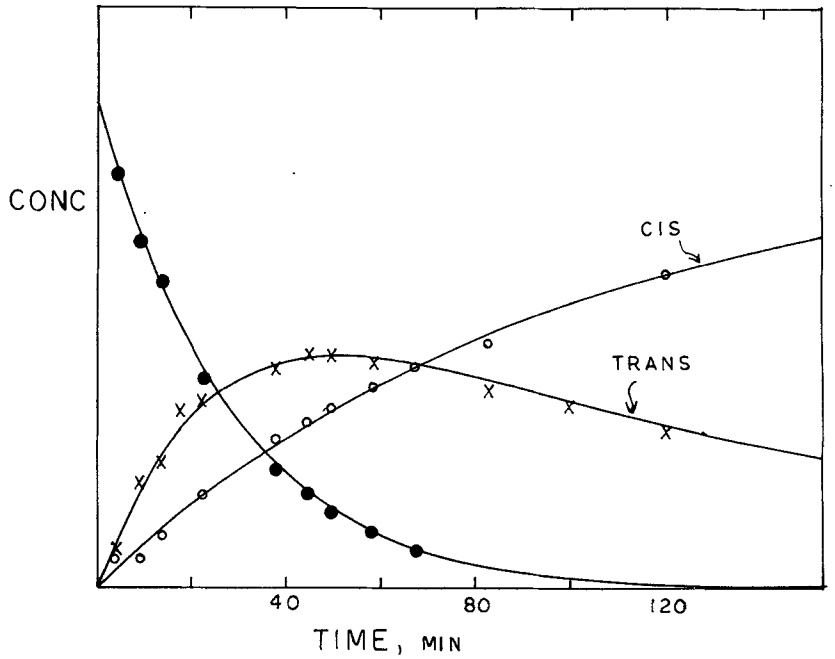


FIGURE 3. Comparison of experimental kinetic data for the reaction of $K[Pt(aba)Cl_2]$ with analog computer simulation (solid lines) at 41° for $k_c = 1.8 \times 10^{-4}$, $k_t = 5.0 \times 10^{-4}$, $k_{ct} = 1.7 \times 10^{-5}$ and $k_{tc} = 1.7 \times 10^{-4}$ sec^{-1}.

variation in peak height of $S(CH_3)_2$ peaks of the *cis* and *trans* products. For $Pt(aba)Cl_2^-$, the net rate of disappearance of starting material was also determined from disappearance of the aba $C(CH_3)_2$ signal for reactions run in DMSO-d_6. When ^{195}Pt satellites overlapped with peaks of interest, appropriate adjustments in peak heights were made. For the $N(CH_3)_2$ complexes, similar data were obtained from changes in amino acid ligand peaks for reactions in DMSO-d_6.

In this way plots of relative concentrations of starting material and *cis* and *trans* products were obtained. Concentration data were fit to the kinetic scheme (Scheme I) involving the four 1st-order rate constants k_c, k_t, k_{ct} and k_{tc}. Although all four rate constants very likely depend on DMSO concentration, since DMSO is the solvent and is present in large excess, the dependence would not be evident in this work. Plots of $\ln(Pt(NO)Cl_2^-)$ vs time were satisfactorily linear for two or more half lives. The slope of such plots yielded $k_c + k_t$. Individual values for k_c and k_t were then calculated from the ratios of initial slopes of plots of *cis* and *trans* isomer concentrations vs time. The ratio k_{tc}/k_{ct} was determined from the equilibrium ratio of *cis*/*trans* products as estimated from peak heights of corresponding DMSO methyl peaks. Individual values of k_{tc} and k_{ct} were then estimated by comparison of observed concentration data for all three species with that calculated by analog computer simulation for various values of k_{tc} and k_{ct} (keeping k_{ct}/k_{tc} = constant) and the previously determined k_c and k_t. Both cathode ray and x-ray recorder output were used in making the comparisons. Typical computer simulation and experimental output for the reaction with $K[Pt(aba)Cl_2]$ are compared in Figure 3.

For the $N(CH_3)_2$ amino acids, the equilibrium ratio of *cis* and *trans* products does not differ perceptibly from the ratio of k_c/k_t. Qualitative experiments, in which ordinary DMSO was added to an equilibrium reaction mixture, confirmed that DMSO incorporation into *cis* and *trans* isomers occurs at a rate which is comparable to the rate of interconversion of *cis* and *trans* products of the reaction of DMSO with $K[Pt(aba)Cl_2]$. Therefore, failure to observe any change in the *cis*/*trans* ratio for $N(CH_3)_2$ amino acids on long standing means that k_c/k_t and k_{tc}/k_{ct} are very similar and not that k_{tc} and k_{ct} are much smaller than k_c or k_t.

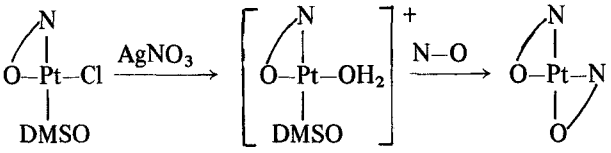
Because of its much lower solubility, good quality kinetic data could not be obtained for the alanine complex. However the rate of chloride displacement

is within a factor of two of the values for aba and glycine complexes. More important, the same general pattern is observed; namely, the *trans* product which predominates initially ultimately is replaced almost entirely by the *cis* product. This conclusion is based entirely on the behavior of the two new peaks observed for coordinated DMSO whose chemical shifts and $^3J_{Pt\text{-}SCH}$ correspond closely to those of corresponding glycine and aba complexes.

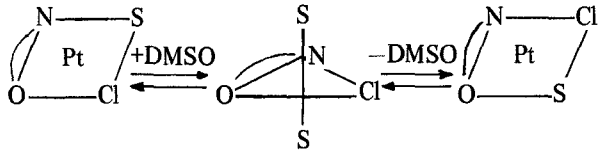
Finally, since Kukushkin's reactions were run with DMSO in aqueous solution, one kinetic run was done with the aba complex in 10% DMSO/D_2O. Although the rate of chloride displacement was significantly slower than in pure DMSO, comparable relative rates and the same strong equilibrium preference for *cis* product were also observed under these conditions.

DISCUSSION

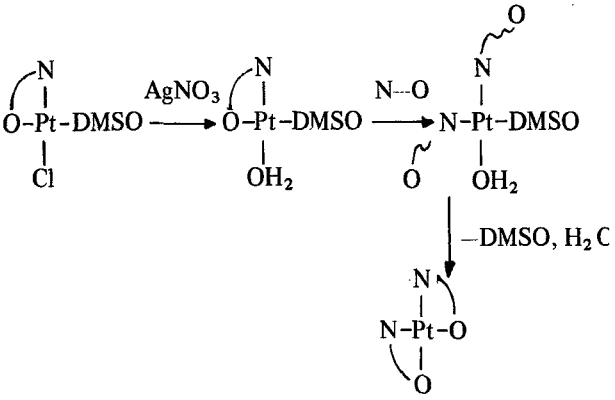
Kukushkin, and Guryamava[2] based their conclusion that the *trans* isomer of Pt(ala) (DMSO)Cl is the preferred isomer on the assumption that the stereochemistry of the reaction of Pt(ala) (DMSO)Cl with $AgNO_3$ in H_2O and the subsequent reaction with alanine is as shown below:



The recovery of pure *cis*-Pt(ala)$_2$ after these two steps was taken as evidence that the initial material was the *trans* isomer shown. In drawing this conclusion, they have made the commonly held assumption that substitution reactions in Pt(II) complexes proceed with retention of configuration.[5] For both Pt(NO) (DMSO)Cl in DMSO and Pt(NO) (DMSO) $(H_2O)^+$ in water, however, equilibration of the two isomers can be achieved via the symmetric trigonal bipyramidal intermediate which contains two solvent molecules; e.g.,

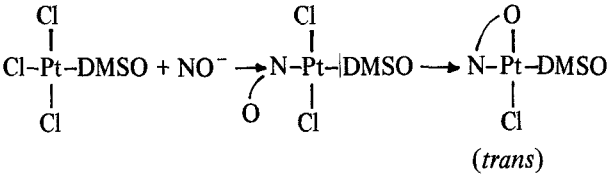


Similarly, under the conditions they used to replace Cl^- by H_2O in Pt(ala) (DMSO)Cl (3–4 days in contact with water solvent before complete precipitation of AgCl) it seems likely that two possible isomers would have a chance to equilibrate so that mainly the *trans* isomer shown was present when the second mole of alanine was added. The role of the solvent in this equilibration would be analagous to that of excess MR_3 in the rapid equilibration of *cis* and *trans*-Pt$(MR_3)_2X_2$.[6] Alternatively *cis*-Pt(ala)$_2$ may have been obtained by the following pathway:



Experiments are in progress to distinguish between these alternatives.

The pathway by which the favored *cis* product of the other four reactions employed by Kukushkin to obtain Pt(ala) (DMSO)Cl can be accounted for similarly. For example, for the reaction of alanine with Pt(DMSO)Cl_3^-, the sequence is probably



to give the kinetically favored *trans* product as they noted. However, subsequent equilibration, involving chloride ion catalysis could have resulted in conversion to the more stable *cis* product which was finally isolated.[7]

The rate of displacement of Cl^- by DMSO in these complexes is within an order of magnitude of rates of displacement of Cl^- by DMSO in similar complexes. For example the rate of displacement of Cl^- from Pt$(py)_2Cl_2$ by DMSO in DMSO at 25° is 3.8×10^{-3} sec^{-1}.[8] More importantly, the small differences in rates permit an evaluation of small differences in the *trans*-effect of CO_2^- and NH_2 or $N(CH_3)_2$ groups of the coordinated amino acid.

In particular, the kinetic data reveals that the *trans* effect of NH_2 in glycine and α-aminoisobutryric acid is greater than that of CO_2^- by a factor of about 3. Substitution of NH_2 by $N(CH_3)_2$ substantially reduces k_t without affecting k_c so that the two chlorides of the dimethyl derivatives are more nearly alike in kinetic lability. This reduction in k_t no doubt reflects the decrease in Pt–N bond strength which is reflected in the observed decrease in $^3J_{Pt-N-C-H}$ to amino acid ligand protons when NH_2 is replaced by $N(CH_3)_2$. The near equality of *trans* influence of CO_2^- and $N(CH_3)_2$ is also reflected in the near equality of $^3J_{Pt-S-C-H}$ for DMSO protons in the *cis* (22 Hz). and *trans* (20 Hz) isomers of Pt(NO) (DMSO)Cl for complexes of N,N-dimethyl amino acids.

Although the data for k_c and k_t can be accounted for readily on the basis of *trans*-effect considerations, greater thermodynamic stability of the *cis*-product cannot be accounted for so easily. A plausible origin of the extra stability of the *cis* isomer could well be intramolecular hydrogen bonding between the oxygen atom of DMSO and adjacent N-H protons of the amino acid moiety. Such stabilization would not be possible for $N(CH_3)_2$ species. However, since the equilibrium isomer ratio is nearly the same in 10% DMSO/D_2O, the large decrease in preference for *cis* isomer associated with replacement of NH_2 by $N(CH_3)_2$ probably reflects the increased steric interaction between $N(CH_3)_2$ and adjacent $S(CH_3)_2$ groups.

The difference in nmr coupling constants to amino acid protons of *cis* and *trans* isomers also provides a quantitative measure of the large *trans*-influence of the DMSO ligand[9], which is so important in determining the products of reaction with DMSO.[10,11,12] Since that coupling is transmitted essentially entirely via the Pt-N bond, 3-bond Pt–N–C–H coupling should be a good measure of the Pt–N bond strength.[13] Replacement of Cl^- trans to N by DMSO decreases this coupling substantially (about 25%); but replacement of Cl^- *cis* to N increases such coupling almost as much (about 15%). Apparently, the weakening of the bond *trans* to S is accompanied by partial strengthening of the bond *cis* to sulfur. This observation agrees with the suggestion that a good *trans*-activating ligand is a poor *cis*-activating ligand.[14] The importance of such large *cis*-effects has recently been noted in a kinetic study of similar DMSO complexes of general formula $Pt(am)_2(DMSO)Cl$, where am = amine ligand.[10]

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