Supplementary Material Available: Arrhenius plots for $Rh_2(PF_3)_8$ and $HRh(PF_3)_4$ (2 pages). Ordering information is given on any current masthead page.

References and Notes

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(20) The Arrhenius plots for $Rh_2(PF_3)_8$ and $HRh(PF_3)_4$ have been included as supplementary material.
(21) A referee has noted that a square-pyramidal geometry for $IrCl(PF_3)_4$, with axial Cl, would also be consistent with the observation of equivalent PF_3 groups. This seems to us unlikely because trigonal-bipyramidal geometry has so far been observed for all compounds studied of the type $YCo(CO)_4$ (Y = various anionic ligands).[7]
(22) It is tempting to suggest that the second "high-temperature" isomer of $Co_2(CO)_8$[11] has the equatorially linked bi(trigonal-bipyramidal) structure.
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Stereochemistry of the Reaction of Dimethyl Sulfoxide with Dichloro(glycinato)platinate(II) and Similar Amino Acid Complexes

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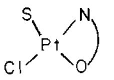
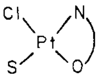
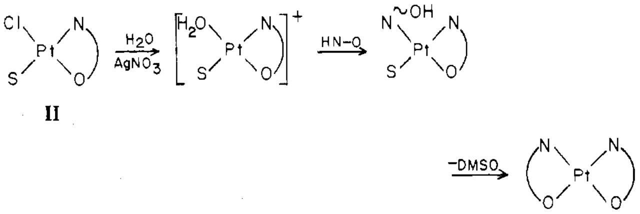
In a recently reported NMR study of the kinetics and stereochemistry of the reaction of K[Pt(amino acid)Cl_2] with dimethyl sulfoxide (DMSO) to form Pt(amino acid)-(DMSO)Cl, we concluded that the thermodynamically preferred isomer of Pt(N–O)(DMSO)Cl is I when N–O = gly


I


II

or aba.[1,2] We concluded further that the single isomer of Pt(ala)(DMSO)Cl obtained by Kukushkin and Gur'yanova[3] by five different reactions was erroneously identified as II, in which DMSO is trans to N. This note reports results of additional NMR experiments which confirm these conclusions and establish the source of discrepancy between the two assignments.

Scheme I. Reaction Sequence Used in Assignment of Structure II by Kukushkin and Gur'yanova[3]



Kukushkin and Gur'yanova based their assignment of structure II to Pt(ala)(DMSO)Cl on the following chemical argument, which is summarized in Scheme I. The chloro complex was first converted by treatment with aqueous $AgNO_3$ to the corresponding aquo complex, which was subsequently converted to $Pt(ala)_2$ by addition of a second mole of alanine. Reaction of the $Pt(ala)_2$ with thiourea was used to demonstrate that it was the cis isomer,[4] from which they concluded that the original chloro complex had structure II. This assignment assumed (a) that water replaces Cl^- of the complex with retention of configuration and (b) that the nitrogen of the second alanine molecule added displaces the water molecule of the aquo complex before the ring closure which eliminates DMSO. Evidence will be introduced to show that assumption (b) is not correct.

Experimental Section

Preparation of K[Pt(DMSO)Cl_3]. A 0.25 M stock solution of K[Pt(DMSO)Cl_3] in D_2O was prepared by adding 6.25 mol of DMSO to 6.25 mmol of K_2PtCl_4 in 20 ml of D_2O and diluting to 25.0 ml.[5] The proton NMR spectrum was monitored as free DMSO was converted essentially completely to $[Pt(DMSO)Cl_3]^-$ (δ 0.80 ppm downfield from free DMSO; $^3J_{Pt-S-CH_3} = 24$ Hz).

Reactions of K[Pt(DMSO)Cl_3] with Glycinate and Other Amino Acid Anions. One millimole of NaOH was added to 1 mmol of free amino acid. The solution was then evaporated to dryness, treated once with 1 ml of D_2O, and evaporated to dryness again to ensure complete exchange of amino protons. Four milliliters of 0.25 M K[Pt(DMSO)Cl_3] was added to dissolve the solid salt and the NMR spectrum of the solution was monitored as the reaction proceeded.

Preparation of [Pt(aba)(DMSO)(OD_2)]$^+$. One millimole of $AgNO_3$ in 5 ml of D_2O was added to 1 mmol of Pt(aba)(DMSO)Cl and the suspension was stirred with warming for about 4 h to precipitate AgCl which was removed by filtration through sintered glass. The NMR spectrum was recorded and the solution was than evaporated to dryness to yield 1 mmol of solid [Pt(aba)(DMSO)(OD_2)]NO_3.

Reaction of [Pt(aba)(DMSO)(OD_2)]$^+$ with Methylamine. The above described solid [Pt(aba)(DMSO)(OD_2)]NO_3 was dissolved quickly in 4 ml of a solution containing 0.25 M NaOD and 0.25 M methylamine in D_2O. The latter solution was prepared by treating 10 mmol of methylamine hydrochloride with 10 mmol of silver nitrate in D_2O to remove the chloride as AgCl and then adding 20 mmol (5 ml of 4 M) NaOD before diluting to 40 ml. The OD^- was included to neutralize the acidic proton of coordinated D_2O ($pK_a \simeq 4.4$).[3]

Results and Conclusions

Reaction of K[Pt(DMSO)Cl_3] with Amino Acid Anions. Spectral changes associated with the reaction of K[Pt-(DMSO)Cl_3] with glycinate anion are illustrated in Figure 1. The spectrum of the freshly mixed solution shows the two strong 1:4:1 triplets (central peak and platinum-195 satellites) typical of coordinated glycinate ($^3J_{Pt-N-C-H} = 28$ Hz) and coordinated DMSO ($^3J_{Pt-S-CH_3} = 20.4$ Hz) and a much smaller peak at δ 0.85 ppm (from free DMSO). After warming of the solution for 5 min at 80 °C, the original triplets have decreased to about half their original intensity while the peak at δ 0.85 has increased correspondingly and a new peak

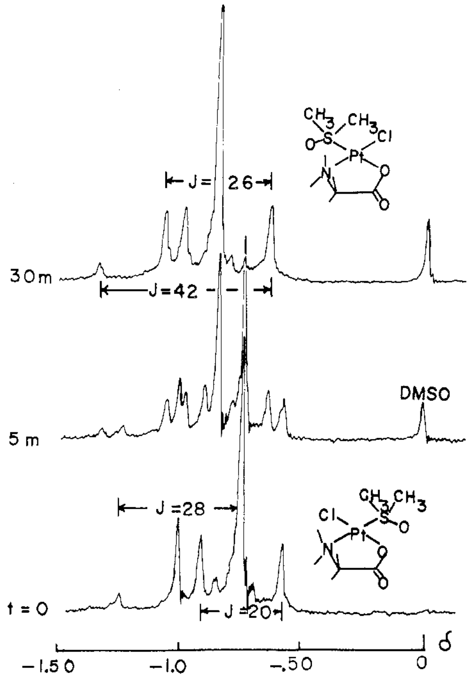
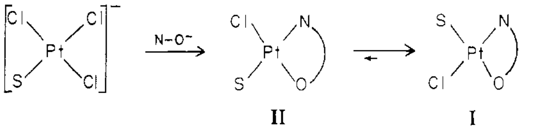


Figure 1. The 60-MHz proton NMR spectra of a K[Pt(DMSO)-Cl_3]-glycinate reaction mixture (0.25 M in each) in D_2O showing the effect of heating at 80 °C on the product distribution.

Scheme II. Reaction of Glycinate with K[Pt(DMSO)Cl_3]



slightly downfield from the original glycinate peak is clearly evident. On longer heating of the solution, the original triplets give way almost completely to two new triplets for coordinated glycinate ($^{3}J_{\text{Pt-N-C-H}} = 42$ Hz) and coordinated DMSO ($^{3}J_{\text{Pt-S-CH}_3} = 25.8$ Hz). After 30 min of heating very little of the original species is present. A small peak from free DMSO is evident in all traces after the first.

The spectral changes of Figure 1 are consistent with the reaction sequence shown in Scheme II. In view of the well-established large trans effect of DMSO,[6] the initial glycine-containing product is certainly II, with N trans to S. The subsequent equilibration to the thermodynamically favored isomer (I) corresponds to our earlier results for the reaction of K[Pt(gly)Cl_2] with DMSO in DMSO.[1,7] The appearance of a small concentration of free DMSO on heating suggests that the equilibration which occurs in the second step involves some conversion to Pt(gly)Cl_2^- which can lose either chloride to yield, ultimately, the equilibrium mixture which strongly favors isomer I.

The reaction was repeated with several other amino acids. In most cases, spectral changes were complicated by complex amino acid spectra or by precipitation of one of the products. However, the characteristic DMSO peaks indicated that isomer II ($^{3}J_{\text{Pt-S-CH}_3} = 20$ Hz) is invariably produced initially and is converted on heating almost completely to isomer I ($^{3}J_{\text{Pt-S-CH}_3} = 26$ Hz).[7] In fact, if the solution is not heated, for most NH_2-type amino acids (glycine being the exception) isomer II precipitates on standing before conversion to isomer I occurs. This reaction can therefore be used to prepare either II (no heating) or I (heating to equilibrate) from K[Pt-(DMSO)Cl_3]. Thus, for a second of the five reactions reported by Kukushkin and Gur'yanova,[3] the anticipated kinetically favored product, II, was converted to the thermodynamically favored isomer, I, before it could be isolated.

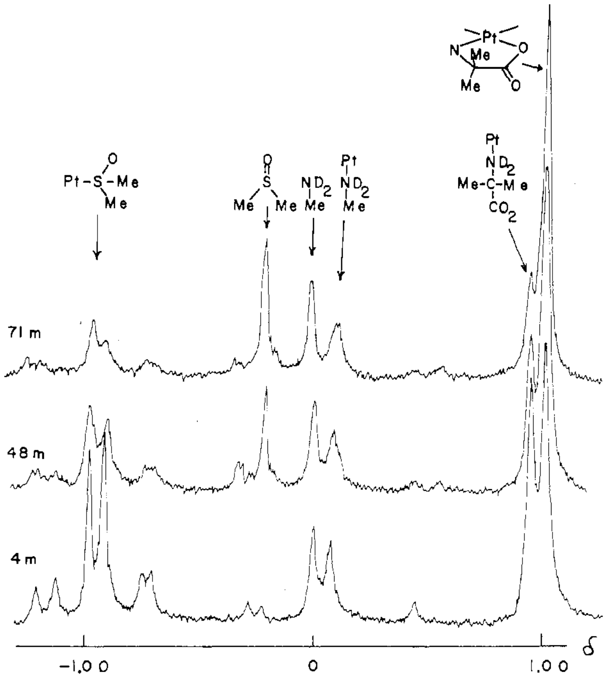
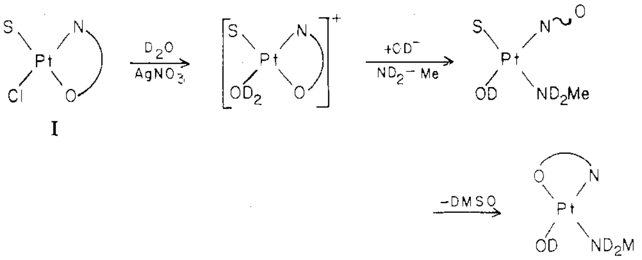


Figure 2. The 60-MHz proton NMR spectra of a [Pt(aba)(DMSO)-(D_2O)]NO_3-methylamine-OD^- reaction mixture (0.25 M in each) in D_2O at 34 °C.

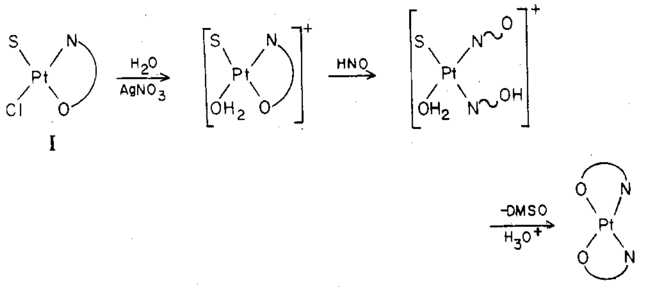
Scheme III. Proposed Reaction Sequence for Conversion of [Pt(aba)(DMSO)Cl] to [Pt(aba)(ND_2Me)(OD)]



Reaction of [Pt(aba)(DMSO)(OD_2)]$^+$ with Methylamine. In order to identify the origin of the error in Kukushkin and Gur'yanova's chemical argument, spectral changes associated with the two reactions employed in Scheme I were examined with a simpler, but analogous, system. First, complexes of gly and aba were used in place of alanine in order to avoid unnecessary spectral complexities. Second, in order to avoid precipitation of Pt(N–O)$_2$ and to be able to follow its coordination fate separately, methylamine was used as the nitrogen donor in the second step. Finally, a second mole of OD^- was added to ensure that methylamine was deprotonated.

The spectral changes associated with the reaction of isomer I of [Pt(aba)(DMSO)(OD)] with ND_2CH_3 in D_2O are shown in Figure 2. In the first trace, 3.75 min after mixing, two species of coordinated DMSO along with two species of coordinated aba are evident at about equal concentrations. Furthermore, platinum-195 satellites show clearly that about half of the methylamine is coordinated to Pt ($^{3}J_{\text{Pt-N-CH}_3} = 43$ Hz). Significantly, only a trace of free DMSO is evident in this trace. On standing of the solution, the peaks due to coordinated DMSO decrease rapidly while that due to free DMSO increases rapidly and the total area due to DMSO peaks also decreases substantially. Although no new N–CH_3 peaks appear, the single peak appears to broaden and a new pair of satellites ($^{3}J_{\text{Pt-N-CH}_3} = 53$ Hz) grows at the expense of the initial pair which indicates conversion of one coordinated

Scheme IV. Reaction Sequence Which Accounts for Isolation of *cis*-Pt(ala)$_2$ from I



methylamine species to a second species, whose chemical shift is nearly identical. At the same time, one peak due to CH_3 protons of aba continues to decline as a second peak grows.

Interpretation of the spectral changes shown in Figure 2 is summarized in Scheme III. The key observations are (a) that methylamine coordinates to platinum before any DMSO is lost and (b) that subsequent appearance of free DMSO is associated with the conversion of one species which contains coordinated methylamine to a second species which also contains coordinated methylamine. Direct displacement of DMSO by methylamine would have required simultaneous appearance of free DMSO and coordinated methylamine. Displacement of OD^- by methylamine should not have led to displacement of DMSO at all. The observed increase in $^3J_{Pt-H}$ for $N-CH_3$ protons from 43 to 53 Hz on replacement of strongly bound trans DMSO by more weakly bound trans carboxylate further supports this interpretation. Finally, the loss of total DMSO-peak area can be attributed to deuterium exchange of the fairly acidic methyl protons of coordinated DMSO at the relatively high pH (~11) of the final solution.[8]

On the basis of this experiment, we conclude that *cis*-Pt(ala)$_2$ was probably obtained from I by Scheme IV. This conclusion emphasizes the great trans-labilizing effect of DMSO which, for this compound, more than compensates for the strong tendency of glycinate rings to remain intact.

Acknowledgment. We wish to acknowledge financial supprt for this project from the Research Corp. and National Science Foundation Grant No. 42192 which provided partial support for purchase of the Perkin-Elmer R-12B NMR spectrometer used in the project.

Registry No. K[Pt(DMSO)Cl$_3$], 21350-35-6; K_2PtCl_4, 10025-99-7; [Pt(aba)(DMSO)(DD$_2$)]NO$_3$, 60338-50-3; Pt(aba)(DMSO)Cl, 60338-48-9; Pt(gly)(DMSO)Cl (isomer I), 60383-64-4; Pt(gly)(DMSO)Cl (isomer II), 60338-47-8; methylamine, 74-89-5.

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(2) The following abbreviations will be used for amino acid anions which are denoted N–O in general structural formulas: gly, glycinate; ala alaninate; aba, α-aminoisobutyrate.

(3) Y. N. Kukushkin and G. P. Gur'yanova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **15** 2761 (1970).

(4) The familiar Kurnakov test for distinguishing cis and trans nitrogen coordination about platinum; see F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science Publishers, London, 1973, p 183.

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(7) The data reported in ref 1 were all for DMSO solutions while the data cited in this paper are for D_2O solutions. The DMSO chemical shift difference between isomers is about 0.05 ppm less in D_2O and the $^3J_{Pt-S-CH_3}$ values are slightly greater (~ 2 Hz) in D_2O.

(8) D. A. Johnson, *Inorg. Nucl. Chem. Lett.*, **5**, 225 (1969).

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Stability of Polymeric Sulfur Nitride, $(SN)_x$, to Air, Oxygen, and Water Vapor

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Recently considerable interest has focused on the remarkable properties of polymeric sulfur nitride (polythiazyl), $(SN)_x$. Solid-state studies show $(SN)_x$ has the properties of a metal[3-8] down to low temperatures,[5] becoming superconducting near 0.3 K.[6] The discovery that this unique material forms oriented thin films[4] on a number of plastic substrates suggests its potential use in optical and microelectronic devices. With regard to the measurement of its chemical and solid-state properties, its stability in air is a matter of critical importance. In this note we report our observations on the stability of partly polymerized and completely polymerized, analytically pure crystals of $(SN)_x$ on exposure to several different atmospheres.

Experimental Section

Synthesis of $(SN)_x$. The $(SN)_x$ crystals used in these studies were obtained by following *exactly* our previously described procedure.[9] This involved slowly growing crystals of S_2N_2 at 0 °C from the vapor phase during 48 h, followed by spontaneous room-temperature solid-state polymerization during 60 h. The lustrous, golden $(SN)_x$ crystals were then pumped in vacuo for (i) 2 h at room temperature, (ii) 1 h as the temperature was raised to 75 °C, and finally (iii) 2 h at 75 °C.

The $(SN)_x$ crystals were exposed to the air for 10 min or less during their weighing and loading in the appropriate pieces of apparatus described in the following paragraphs. These crystals are referred to as "unexposed crystals".

Exposure of $(SN)_x$ to Air. $(SN)_x$ crystals were placed in a 500-ml beaker covered loosely with filter paper to exclude dust and were permitted to stand undisturbed for 7 days at room temperature in normal laboratory lighting. The analytical results obtained after this time are given in Table I. The crystals underwent no detectable visual change. Similar results were obtained in duplicate experiments where time periods of 1, 2, and 48 h were employed.

Exposure of $(SN)_x$ to Dry Oxygen. Commercial grade oxygen (Airco, Inc., 99.5% O_2, 0.5% Ar) was passed through a drying train consisting of Linde 4A molecular sieve, followed by silica gel (Fisher; Grade 42, 6–16 mesh), before being allowed to contact the $(SN)_x$ crystals held in a 20-ml bulb connected to the oxygen supply by a "T"-tube. The oxygen flow was maintained for 7 days and was vented to the air through a paraffin oil bubbler. After 7 days at room temperature in normal laboratory lighting there was no visual change in the appearance of the $(SN)_x$ crystals. Pertinent analytical data are given in Table I.

Exposure of $(SN)_x$ to Moist Oxygen. This experiment was carried out as described for the experiment using dry oxygen except that the drying train was replaced by a bubbler fitted with a fine glass frit and filled with distilled water. The oxygen was saturated with water by passing it through the bubbler held at 0 °C (vapor pressure of water at 0 °C 4.6 Torr). No change in appearance of the $(SN)_x$ was noted. Pertinent analytical data are given in Table I.

Exposure of $(SN)_x$ to Water Vapor. The $(SN)_x$ crystals were held in a previously evacuated tube at room temperature in normal laboratory lighting for 7 days under a constant atmosphere of 4.6 Torr of water vapor, maintained by a bulb of degassed, distilled water held at 0 °C, which was connected to the tube containing the $(SN)_x$. No change in appearance of the $(SN)_x$ crystals was noted. Pertinent analytical data are given in Table I.

Exposure of Incompletely Polymerized S_2N_2 to Air. Golden $(SN)_x$ crystals, obtained by the solid-state room-temperature polymerization of S_2N_2 for a period of only 27 h, were exposed, without any previous pumping or heating treatment, to the normal laboratory atmosphere for 1 h in a dish covered loosely with filter paper. The crystals