between *trans*-$Co(en)_2H_2OBr^{2+}$, $k = 9.4 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25°, and *cis*-$Co(en)_2NH_3Br^{2+}$, $k = 6.1 \times 10^{-6}\ M^{-1}\ sec^{-1}$, is caused primarily by the change in $\Delta H^{\ddagger}$. Indeed, if one compares only the oxidants with a dipositive charge $\Delta S^{\ddagger}$ ranges only from −20.4 to −23.2 cal mol^{-1} deg^{-1}. $\Delta S^{\ddagger}$ for *trans*-$Co(en)_2Br_2^+$, the only monopositive ion studied, is only −16.7 cal mol^{-1} deg^{-1}. These results mean that over a range of temperature, the efficiency of the nonbridging ligand will be maintained in substantially the same order as found at 25°. The perturbation caused by a change in the nonbridging ligands is primarily electronic in nature. The effect can be visualized as proportional to the energy measured by the charge-transfer transition (a process governed by the Franck–Condon principle)

$$\underset{\text{I}}{Fe^{II}(H_2O)_5BrCo^{III}L_5} \longrightarrow \underset{\text{II}}{Fe^{III}(H_2O)_5BrCo^{II}L_5}$$

The perturbation of the Co(III) center by the nonbridging ligand changes the energy of the acceptor orbital and changes the charge-transfer energy, which in turn affects the point of intersection of the two zero-order states represented by I and II. Such an effect should manifest itself through the enthalpy of activation as is observed in the data presented here. This analysis is based upon that presented more quantitatively by Hush.[31]

Mechanistic Conclusions with Nonbridging Ligand Effects.—The close correspondence in the rate of reduction of the complexes with Br^- as the possible bridge as compared to the rate of reduction of those with Cl^- as the possible bridge strongly implies a similar mechanism for both systems. If the mechanisms differed, one would expect at least a slope in Figure 1 different from 1.0.[1] In addition, the strong implication to be drawn from the temperature dependence data is that all the Co^{III}–Br^- complexes react by the same mechanism.

Figure 1 also illustrates what may become a relatively useful means of distinguishing between two possible bridges in a given complex. The case in point is the geometry of the activated complex for the Fe^{2+} reduction of *trans*-$Co(en)_2BrCl^+$. The rates of reduction of *trans*-$Co(en)_2Br_2^+$ and *trans*-$Co(en)_2Cl_2^+$, corrected for the statistical factor of 2, give measures of the respective nonbridging abilities of Br^- and Cl^-. The arrow marked A in Figure 1 indicates how the rate of a Br^- nonbridging ligand with a Br^- bridge predicts the rate for a Cl^- bridge and Br^- nonbridging ligand. Similarly the arrow marked B indicates the predicted ability of Cl^- to function as a nonbridging ligand when Br^- is the bridge. These considerations indicate that Br^- is a more efficient nonbridging ligand than is Cl^- (a conclusion consistent with the σ-bonding model of nonbridging ligand effects in which similar molecules and ions are compared by consideration of their pK's[32]). Thus both the bridging efficiency, $Cl^- > Br^-$, and the nonbridging efficiency, $Br^- > Cl^-$, are such as to make the transition state geometry $[BrCoL_4ClFe^{3+}]^{\ddagger}$ more stable than the Br^- bridged transition state $[ClCoL_4BrFe^{3+}]^{\ddagger}$. Nevertheless, the difference in stability of these two transition states is, as Benson and Haim originally suggested might be possible,[19] small. Further work on other systems is needed to establish this point in a more quantitative fashion.

Acknowledgment.—This research was sponsored by the National Science Foundation under Grant GP-8318. I am grateful for that support.

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Infrared and Nuclear Magnetic Resonance Spectra of Thiocyanatotrimethylplatinum(IV) and Its Pyridine Adducts

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Infrared and nmr methods are used to deduce the structure of tetrameric thiocyanatotrimethylplatinum(IV). This unusual structure contains SCN bridging ligands with the sulfur bound to two platinum atoms and the nitrogen to one platinum atom. The 1:1 and 2:1 pyridine adducts (per platinum atom) were prepared and studied to assist in making assignments.

In extending our studies of tetrameric trimethylplatinum derivatives[2] we have considered bridging ligands containing sulfur, including thiocyanate. The ability of platinum compounds to exhibit several bonding modes with thiocyanate ions has been reported.[3] The occurrence of terminal sulfur- and nitrogen-bonded ligands as well as bridging SCN ligands has been reported.[4–6]

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[1] NSF Undergraduate Research Participant.

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[3] J. Burmeister and F. Basolo, *ibid.*, **3**, 1587 (1964).

[4] D. Forster and D. M. L. Goodgame, *ibid.*, **4**, 715 (1965).

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[6] P. Kinell and B. Strandberg, *Acta Chem. Scand.*, **13**, 1607 (1959).

Experimental Section

Preparation of Compounds.—Iodotrimethylplatinum(IV) was prepared by the method of Gel'man and Ivanova[7] and converted to sulfatobis(trimethylplatinum(IV)) tetrahydrate by the method of Pope and Peachey.[8]

Thiocyanatotrimethylplatinum(IV) was formed by the reaction of 0.1418 g of sulfatobis(trimethylplatinum(IV)) tetrahydrate dissolved in 20 ml of water with 0.057 g of barium thiocyanate obtained from K & K Chemical Co. The barium salt was added with stirring. Twenty milliliters of benzene was added and the mixture was heated at reflux for 24 hr with stirring. A yellow white precipitate was obtained by evaporation of the benzene layer. The product is only slightly soluble in cold benzene. The reaction yielded 0.095 g of product which represents a 72% yield based upon the amount of sulfatobis(trimethylplatinum(IV)) tetrahydrate.

An alternative method of synthesis was the reaction of sodium thiocyanate with iodotrimethylplatinum(IV) dissolved in a benzene–dimethylformamide mixture. The reaction mixture was stirred for 4 hr at room temperature followed by addition of water. The yellow crystals which immediately formed were only slightly soluble in benzene. Several recrystallizations were necessary to free the crystals from all impurities. The infrared and nmr spectra were identical with those for the product of the first method.

An osmometric determination of the molecular weight was attempted, but the results although indicative of the tetramer are by no means definitive. The range of values for five runs yields an average molecular weight of 1484 (1192 calculated for the tetramer). Because of the very low solubility of the compound, the only conclusion that can be drawn is that the molecular weight is in excess of 1000 and the tetrameric structure is indicated.

An elemental analysis was performed by Schwarzkopf Microanalytical Laboratory. *Anal.* Calcd for $(CH_3)_3PtSCN$: Pt, 65.4; C, 16.1; H, 3.0; S, 10.4; N, 4.6. Found: Pt, 65.5; C, 16.3; H, 2.2; S, 11.0; N, 4.6. All the data are consistent with $((CH_3)_3PtSCN)_4$.

Chlorotrimethylplatinum(IV) tetramer was prepared by the addition of a large excess of sodium chloride to an aqueous solution of sulfatobis(trimethylplatinum(IV)) tetrahydrate. The solution was heated on the steam bath and evaporated to dryness. The residue was extracted with benzene and the nmr spectrum of the benzene solution was recorded. The product was identified as chlorotrimethylplatinum(IV) tetramer by comparison of the chemical shift and the coupling constant with the values obtained by Rennick.[9]

Bromotrimethylplatinum(IV) tetramer was prepared by the addition of an excess of potassium bromide to an aqueous solution of sulfatobis(trimethylplatinum(IV)) tetrahydrate. The solution was heated and evaporated to dryness on the steam bath and the residue was extracted with hot benzene. Comparison of the nmr data obtained from the benzene extract with the values reported by Rennick confirmed the formation of bromotrimethylplatinum(IV) tetramer.[9]

The 2:1 pyridine adducts of chloro- and bromotrimethylplatinum were formed by addition of pyridine to the original analytical nmr samples in the nmr tubes. The spectra of the adducts were obtained, the solutions were evaporated, and the infrared spectra were obtained.

Iododipyridinetrimethylplatinum(IV) monomer was prepared by dissolving tetrameric iodotrimethylplatinum(IV) in an excess of pyridine and allowing the solution to evaporate to dryness. The compound was also prepared in an nmr tube by dissolving the iodide in a mixture of benzene and pyridine. The nmr spectra of the products made by both methods were identical. The infrared spectrum of a Nujol mull was found to agree with the spectrum reported by Hoechstetter.[10]

Dimeric iodopyridinetrimethylplatinum(IV) was prepared by stepwise addition of a 1:100 pyridine–benzene solution to tetrameric iodotrimethylplatinum(IV) in an nmr tube. The nmr spectrum was recorded and a mixture of 1:1 and 2:1 pyridine adducts was found. The compounds were not isolated. The synthesis was repeated using a smaller quantity of pyridine and the resultant spectrum demonstrated the presence of a mixture of the 1:1 adduct and the tetrameric starting material.

Thiocyanatodipyridinetrimethylplatinum(IV) monomer was prepared by the addition of a 1:1 pyridine–benzene solution to an nmr tube containing tetrameric thiocyanatotrimethylplatinum(IV).

A set of samples was prepared for the dimeric 1:1 pyridine adduct of thiocyanatotrimethylplatinum(IV) analogous to the method used to prepare the dimeric iodide complex. A sample of solid tetrameric thiocyanatotrimethylplatinum(IV) was dissolved in a 1:100 pyridine–benzene mixture in an nmr tube and the nmr spectrum was recorded. The procedure was repeated with further addition of pyridine until signals resulting from both the 1:1 and the 2:1 adducts were recorded. The infrared spectra of the solutions were also recorded at various stages of the experiment. The solutions were allowed to equilibrate for 24 hr after addition of pyridine before the nmr spectrum was recorded. The infrared spectra were recorded immediately after the nmr spectra were recorded. An infrared spectrum of the solid was obtained by evaporating the product of the first addition of pyridine and recording the infrared spectrum.[11]

Molecular Weight Apparatus.—The molecular weight data obtained in this study were obtained using a vapor-phase osmometer manufactured by Mechrolab Inc. of Mountain View, Calif. The instrument was calibrated with solutions of benzil in benzene.

The molecular weight data were obtained by saturating a benzene solution of the compound and withdrawing an aliquot into a tared vessel. This solution was used to obtain the data. After the data were gathered, the container plus samples plus solvent was weighed. The solvent was removed and the weights of solvent and solute were obtained by difference. The density of the solvent was employed to convert the weight of solvent to the corresponding volume and the concentration of the solution was calculated.

Nuclear Magnetic Resonance Spectrometer.—Proton magnetic resonance spectra were recorded on a Varian Associates HA 100 spectrometer using standard thin-wall Pyrex sample tubes sealed with the plastic caps supplied with the tubes. Chemical shifts were measured relative to the benzene resonance which was assigned a τ value of 2.74 and are accurate to within 0.01 ppm. The coupling constants are accurate to ±0.1 Hz. All spectra reported in this study were run in benzene.

Infrared Spectrophotometer.—The infrared spectra presented in this work were recorded on a Perkin-Elmer Model 621 grating spectrophotometer. Spectra of solid samples were obtained as Nujol mulls on cesium bromide plates in the region from 4000 to 300 cm^{-1}. Fluorolube mulls were used for the regions of Nujol absorption, 2800–3000 and 1360–1470 cm^{-1}. The region below 300 cm^{-1} to the limit of the optics of the spectrophotometer was scanned using polyethylene plates. Expanded spectra in the region below 450 cm^{-1} were recorded while purging the instrument with dried nitrogen.

Solution spectra were obtained using a Beckman F-05 sealed potassium bromide liquid cell (0.1-mm thickness) which was compensated by an adjustable potassium bromide wedge cell filled with the solvent and placed in the reference beam. The wedge cell was adjusted until the solvent signals were canceled.

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[7] O. M. Ivanova and A. D. Gel'man, *Zh. Neorg. Khim.*, **3**, 1334 (1958).

[8] W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, **95**, 571 (1909).

[9] R. D. Rennick, M.S. Thesis, University of Wyoming, 1965.

[10] M. N. Hoechstetter, Ph.D. Thesis, Michigan State University, 1960, p 48.

[11] At the suggestion of a referee we sent out a sample of the "2:1" adduct for analysis. The elemental analysis and molecular weight data indicated that the sample was a mixture of 1:1 and 2:1 adducts. The 1:1 and 2:1 pyridine adducts of iodotrimethylplatinum(IV) have been isolated; however, an equilibrium between them has been reported in solution: M. E. Foss and C. S. Gibson, *J. Chem. Soc.*, 299 (1951). Thus we feel that the postulation of analogous adducts between pyridine and thiocyanatotrimethylplatinum(IV) is not unreasonable and that the 2:1 adduct most certainly exists in solutions containing an excess of pyridine.

The frequency counter attached to the instrument was used to calibrate the spectra to ±0.2 cm^{-1}.

Results and Discussion

Thiocyanatotrimethylplatinum(IV).—The only platinum nuclide with a spin is ^{195}Pt ($I = ^1/_2$) with an isotopic abundance of 33.8%. Trimethylplatinum derivatives thus exhibit a methyl resonance consisting of an unsplit central peak plus a doublet, the latter having 33.8% of the total area of the three peaks (herein called a pseudotriplet).

The proton magnetic resonance spectrum of a benzene solution of thiocyanatotrimethylplatinum(IV) was obtained using the solvent as a locking signal. The spectrum consisted of two sets of pseudotriplets in a 2:1 ratio. The lower field satellite of the high-field resonance overlapped the center peak of the low-field pseudotriplet and *vice versa*, and the coupling constants were obtained by doubling the distance from the center of the pseudotriplet to the unobscured satellite. The ratio of areas was also obtained from measurements on these satellites since the more intense main peaks are not a single resonance signal but also include the satellite of the other pseudotriplet. The more intense peak, found at τ 8.52, exhibits a coupling constant of 75.0 Hz, while the other pseudotriplet, centered at τ 8.94, shows a coupling constant of 74.2 Hz. These values were obtained at a sweep width of 100 Hz with peak maxima measured on a frequency counter.

The infrared spectrum of thiocyanatotrimethylplatinum(IV) tetramer must be interpreted on the basis of a low-symmetry model. The proposed structure is used here to assign the vibrational modes. The structure postulated for this compound has a local platinum environment of $(CH_3)_3PtS_2N$ with the carbon atoms mutually cis and the two sulfurs and the nitrogen atom occupying the other three positions. This portion of the molecule has only a single plane of symmetry. The point group is thus C_s and all 42 vibrations are predicted to be fundamentals and to be infrared active. The symmetry predicts no degeneracies and no inactive modes. Many of these modes lie below the effective range of the instrument and only the platinum–carbon stretching frequencies, the carbon–hydrogen modes, and the internal vibrations of the anionic ligand occur above 300 cm^{-1}. Two sets of platinum–carbon stretching frequencies should be observed since two different types of methyls are present.

Table I lists the band locations and the assignments which are made by analogy to other platinum compounds. The extra methyl modes assigned are due to the presence of different types of methyl groups in the compound; therefore we find three additional methyl deformation bands and one additional platinum–carbon mode relative to iodotrimethylplatinum(IV).

The internal ligand vibrations were assigned by analogy to the spectrum of polymeric silver thiocyanate[6] and to the spectra of other platinum–thiocyanato and –isothiocyanato complexes. These data are more completely discussed below, where they are used to demonstrate the structure of this compound.

TABLE I

INFRARED SPECTRUM AND VIBRATIONAL ASSIGNMENTS FOR SOLID THIOCYANATOTRIMETHYLPLATINUM(IV)

$((CH_3)_3PtSCN)_4$	$((CH_3)_3PtI)_4$[9]	Assignment
(234 v)		Pt–N str
(224 w)		Pt–N str
541 vw	548 b, w	Sym Pt–C
563 w	558 w	Asym Pt–C str
570 vw		Asym Pt–C str
866 sh	830 b, vw	Asym methyl rock
880 m	850 b, w	Sym methyl rock
1220 vs	1223 vs	Asym methyl def
1235 vs		Asym methyl def
1268 s	1260 vs	Total sym methyl def
1273 s		Total sym methyl def
	1326 b, vw	CH def
1408 m		
1416 m	1416 s	CH def
2123 m		880 + 1235 = 2115
2800 m	2790 m	Sym CH str
2901 s	2890 s	Sym CH str
2920 sh		Asym CH str
2960 s	2963 s	Asym CH str
Internal Ligand Vibrations of SCN		
446 m		SCN rock
743 s		Carbon–sulfur str
904 w		Overtone of 446 cm^{-1}
2176 vs		Carbon–nitrogen str

Since thiocyanatotrimethylplatinum(IV) is the first reported tetrameric alkylplatinum compound to use a simple ambidentate ligand in the bridging position, it was necessary to determine the structure and the type of bonding in the compound. Three types of bonding have been reported for the thiocyanate anion: nitrogen-bonded terminal isothiocyanate,[3–5] sulfur-bonded terminal thiocyanate,[3–5,12] and sulfur–nitrogen bridged bonded thiocyanate.[6,13] In addition several examples of sulfur-bonded thiocyanate bridges have been reported by Dehnicke. This latter structure is assigned to phenylmercury thiocyanate dimer[14] and the diethylthiocyanato trimers of aluminum, gallium, and indium.[15] Although the data cited by Dehnicke in assigning the structures are consistent with the postulated structure,[15] they are also consistent with the SCN bridging structure, which would be sterically favored.

Since chemical analysis data indicate that our compound is consistent with the formula $(CH_3)_3PtSCN$ and at least tetrameric in solution (mol wt >1000 by osmometer), possible structures were postulated consistent with these data.

Goodall has reported spectral data of platinum(II) compounds which have a ligand bonded both through a selenium atom and through an attached double bond.[16] The infrared absorption of the carbon–carbon double bond stretching frequency was lowered from 1637 cm^{-1} in free ligand to 1500 cm^{-1} when complexed. In view of this possible interaction, structures involving triple

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(12) J. Chatt and L. A. Duncanson, *Nature (London)*, **178**, 997 (1956).

(13) (a) J. Chatt, L. A. Duncanson, F. A. Hart, and P. G. Owston, *ibid.*, **181**, 43 (1958); (b) D. L. Tibbetts and T. L. Brown, *J. Amer. Chem. Soc.*, **91**, 1108 (1969).

(14) K. Dehnicke, *J. Organometal. Chem.*, **9**, 11 (1967).

(15) K. Dehnicke, *Angew. Chem., Int. Ed. Engl.*, **6**, 947 (1967).

(16) D. C. Goodall, *J. Chem. Soc. A*, 890 (1969).

bond ($\equiv$) participation are included in Table II. The table lists the local environment of the platinum and the number of different types of methyl groups.

TABLE II

POSSIBLE PLATINUM ENVIRONMENTS CONSISTENT WITH $((CH_3)_3PtSCN)_4$ ENVIRONMENTS

Environment	No. of methyl environments	Environment	No. of methyl environments
$(CH_3)_3PtS_3$	1	$(CH_3)_3PtS_2$ ($\equiv$)	2
$(CH_3)_3PtS_2N$	2	$(CH_3)_3PtSN$ ($\equiv$)	3

In Table II the environment of each platinum atom in the tetramer is the same. Environments such as $(CH_3)_3PtN_2S$ and $(CH_3)_3PtN_3$ are neglected since the nitrogen atom has only a single lone pair of electrons available for donation, and these bonding arrangements require either nonequivalence of the four platinum atoms or a bridging nitrogen.

The infrared spectrum of the platinum skeleton of thiocyanatotrimethylplatinum(IV) has been presented and assigned above; the vibrations of the anion are discussed here. Three fundamental vibrations and one overtone are of sufficient intensity to be assigned (Table III). The values for KSCN[17] are included for comparison with the values obtained for the platinum compound.

TABLE III

REPRESENTATIVE LIGAND VIBRATION MODES AS A FUNCTION OF THE BONDING

Compound	ν(C–N), cm^{-1}	ν(C–S), cm^{-1}	δ(SCN), cm^{-1}	Bonding
$((CH_3)_3PtSCN)_4$	2176 vs	743 s	446 m	...
$(AgSCN)_n$	2169 vs	746 m, 723 m	446 m, 423 m	SCN bridge
$K_2Pt(SCN)_6$[5]	2130 s	699 sh, 695 w	462 vw, 433 sh, 418 m	S terminal
$((n\text{-}C_3H_7)_3P)_2Pt(SCN)_4$[12]	2182 (bridged) 2105 (terminal)	...	...	SCN bridge
$((C_6H_5)_3P)_2Pt(NCS)_2$[3]	2097 s,b	841 w	...	N terminal
KSCN[17]	2053 vs	749 m	484, 470 m	

Burmeister[3] reported the generalization that for sulfur-bonded thiocyanate, the carbon–nitrogen stretch frequency is at higher wave numbers than for the corresponding nitrogen-bonded isothiocyanate and the values of the rocking frequency and the carbon–sulfur stretch modes are also affected. The carbon–sulfur stretch is usually at lower frequency than for KSCN when sulfur bonded and at higher frequency when the ligand is nitrogen bonded. The values of the rocking mode for the sulfur-bonded ligand are 60 cm^{-1} lower than the free ion while the nitrogen-bonded ligand has the rocking mode approximately in the same location as the free ion. Most sulfur-bonded compounds, especially those with a terminal SCN, have four weak peaks between 460 and 415 cm^{-1} with the most intense at about 420 cm^{-1}. The additional peaks are caused by the loss of linearity when the bonding is to nitrogen rather than to sulfur.

No data have been found for the carbon–sulfur stretching frequency of the rocking mode in platinum compounds where the thiocyanate is bridging, but the vibrational spectrum for silver thiocyanate, which is polymeric, has been reported.

The table includes nitrogen-bonded isothiocyanate, sulfur-bonded thiocyanate, and bridge sulfur- and nitrogen-bonded thiocyanate. The most completely tabulated region is that of the carbon–nitrogen stretch, where the most intense band in the spectrum occurs. This band is doubly useful since, in addition to the relationship of the frequency to the mode of bonding, the intensity of the band is also dependent upon the mode of bonding. Burmeister and coworkers[18] have reported that the magnitude of the integrated intensity of the CN vibrational band is an order of magnitude larger for nitrogen-bonded compounds than the sulfur-bonded isomers. Where accurate data are available for a series of compounds using the same metal, an approximate value of relative intensity should indicate the type of bonding. This is especially true when the position of the band does not allow conclusive assignment and the remainder of the ligand vibrations are obscured by other bands. This phenomenon will prove useful when the infrared spectrum of derivatives of the parent compound are discussed.

Comparison of the data for thiocyanatotrimethylplatinum(IV) with the data for polymeric silver thiocyanate,[6] which contains bridging SCN, shows very close correspondence; the frequencies of all of the vibrations are very much in agreement with each other. The frequencies for the other platinum compounds vary considerably. For example, the value of the carbon–sulfur stretching mode is much higher for thiocyanatotrimethylplatinum(IV) than for potassium tetrathiocyanatoplatinum(II) (743 cm^{-1} *vs.* 690 cm^{-1}).[5] While the platinum(II) compound has the usual pattern of four weak bands in the SCN rocking region, the thiocyanatotrimethylplatinum(IV) has only a single peak of medium intensity at 446 cm^{-1}. The degeneracy in the tetrameric compound is an indication of a more symmetrical environment of the thiocyanate than in the usual sulfur-bonded complexes.

By consideration of these infrared data, it is possible to arrive at certain conclusions. Based upon the value of the carbon–nitrogen stretch the compound contains an SCN bridging ligand. The compound does not utilize structures with significant triple bond participation since that would lower the stretching frequency of

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[17] L. H. Jones, *J. Chem. Phys.*, **25**, 1069 (1956).

[18] J. L. Burmeister, E. A. Deardorff, and C. E. Van Dyke, *Inorg. Chem.*, **8**, 170 (1969).

the multiple bond. The frequency on the contrary is raised. The only compounds with stretching frequencies in this region (above 2150 cm^{-1}) are those containing bridging SCN ligands.

The nmr spectrum is consistent with a structure containing platinum bonded to two sulfurs and one nitrogen. This structure, with bridging SCN, would be consistent with the infrared data cited above and would explain the observed nmr spectrum. The nmr spectrum consisted of two sets of pseudotriplets in a 2:1 ratio. The low-field peak at τ 8.52 is assigned to methyl protons trans to the more abundant sulfur and the high-field peak at τ 8.91 is assigned to methyl groups trans to the nitrogen atom of the anionic ligand.

The postulated structure is diagrammed in Figure 1.

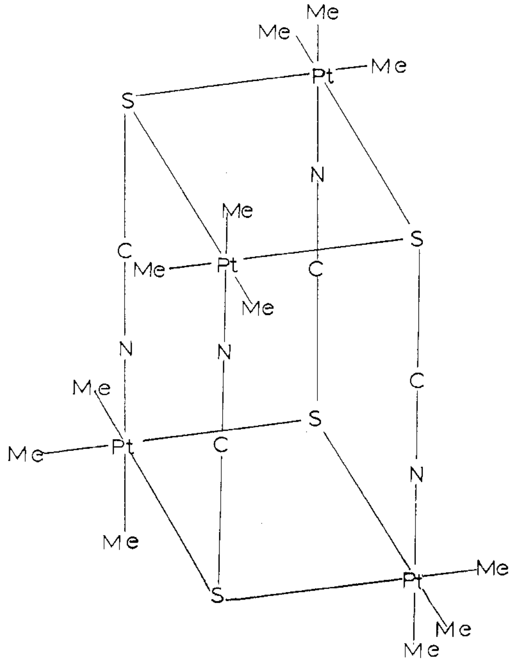

Figure 1.—Postulated structure of tetrameric thiocyanatotrimethylplatinum(IV).

The structure consists of two sets of planes in each of which the two platinums are bound to two sulfurs. The sixth coordination site is filled by the nitrogen end of a thiocyanate ligand in the other plane.

In order to test the postulated structure of the thiocyanate compound and in order to eliminate the possibility that a mixed tetramer of two different compounds, as reported by Morgan[2] for an intermediate product between hydroxytrimethylplatinum(IV) and iodotrimethylplatinum(IV), was formed, the pyridine adducts were prepared. A mixed tetramer would form more than one type of 2:1 pyridine adduct since each component of the mixed tetramer would yield a 2:1 pyridine adduct.

Pyridine Adducts of the Trimethylplatinum(IV) Compounds.—The pyridine study of the trimethylplatinum(IV) halides provided several generalizations which will be helpful in assigning the peaks for the pyridine adducts of thiocyanatotrimethylplatinum(IV). The methyl groups trans to pyridine were shifted to lower field relative to the tetramer while the methyls trans to the halide were shifted to higher field. The coupling constant for the methyl groups trans to pyridine was relatively insensitive to the degree of association and to the identity of the halide. The relative areas were used to assign the peaks in the 2:1 adducts since a large excess of pyridine was added to ensure the complete transformation to the 2:1 adduct. The 1:1 adduct was prepared for only the iodide and thiocyanate and the assignments were made on the basis of the known spectra of the tetramers and of the 2:1 adducts.

A sample of the solid thiocyanatotrimethylplatinum(IV) tetramer was dissolved in benzene–pyridine solution and the spectrum was recorded. The addition of pyridine was continued gradually followed by recording the nmr spectrum. Figure 2 is the observed spectrum when the concentration of pyridine was small. Some unreacted tetramer is present and a small amount of a postulated isomer is also present at low field (τ 8.01) (*vide infra*). This extra peak disappears as the concentration of pyridine increases. The three peaks that are labeled are assigned to three methyls comprising the 1:1 adduct. Table IV summarizes the data and lists the assignments to be discussed below. The assignments listed are derived by consideration of the spectrum of the tetramer and by analogy with the spectral change in the pyridine adducts of the trimethylplatinum(IV) halides relative to the uncomplexed compound. The relative area of the peaks assigned to a given adduct also provided information which was helpful in making the assignments. Using the generalizations derived from the pyridine complexes of the tetrameric trimethylplatinum halides, the 2:1 pyridine adduct of thiocyanatotrimethylplatinum(IV) was easily assigned. The more intense low-field peak (τ 8.53; J = 70.5 Hz) was assigned to the methyls trans to the pyridine. This peak is relatively unshifted from the position of one of the peaks in the original tetramer. The other peak (τ 9.04; J = 68.8 Hz) is assigned to the methyls trans to the anion. The anion is assumed to be isothiocyanate; that is, the anion is bonded through nitrogen. The infrared data presented below are consistent with this assignment. With a large excess of pyridine an extra peak is seen at τ 8.82. The peak is fairly weak and if it is a pseudotriplet, the satellites are in the noise.

Assignment of the 1:1 adduct is less straightforward. The spectrum is composed of three sets of pseudotriplets in an apparent ratio of 1:1.3:1.2. The low-field peak is assigned to the methyls trans to pyridine (τ 8.40; J = 70.0 Hz) on the basis of the coupling constant and the downfield shift relative to the tetramer. The middle and most intense peak is assigned to the methyls trans to the sulfur end of thiocyanate (τ 8.61; J = 72.2 Hz). The assignment is based on the assignment of the low-field peak in the spectrum of the tetramer to methyls trans to the sulfur atom of SCN and the shift upfield upon the addition of the pyridine. The third peak is assigned to the methyl groups trans to the nitrogen atom of the thiocyanate (τ 8.86; J = 73.0 Hz). The cou-

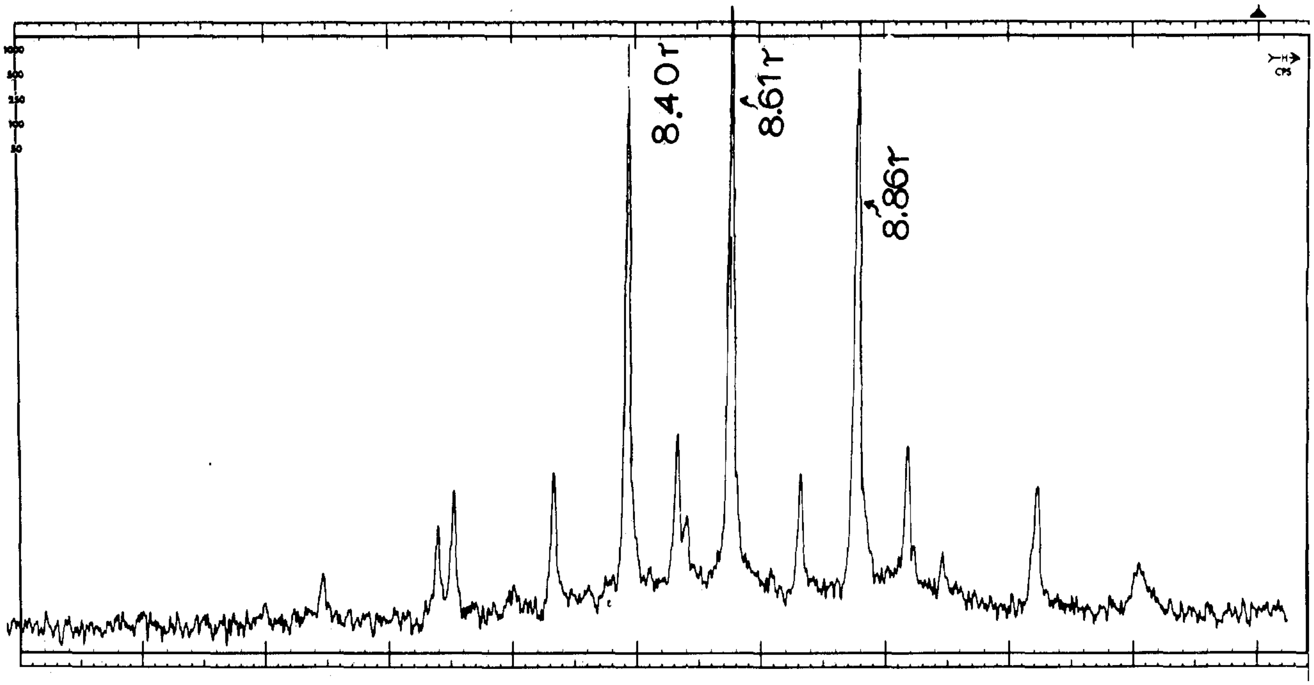

Figure 2.—Nuclear magnetic resonance spectrum of thiocyanatotrimethylplatinum(IV) plus pyridine.

TABLE IV
NUCLEAR MAGNETIC RESONANCE FOR THE TRIMETHYLPLATINUM COMPOUNDS AND THEIR PYRIDINE ADDUCTS

Compound	Ligand trans to methyl	Chem shift, τ, ppm	Coupling constant, Hz	Rel area
$((CH_3)_3PtI)_4$	I	8.16	78.4	. . .
$(Py(CH_3)_3PtI)_2$	Pyridine	8.01	71.0	1.0
	I	8.34	74.4	2.0
$Py_2(CH_3)_3PtI$	Pyridine	8.01	70.7	2.0
	I	8.67	68.2	1.0
$((CH_3)_3PtBr)_4$	Br	8.36	79.0	. . .
$Py_2(CH_3)_3PtBr$	Pyridine	8.06	70.2	2.0
	Br	8.72	69.5	1.0
$((CH_3)_3PtCl)_4$	Cl	8.47	79.7	. . .
$Py_2(CH_3)_3PtCl$	Pyridine	8.20	70.5	2.0
	Cl	8.77	70.0	1.0
Tetramer	*S*CN	8.52	75.0	2.0
	*N*CS	8.91	74.2	1.0
1:1 adduct	Pyridine	8.40	70.0	1.0
	*S*CN	8.61	72.2	1.3
	*N*CS	8.86	73.0	1.2
	a	8.01	70.0	. . .
2:1 adduct	Pyridine	8.53	70.5	2.0
	*N*CS	9.04	68.8	1.0
	b	8.82	. . .	. . .

[a] An unidentified pseudotriplet present at low pyridine concentration. [b] An unidentified, weak peak present at high pyridine concentration.

pling constant is not greatly affected since these methyl groups still are trans to a nitrogen of a bridged thiocyanate. The coordination change, occurring when the sulfur becomes two-coordinate instead of three-coordinate, is rather distant from this bond.

In addition to the three intense pseudotriplets found in the solution when the concentration of pyridine is small, a much weaker pseudotriplet is seen when the solution consists of a mixture of tetramer and 1:1 adduct. This peak (τ 8.01; J = 70.0 Hz) is at a very low field and is thought to represent another isomer of the 1:1 adduct. The presence of other peaks under the more intense peaks already assigned is indicated by the difference between the relative areas of the three most intense peaks. Possible isomers are further indicated by infrared evidence.

The complex vibrational spectrum of pyridine makes the complete assignment of all the bands in the spectra of the pyridine adducts extremely difficult. It is, however, possible to separate the bands due to the anion from those due to the platinum methyl and pyridine modes. Table V lists the bands due to thiocyanate ligand in various phases for the different compositions analyzed.

TABLE V
INFRARED DATA FOR THE THIOCYANATE LIGAND IN THE PYRIDINE ADDUCTS OF THIOCYANATOTRIMETHYLPLATINUM(IV)

Compn of sample	ν(C–N), cm^{-1}	ν(C–S), cm^{-1}	δ(SCN), cm^{-1}
1:1 adduct (mull)	2125 vs	. . .	. . .
Mixture of 1:1 and 2:1 adducts (benzene solution); approximately equal concn	2140 m 2084 vs	. . .	. . .
2:1 adduct (mull)	2096 vs	804 m 801 m	469 m
Tetramer (mull)	2176 vs	743 m	446 m

The most useful band is the carbon–nitrogen stretching frequency since it is of high intensity and appears in a region where pyridine does not absorb strongly. As was noted above, the intensity of this band is greater for the nitrogen-bonded isomer than for the sulfur-bonded isomer. This was especially apparent in the mixture of the 2:1 and 1:1 adducts. The nmr spectrum of this solution indicated that the amount of 1:1

adduct was greater than the amount of 2:1 adduct, yet the peak at 2084 cm^{-1} assigned to the nitrogen-bonded 2:1 isomer is much more intense than the peak at 2140 cm^{-1} assigned to the more abundant 1:1 isomer.

The assignments of the structures are made on the following basis. The tetramer has a band at 2176 cm^{-1} and has been assigned the bridging structure; the 2:1 adduct is assigned the isothiocyanato structure by examination of the carbon–nitrogen stretch and the relative position of the nmr peak assigned to the methyl groups trans to the anion. Both observations lead to its assignment as the nitrogen-bonded isomer. The structure of the predominant form of the 1:1 isomer is based upon the small reduction in the stretching frequency and the evidence for three methyl environments in the compound. The 1:1 adduct is therefore assigned a bridged structure analogous to the tetramer except for one less bond to each sulfur. This structure is illustrated in Figure 3.

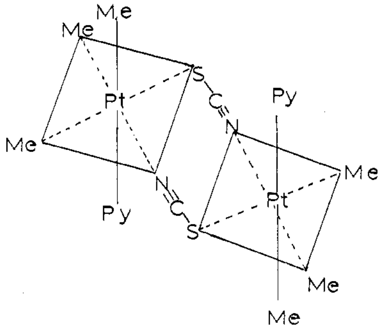

Figure 3.—Postulated structure of the predominant 1:1 pyridine adduct.

The spectral evidence seems also to indicate the presence of an isomeric form of the 1:1 adduct. The lowering of the carbon–nitrogen stretching frequency for the mull of the 1:1 adduct relative to the benzene solution would seem to indicate the presence of a different form of the compound in the solid. The frequency has been shifted from 2140 cm^{-1} in solution to 2125 cm^{-1} as the solid. A solubility-governed isomerization is postulated to account for this change. The more soluble form has a peak at 2140 cm^{-1} and three separate methyl environments. As the solution is evaporated, the equilibrium is shifted to favor the other isomer. This would explain the previously noted extra pseudotriplet at low field and the other abnormalities in the nmr spectrum at a low pyridine concentration in the solution.

The reduction in the carbon–nitrogen stretching frequency for the less soluble isomer of the 1:1 adduct may be interpreted as the result of the formation of a dimer with bridging sulfurs. The vibration is in the range associated with sulfur-bonded thiocyanate.

This type of structure would explain some of the anomalies encountered with relative areas in the nmr spectrum of the solution of the 1:1 adduct. The low-field peak could represent methyls trans to pyridine while the high-field component lies under another peak at high field. The approximate value of the coupling constant for the lower field peak (*ca.* 70.0) is in the range of values found for other pyridine adducts. Another isomeric structure which can be considered is the dimeric bridging thiocyanate which has one platinum bonded to two nitrogen atoms of thiocyanate while the other platinum atom is bonded to the sulfur end of the ligand. The data are not sufficient to determine the extent nor the type of isomers that are formed in addition to the predominant form.

The infrared spectrum of the mull of the 2:1 adduct provides other evidence for the assigned isothiocyanate bonding. The carbon–sulfur stretch is found as a doublet at 801 and 804 cm^{-1} compared with 743 cm^{-1} in the bridged species and the rocking mode is shifted from 446 cm^{-1} in the tetramer to 469 cm^{-1} in the 2:1 adduct. Both of these changes are in the direction expected for a change to the nitrogen-bonding mode.

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