Alternately, it might be argued that the substitution reaction does not proceed by an S_N1 mechanism, at least when the substituting nucleophile is py. Completion of studies of the rate of exchange of $Co(CN)_5OH_2^{2-}$ with O^{18}-labeled H_2O should clarify this point.

The present studies considerably extend our knowledge of the factors which parallel nucleophilic reactivity in the displacement of H_2O in $Co(CN)_5OH_2^{2-}$. The NH_3 ligand, with an experimental value of $k_2/k_3 = 6.4$, is appreciably more reactive than N_2H_4, an indication that an unshared pair of electrons on the atom α to the reactive site does not result in exceptional reactivity in the present system.[4] Basicity is also apparently not of major importance. The py molecule is much more reactive than NH_3, despite its lower basicity, presumably because of its ability to form metal-to-ligand π bonds in the activated complex, a phenomenon which may also contribute to the reactivity series $I^- > Br^- > Cl^-$. A comparison of the relative reactivity of N_2H_4 and $N_2H_5^+$ also demonstrates the lack of correlation of basicity and reactivity and suggests that electrostatics may play an appreciable role in determining nucleophilicity. Alternately, the unexpected reactivity of $N_2H_5^+$ may arise from especially favorable hydrogen bonding in the activated complex.

It is of interest, finally, to compare the acid properties of $Co(CN)_5N_2H_5^-$ with those of structurally related ions. It is generally recognized that substitution of a proton by a Co(III) linkage is acid weakening, particularly when the Co(III) is present in a complex with a negative charge. A pertinent example is a comparison of the acidity of H_3O^+ with that of $Co(CN)_5OH_2^{2-}$, with the latter species having a pK of 9.8. It might be anticipated, therefore, that the acidities of $N_2H_6^{2+}$ and $Co(CN)_5N_2H_5^-$ would be related in an analogous fashion, with the latter species being much less acidic in agreement with prediction.[12] The effect of substitution on the $N_2H_6^{2+}$ ion is, as expected, less than that in H_3O^+, because the substitution in $N_2H_6^{2+}$ presumably occurs on an atom in the α position to that bearing the acidic proton. In an alternative comparison of acidity, it may be noted that the addition of $Co(CN)_5^{2-}$ to the basic nitrogen atom of $N_2H_5^+$ decreases the pK of the latter species from 8.0 to 4.35.

Acknowledgment.—The preparation of $K_2Co(CN)_5py$ and the study of its aquation was carried out by Dr. Ingo Stolz. Dr. Richard W. Gaver carried out the least-squares computations.

[12] At ordinary acidities $N_2H_6^{2+}$ dissociates completely to form $N_2H_5^+$ and H^+. The data of G. Schwarzenbach, *Helv. Chim. Acta*, **19**, 178 (1936), reported as basicity constant, correspond to an acidity constant of 1.0×10^2.

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The Replacement of Thiocyanate Ion in the *trans*-Dithiocyanatotetraammineplatinum(IV) Cation by Chloride Ion[1]

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The predominant paths for the stepwise replacement of the two thiocyanate ions in *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$ by chloride ion have third-order rate laws with rate dependences on the reactant platinum(IV) complex, $Pt(NH_3)_4^{2+}$, and chloride ion, The third-order rate constants at 25.0° are 1.8×10^2 and 2.7 M^{-2} sec^{-1}, respectively. The thiocyanate ions in both *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$ and the intermediate product *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$ were found to be S bonded. These results are explained in terms of a bridged inner-sphere redox mechanism in which the sulfur atom of a thiocyanate ion links the platinum(II) and platinum(IV) complexes. Activation parameters for the reactions are reported. The equilibrium constants for the stepwise replacement of thiocyanate ions are 0.084 and 0.0028 at 35.0°.

Introduction

A variety of substitution reactions of *trans*-dihalotetraammineplatinum(IV) cations are catalyzed by the tetraammineplatinum(II) cation.[2-5] The rate behavior of these reactions is consistent with a mechanism proposed by Basolo and Pearson, which involves an inner-sphere, two-electron redox process, eq 1–3. The four

$$Pt^{2+} + Z^- = Pt\text{–}Z^+ \tag{1}$$

$$Y\text{–}Pt\text{–}X^{2+} + Pt\text{–}Z^+ = Y\text{–}Pt\text{–}X\text{–}Pt\text{–}Z^{3+} \tag{2}$$

$$Y\text{–}Pt\text{–}X\text{–}Pt\text{–}Z^{3+} = Y^- + Pt^{2+} + X\text{–}Pt\text{–}Z^{2+} \tag{3}$$

ammonias in the plane of each complex are omitted; X, Y, and Z are halogens. Studies in this laboratory have been aimed at a detailed investigation of this mechanism and its applications in the chemistry of platinum(IV).

In terms of this mechanism, an intriguing situation can be visualized for the ambidentate thiocyanate ligand. A thiocyanate situated in the bridging position of the activated complex (group X in eq 2) might

[1] Based on part of the Ph.D. Dissertation of W. R. M., Emory University, 1966.

[2] F. Basolo, M. L. Morris, and R. G. Pearson, *Discussions Faraday Soc.*, **29**, 80 (1960).

[3] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 35 (1961).

[4] R. R. Rettew and R. C. Johnson, *Inorg. Chem.*, **4**, 1565 (1965).

[5] R. C. Johnson and E. R. Berger, *ibid.*, **4**, 1262 (1965).

be expected to give either an N-bonded isothiocyanatoplatinum(IV) complex or an S-bonded thiocyanato complex. The nature of the product will depend upon whether the $Pt(NH_3)_4Z^+$ species attacks the sulfur atom adjacent to the platinum(IV) or the nitrogen atom remote from it. Haim and Sutin[6] have demonstrated that the reaction of $FeNCS^{2+}$ or $Co(en)_2H_2ONCS^{2+}$ with Cr^{2+} yields both $CrNCS^{2+}$ and $CrSCN^{2+}$ and have postulated that both remote and adjacent attack on the coordinated thiocyanate occurs.

This paper presents the results of studies in which the rate behavior, equilibrium constants, and products of reactions 4 and 5 were determined.

$$\textit{trans}\text{-}Pt(NH_3)_4(SCN)_2^{2+} + Cl^- \longrightarrow \textit{trans}\text{-}Pt(NH_3)_4(SCN)Cl^{2+} + SCN^- \quad (4)$$

$$\textit{trans}\text{-}Pt(NH_3)_4(SCN)Cl^{2+} + Cl^- \longrightarrow \textit{trans}\text{-}Pt(NH_3)_4Cl_2^{2+} + SCN^- \quad (5)$$

Experimental Section

Preparation of Compounds.—Tetraammineplatinum(II) perchlorate and *trans*-dichlorotetraammineplatinum(IV) chloride were prepared as described in a previous paper.[4]

trans-Dithiocyanatotetraammineplatinum(IV) perchlorate was prepared by dissolving 3.2 g (7.8 mmoles) of $[Pt(NH_3)_5Cl]PO_4$[7] in 100 ml of dilute acetic acid (1 *M*) and adding 40 g (0.4 mole) of KSCN at room temperature. The clear solution turned orange and 1.8 g (3.6 mmoles) of *trans*-$[Pt(NH_3)_4(SCN)_2](SCN)_2$ precipitated after about 30 min. The product was collected, washed with alcohol and ether, and dried under vacuum. The thiocyanate salt was converted to the perchlorate salt by dissolving the above product in a minimum amount of cold dilute $HClO_4$ (0.01 *M*). The perchlorate salt was precipitated with 72% $HClO_4$ at ice bath temperature; the product was collected and washed with a minimum amount of alcohol and ether. The yield of 1.0 g (1.7 mmoles) was dried under vacuum and analyzed. *Anal.* Calcd for $[Pt(NH_3)_4(SCN)_2](SCN)_2$: Pt, 33.74; SCN^-, 20.09. Found: Pt, 34.04, SCN^-, 19.11.

Many attempts were made to prepare *trans*-chlorothiocyanatotetraammineplatinum(IV) chloride, but the highest purity that was obtained was about 70%. A 100-mg sample (0.17 mmole) of *trans*-$[Pt(NH_3)_4(SCN)_2](ClO_4)_2$ was treated with 300 ml of a 0.200 *M* solution of HCl containing $Pt(NH_3)_4^{2+}$ catalyst (0.012 mmole) ot 8°. The formation of the *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$ cation was followed by observing the increase in its absorption maximum at 252 mμ. When the reaction was complete (120 min), a stoichiometric amount of $AgNO_3$ was added. The AgCl–AgSCN precipitate was removed and the solution was concentrated tenfold under vacuum at a temperature below 15°. The chloride product was precipitated at ice bath temperature with cold, concentrated HCl. The yield of 51 mg was washed with alcohol and ether and air dried. Analysis of the ultraviolet spectrum of the product was consistent with a mixture of *trans*-$[Pt(NH_3)_4(SCN)Cl]Cl_2$ (70%) and *trans*-$[Pt(NH_3)_4Cl_2]Cl_2$ (30%). This analysis was in agreement with direct analysis for SCN^-.

Sodium perchlorate used to control ionic strength in kinetic experiments was prepared from reagent Na_2CO_3 and $HClO_4$. All materials used were reagent grade.

Concentrations of $Pt(NH_3)_4(ClO_4)_2$ solutions were determined by Ce(IV) titration in dilute H_2SO_4 containing 1 *M* NaCl.

The ultraviolet spectra of neutral solutions of *trans*-$[Pt(NH_3)_4(SCN)_2](ClO_4)_2$ changed appreciably when they were stored at room temperature longer than 12 hr or exposed to strong sunlight. Therefore solutions of *trans*-$[Pt(NH_3)_4(SCN)_2](ClO_4)_2$ were prepared fresh daily in acid and were protected from excessive exposure to light. These solutions were stored in a refrigerator at 10° until they were used. Under these conditions there was no noticeable change in the ultraviolet spectra for periods as long as 48 hr. A variety of artificial lighting conditions was used during these experiments and there was no evidence that the rates of the reactions investigated were influenced by light.

Spectral Measurements.—Ultraviolet and visible spectral measurements were made on a Cary 14 recording spectrophotometer with 1.00-cm quartz cells. Spectra of the Pt(IV) complexes were run in dilute $HClO_4$ at concentrations of 0.05–1.0 *M*. There was no change in spectra as a function of acid concentration.

Infrared spectra were recorded on Perkin-Elmer Infracord spectrometers with NaCl and KBr prisms, and also on a Perkin-Elmer Model 21 spectrometer. Spectra were run using paraffin oil mulls and KBr or KCl disks.

Kinetic Measurements.—Kinetics were followed spectrophotometrically using a Cary 14 spectrophotometer equipped with a thermostated cell compartment. The temperatures reported are accurate to ±0.1°. The details of the kinetic method used are published elsewhere.[4] The reactions were studied in acid media under conditions of excess Cl^- to make them pseudo first order in Pt(IV).

Reaction 4 was followed at 284 mμ which corresponds to a maximum of *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$. The products of this reaction do not absorb appreciably at this wavelength. The infinite time spectrum of reaction 4 was assigned to *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$; it was entirely different from that of *trans*-$Pt(NH_3)_4Cl_2^{2+}$ and *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$. The ionic strength was controlled at 0.2 *M* with $NaClO_4$ or $HClO_4$.

Reaction 5 was run using *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$ as starting material, but under the conditions of the experiments the first SCN^- replacement (reaction 4) occurred very rapidly and was essentially complete on mixing the reactants. The replacement of the second SCN^- was then followed at 252 mμ which corresponds to a maximum of *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$. The products of reaction 5 absorb much less at this wavelength. Infinite time spectra of the reaction mixture were identical with the spectrum of the *trans*-$Pt(NH_3)_4Cl_2^{2+}$ cation. The ionic strength of reaction 5 was adjusted to 1.10 *M* with $NaClO_4$ or $HClO_4$.

Rate data were evaluated by using a least-squares treatment of data covering 4 half-lives by the Guggenheim method.[8] Linear plots were obtained in all cases. Rate constants for reaction 4 were evaluated from plots of $k_{\text{obsd}}/[Pt(II)][Cl^-]$ *vs.* $[Cl^-]$, where k_{obsd} is the pseudo-first-order rate constant. These plots were linear; the slope corresponds to a fourth-order rate constant and the intercept to a third-order constant. The third-order constants are self-consistent to ±5%; the fourth-order constants are not so precise.

Rate constants for reaction 5 measured at an ionic strength of 1.10 *M* were calculated by plotting $k_{\text{obsd}}/[Cl^-]$ *vs.* [Pt(II)]. The slope of the line generated corresponds to a third-order rate constant and the intercept to a second-order constant. Rate data taken at very low $Pt(NH_3)_4^{2+}$ concentrations do not fit this rate treatment well. Therefore, although the third-order constants are reliable, the process responsible for the intercept needs further study. The third-order constants are self-consistent to ±10%.

Reaction 5 was also investigated at 0.2 *M* ionic strength using a ×0.1 slide wire in the Cary 14 and one-tenth the concentration of Pt(IV) (5×10^{-6} *M*). These conditions were required to drive the reaction to completion. Erratic results were observed; the noise level of the instrument alone was sufficient to introduce considerable uncertainty in absorbance *vs.* time measurements. The data collected under these conditions were treated by determining k_{obsd} from slopes of plots of $\ln (A - A_\infty)$ *vs.* time. Initial curvature was observed in some plots, but after about 0.5 half-life, the plots were linear.

Activation parameters were calculated for the rate data corre-

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[6] A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **87**, 4210 (1965); **88**, 434 (1966).

[7] "Gmelin's Handbuch der Anorganischen Chemie," 68D, Verlag Chemie, Weinheim/Bergstrasse, Germany, 1957, p 480.

[8] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

sponding to the third-order path at three temperatures—25, 35, and 45°.

Equilibrium Measurements.—Equilibrium measurements for reaction 5 were made spectrophotometrically at 252 mμ on reaction mixtures containing *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$, $Pt(NH_3)_4^{2+}$, SCN^-, and Cl^-. The reactants were mixed and placed in the thermostated spectrophotometer cell at 35°. The absorbance was observed as a function of time as equilibrium was approached. The equilibrium constant, K_2, was evaluated from

$$K_2 = \frac{(\epsilon_{ClSCN}[Pt(IV)] - A_\infty)\{(\epsilon + \epsilon_{ClSCN})[Pt(IV)] + \epsilon[SCN^-]_0 - A_\infty\}}{\epsilon[Cl^-](A_\infty - \epsilon_{Cl_2}[Pt(IV)])} \qquad (6)$$

where [Pt(IV)] is the total Pt(IV) concentration, $[Cl^-]$ is the concentration of uncomplexed Cl^-, $[SCN]_0$ is the concentration of added NaSCN, ϵ_{Cl_2} is the molar absorptivity of *trans*-$Pt(NH_3)_4Cl_2^{2+}$ at 252 mμ (=600), ϵ_{ClSCN} is the molar absorptivity of *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$ at 252 mμ ($=2.8 \times 10^4$), $\epsilon = \epsilon_{ClSCN} - \epsilon_{Cl_2} = 2.74 \times 10^4$, and A_∞ is the absorbance of the reaction mixture at 252 mμ at equilibrium corrected for absorbance due to Pt(II). The derivation of eq 6 is tedious but straightforward. It is valid only for 1.00-cm cells. The derivation involves the assumption that the concentration of *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$ is negligibly small; this is in accord with the absence of the absorption maximum at 284 mμ of this complex in the experimental spectra. The value of ϵ_{Cl_2} was measured directly from a spectrum of the pure material. The value of ϵ_{ClSCN} was estimated from absorbance *vs.* time curves of kinetic experiments on reaction 5. It is the least reliable parameter used and is probably good to ±10%. Values of K_2 were self-consistent to ±5%.

The equilibrium constant K_1 for reaction 4 was determined in a similar manner but at 284 mμ; K_1 was calculated from

$$K_1 = ([Pt(IV)]\epsilon_{(SCN)_2} - A_\infty)[SCN^-]_0/(A_\infty - \epsilon_{ClSCN}[Pt(IV)])[Cl^-] \qquad (7)$$

where $\epsilon_{(SCN)_2}$ is the molar absorptivity of *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$ at 284 mμ ($=3.65 \times 10^4$), ϵ_{ClSCN} is the molar absorptivity of *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$ at 284 mμ ($=3.0 \times 10^3$), A_∞ is the absorbance at 284 mμ at equilibrium corrected for absorbance due to Pt(II), and $[SCN^-]_0$ is the concentration of added SCN^-. All other symbols have the same meaning as in eq 6. The derivation of eq 7 involves the assumption that the concentration of *trans*-$Pt(NH_3)_4Cl_2^{2+}$ is negligibly small at equilibrium; this is consistent with the values of K_1 and K_2 and the equilibrium spectra. Equation 7 is valid only for measurements in 1.00-cm cells. The value of $\epsilon_{(SCN)_2}$ was measured directly from pure material. The value of ϵ_{ClSCN} was estimated from a spectrum of 70% pure *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$ and is probably reliable to ±10%. The values of K_1 were self-consistent to ±1%.

Results

The ultraviolet and visible spectra of *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$, *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$, and *trans*-$Pt(NH_3)_4Cl_2^{2+}$ are presented in Figure 1. Infrared thiocyanate bands together with visible and ultraviolet spectral bands are tabulated in Table I. The infrared spectrum of *trans*-$[Pt(NH_3)_4(SCN)Cl]Cl_2$ (70%) was carefully searched for the thiocyanate C–S stretching frequency. There were no bands at all in the 900–750-cm^{-1} region of the spectrum, both in mulls and disks. The mulls showed a weak paraffin oil band at 725 cm^{-1} and the disks showed only a gradual increase in background absorption at 850–650 cm^{-1}.

Rate data for reactions 4 and 5 are presented in Tables II and III; a comparison of the activation parameters and rate constants at 25° is presented in Table IV. Many kinetic experiments listed in Tables II and III represent average values of several runs; agreement was of the order of a few per cent in all cases.

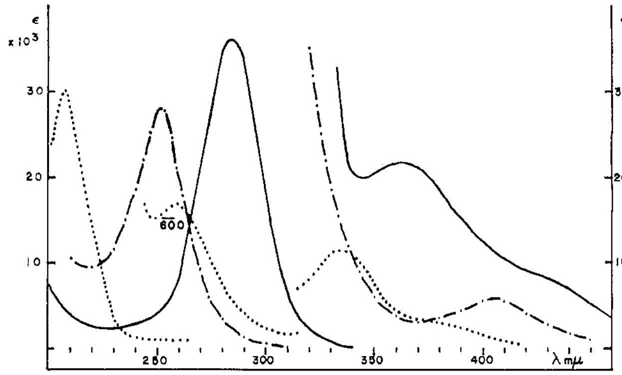


Figure 1.—The visible and ultraviolet spectra of *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$ (—), *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$ (· — ·), and *trans*-$Pt(NH_3)_4Cl_2^{2+}$ (· · · ·).

Table I

Spectral Bands[c]

Infrared (SCN^-), cm^{-1}

Matrix	*trans*-$[Pt(NH_3)_4(SCN)_2](ClO_4)_2$	*trans*-$[Pt(NH_3)_4(SCN)Cl]Cl_2$[a]
Paraffin oil	2120 s, sp	2120, s, sp, 2060 m, sh
Mull	697 mw	. . .
KCl disk	2130 s, sp, 2062 s, sp	2125 s, sp, 2070 m, sh
	694 mw	. . .
	462 w, 450 w	. . .
KBr disk	2124 s, sp, 2063 s, sp	2130 s, sp, 2070 s, sp
	692 mw	. . .
	458 w, 448 w, 412 w	. . .

Visible and Ultraviolet λ_{max}, mμ (ϵ_{max})

Compound	
trans-$[Pt(NH_3)_4(SCN)_2](ClO_4)_2$	435 (70 sh), 362 (215), 284 (3.65×10^4)
trans-$[Pt(NH_3)_4(SCN)Cl]Cl_2$[a]	408 (60), 252 (2.8×10^4)[b]
trans-$[Pt(NH_3)_4Cl_2]Cl_2$	333 (116), 259 (673), 208 (3.0×10^4)

[a] 70% *trans*-$[Pt(NH_3)_4(SCN)Cl]Cl_2$–30% *trans*-$[Pt(NH_3)_4Cl_2]Cl_2$ (see Experimental Section). [b] Estimated from kinetic experiments. [c] s = strong, m = medium, w = weak, sp = sharp, sh = shoulder.

A rate law for reaction 4 is given in eq 8. The Cl^-

$$-d[trans\text{-}Pt(NH_3)_4(SCN)_2^{2+}]/dt = (k_3 + k_4[Cl^-])[Cl^-][Pt(II)][Pt(IV)] \qquad (8)$$

concentrations used in the study of this reaction were such that the greater than first-order path for this reaction contributed less than 25% to the observed rate. Data in addition to that reported in Table II confirm the need for a rate term in addition to the third-order one. However, the k_4 values are not sufficiently accurate to ensure that this path is second order in Cl^-. The reaction was found to be independent of $[H^+]$ over the small range investigated, and ionic strength effects were found to be almost negligible.

The rate law used to evaluate rate constants for reaction 5 is presented in eq 9.

$$-d[trans\text{-}Pt(NH_3)_4(SCN)Cl^{2+}]/dt = (k_2 + k_3[Pt(II)])[Cl^-][Pt(IV)] \qquad (9)$$

The validity of the second-order term in eq 9 is uncertain. It is clear that some process other than that

TABLE II

RATE DATA

rans-$Pt(NH_3)_4(SCN)_2^{2+} + Cl^- \longrightarrow$ *trans*-$Pt(NH_3)_4(SCN)Cl^{2+} + SCN^-$

$10^4[Pt(NH_3)_4^{2+}]$,[a] M	10^3k_{obsd}, sec^{-1}	k_3, M^{-2} sec^{-1}	$10^4[Pt(NH_3)_4^{2+}]$,[a] M	10^3k_{obsd}, sec^{-1}	k_3, M^{-2} sec^{-1}
25.0°[h]			45.0°[j]		
4.00	8.38	184	1.00	4.45	321
2.00	4.01	175	2.00	9.2	334
1.00	1.98	173	3.00	14.1	345
4.00	1.40[b]	170	4.00	5.95[c]	321
4.00	2.94[c]	176	4.00	2.87[b]	333
2.00	4.02[d]	178			
2.00	4.07[e]	173	35.0°[i]		
2.00	3.96[f]	173	1.00	3.06	261
2.00	4.15[g]	182	2.00	6.21	263
			3.00	9.3	264
			4.00	4.46[c]	259
			4.00	2.16[b]	260

[a] $[Pt(IV)] = 2.4 \times 10^{-4}\ M$, $[H^+] = 0.20\ M$, $\mu = 0.20\ M$, $[Cl^-] = 0.100\ M$. [b] $[Cl^-] = 0.020\ M$. [c] $[Cl^-] = 0.040\ M$. [d] $[Pt(IV)] = 4.8 \times 10^{-4}\ M$. [e] $\mu = 0.54\ M$. [f] $[H^+] = 0.100\ M$. [g] $[H^+] = \mu = 0.34\ M$. [h] $k_4 = 2.5 \times 10^2\ M^{-3}\ sec^{-1}$. [i] $k_4 = 4.7 \times 10^2\ M^{-3}\ sec^{-1}$. [j] $k_4 = 1.24 \times 10^3\ M^{-3}\ sec^{-1}$.

TABLE III

RATE DATA

trans-$Pt(NH_3)_4(SCN)Cl^{2+} + Cl^- \longrightarrow$ *trans*-$Pt(NH_3)_4Cl_2^{2+} + SCN^-$

$10^4[Pt(NH_3)_4^{2+}]$, M	10^3k_{obsd}, sec^{-1}	k_3, M^{-2} sec^{-1}	$10^4[Pt(NH_3)_4^{2+}]$, M	10^3k_{obsd}, sec^{-1}	k_3, M^{-2} sec^{-1}
25.0°[a]			35.0°[a,h]		
			4.00	1.25[b]	5.0
			4.00	0.77[d]	4.6
2.00	0.53	2.7	4.00	2.0[e]	4.3
4.00	1.02	2.5	4.00	2.8[f]	6.2
4.00	0.62[b]	2.8	4.00	2.1[g]	4.5
			10.00	2.5[b]	4.3
35.0°[a,h]			45.0°[a,i]		
10.0	0.5[c]	...	1.00	1.04	7.8
25.0	1.1[c]	...	2.00	1.9	8.2
50.0	3.0[c]	...	4.00	3.5	8.1
			4.00	1.9	8.0
1.00	0.55	2.8	6.00	5.1	8.1
2.00	1.07	4.0			
4.00	1.98	4.3			
6.00	2.8	4.2			
8.00	3.7	4.3			
10.0	4.3	4.0			

[a] $[Pt(IV)] = 4.0 \times 10^{-5}\ M$, $[H^+] = 0.200\ M$, $\mu = 1.10\ M$, $[Cl^-] = 1.00\ M$. [b] $[Cl^-] = 0.55\ M$. [c] $[Pt(IV)] = 4.0 \times 10^{-6}\ M$, $\mu = 0.20\ M$, $[Cl^-] = 0.100\ M$, $[H^+] = 0.200\ M$. [d] $[Cl^-] = 0.369\ M$. [e] $[Pt(IV)] = 2.0 \times 10^{-5}\ M$. [f] $\mu = 1.63\ M$. [g] $[H^+] = 0.100\ M$. [h] $k_2 = 2.7 \times 10^{-4}\ M^{-1}\ sec^{-1}$. [i] $k_2 = 2.6 \times 10^{-4}\ M^{-1}\ sec^{-1}$.

TABLE IV

THIRD-ORDER RATE CONSTANTS AT 25°
AND ACTIVATION PARAMETERS

Reaction	ΔH^*, kcal mole^{-1}	ΔS^*, cal mole^{-1} deg^{-1}	k_3, M^{-2} sec^{-1} (25°)
4	5	−30	175[a]
5	10	−20	2.7[b]

[a] $\mu = 0.20\ M$. [b] $\mu = 1.10\ M$.

corresponding to the third-order rate term is occurring, but it contributes little to the reaction under the conditions of the present study and hence was not well characterized. Reaction 5 was found to be independent of $[H^+]$ in the small range investigated. Ionic strength increases above 1.10 M were found to cause a slight increase in rate.

Results of equilibrium measurements for reactions 4 and 5 are presented in Table V. Rate constants for the reverse of reactions 4 and 5 at 35° can be calculated from the equilibrium constants and rate constants for the forward reactions. The values for the third-order constants are 3.1×10^3 and $1.5 \times 10^3\ M^{-2}\ sec^{-1}$.

TABLE V

EQUILIBRIUM CONSTANTS AT 35.0°

$$K_1 = \frac{[Pt(NH_3)_4(SCN)Cl^{2+}][SCN^-]}{[Pt(NH_3)_4(SCN)_2^{2+}][Cl^-]}$$

$[Cl^-]$, M	$[SCN^-]_0$, M	A	10^2K_1[a]
0.100	0.0100	0.874	8.47
0.050	0.0100	1.102	8.33
0.100	0.0050	0.639	8.44

$$K_2 = \frac{[Pt(NH_3)_4Cl_2^{2+}][SCN^-]}{[Pt(NH_3)_4(SCN)Cl^{2+}][Cl^-]}$$

$[Cl^-]$, M	$10^4[SCN^-]_0$, M	A	10^3K_2
1.00	5.00	0.215	2.72
0.55	5.00	0.317	2.84
1.00	10.0	0.313	2.99

[a] $[Pt(IV)] = 4.14 \times 10^{-5}\ M$, $\mu = 0.200\ M$, $[H^+] = 0.200\ M$, $[Pt(NH_3)_4^{2+}] = 4.0 \times 10^{-4}\ M$. [b] $[Pt(IV)] = 4.00 \times 10^{-5}\ M$, $\mu = 1.10\ M$, $[H^+] = 0.200\ M$, $[Pt(NH_3)_4^{2+}] = 2.0 \times 10^{-4}\ M$.

Discussion

A basic feature of the mechanism for reaction 10 is the stoichiometry and structure of the intermediate product formed. The reaction occurs in two steps,

$$trans\text{-}Pt(NH_3)_4(SCN)_2^{2+} + 2Cl^- \longrightarrow trans\text{-}Pt(NH_3)_4Cl_2^{2+} + 2SCN^- \quad (10)$$

the first being much more rapid than the second. Repetitive scans of the 350–200-mμ region of the spectra of reaction mixtures show an isosbestic point at 265 mμ during the fast step of the reaction and an isosbestic point at 227 mμ during the slow step. This suggests that only one intermediate product is formed or that all other intermediates are very short-lived. The spectrum of the intermediate is identical with that of the initial product formed when *trans*-$Pt(NH_3)_4Cl_2^{2+}$ reacts with thiocyanate ion. This indicates that the intermediate is $Pt(NH_3)_4(CNS)Cl^{2+}$ and it suggests that it is the stable linkage isomer. A *trans* geometry seems certain since the starting material $Pt(NH_3)_4(SCN)_2^{2+}$ and the ultimate product $Pt(NH_3)_4Cl_2^{2+}$ are both *trans* isomers and *cis–trans* isomerization has not been observed in platinum(IV) systems.

The mode of attachment of the SCN^- ligand to platinum(IV) in both *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$ and *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$ has been determined on the basis of infrared and ultraviolet spectral studies. Infrared spectroscopy has been the prime method for determining the type of bonding in metal thiocyanate complexes.[9-11] The weak C–S stretching frequency is most widely used; S-bonded thiocyanate complexes show C–S stretching frequencies between 670 and 740 cm^{-1}, whereas for N-bonded isothiocyanate complexes, the bands come at a higher frequency, 780–860 cm^{-1}. The C–N stretching band (2030–2160 cm^{-1}), while stronger and sharper, is less useful in structure assignment. There is considerable overlap in the frequencies for thiocyanate and isothiocyanate complexes. Generally S-bonded thiocyanate complexes have strong, sharp bands which lie at higher frequency than the slightly broader bands of isothiocyanate complexes.

On the basis of its infrared spectrum *trans*-[$Pt(NH_3)_4(SCN)_2$]$(ClO_4)_2$ is clearly an S-bonded complex. The structural assignment in *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$ is less straightforward because a band due to C–S stretching was not observed. The C–N bands of this complex are seen however to be quite similar to those of *trans*-[$Pt(NH_3)_4(SCN)_2$]$(ClO_4)_2$, which suggests the bonding is Pt–SCN. If the bonding were different, these two complexes would be similar to linkage isomers. However for linkage isomers the N-bonded isomer has a lower C–N stretching frequency than the S-bonded isomer.[12-14]

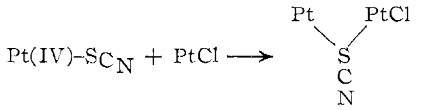
Additional evidence for an S-bonded assignment for both *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$ and *trans*-$Pt(NH_3)_4(SCN)_2{}^{2+}$ is the relative positions of the ultraviolet and visible spectral bands of *trans*-$Pt(NH_3)_4Cl_2{}^{2+}$, *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$, and *trans*-$Pt(NH_3)_4(SCN)_2{}^{2+}$. As chlorides are replaced by thiocyanate ion, the spectral bands shift to longer wavelengths. If the thiocyanate ion was N-bonded, a blue shift would be expected.[15] Spectral shifts of this type have been used previously to ascertain the coordination of SCN^- in metal complexes [6,16,17]

The S-bonded character of these two complexes is in line with structural studies on other platinum(IV) thiocyanate complexes All those on which studies have been reported are S bonded [9,10,18]

The rate data collected permit a more complete analysis of the mechanisms for reactions 4 and 5. The mechanism postulated by Basolo and Pearson, eq 1–3, is consistent with the third-order step in the rate laws for these reactions. The greater than first-order chloride dependence found for reaction 4 can be explained by assuming that a small part of the reaction involves platinum(II)-catalyzed chloride substitution on an ion pair of *trans*-$Pt(NH_3)_4(SCN)_2{}^{2+}$ and Cl^-. Rettew and Johnson[4] have reported evidence for ion pairs in bromide solutions of *trans*-$Pt(NH_3)_4Br_2{}^{2+}$. It is possible that the fourth-order rate term is simply a consequence of the change in solution environment which results from the replacement of HCl with $HClO_4$.

The formation of *trans*-$Pt(NH_3)_4(SCN)Cl^{2+}$ in reaction 4 can be explained in either of two ways, if one assumes the basic mechanism of eq 1–3 is appropriate. The first assumes that the thiocyanate bridge in the activated complex is triatomic with platinum atoms attached to both the sulfur and nitrogen ends. A subsequent rapid isomerization of the N-bonded thiocyanate complex initially produced would explain the S-bonded product observed. A very rapid isomerization is possible but does not seem very probable. Neither a platinum(II)-independent nor a platinum(II)-dependent mechanism would be likely to produce a rate much greater than that of reaction 4 (which is rather rapid for a substitution reaction of this type of complex).

The second explanation asserts that the thiocyanate bridge is monatomic involving interaction of only the sulfur atom with the two platinum atoms, eq 11. Such



$$\mathrm{Pt(IV)\text{–}SC_N + PtCl \longrightarrow \overset{Pt\quad PtCl}{\underset{\underset{N}{C}}{S}}} \qquad (11)$$

an activated complex would give the S-bonded product directly. X-Ray studies on metal thiocyanate complexes have shown that S-bonded thiocyanate is coordinated in an angular fashion with M–S–C bond angles of approximately 120°.[10,19] Such an arrangement would leave the sulfur atom exposed to interact with an approaching $Pt(II)\cdot Cl^-$ ion pair. The reaction of $FeNCS^{2+}$ or $Co(en)_2H_2ONCS^{2+}$ with Cr^{2+} produces both $CrNCS^{2+}$ and $CrSCN^{2+}$. The formation of $Cr\text{–}NCS^{2+}$ was explained in terms of bridging through only the nitrogen atom of the thiocyanate ion. Since M–NCS axes are relatively linear,[6] this suggests both that adjacent attack is possible and that it should be more favorable in the case of the angular M–SCN system.

The relative activation parameters for bromide and chloride ions and chloride and thiocyanate ions functioning as bridging groups can be used to support a mechanism involving bridging through the sulfur atom of thiocyanate ion. See Table VI. If ΔH^* determined the relative bridging ability of Br^- and SCN^-, they would react at comparable rates. However the ΔS^* associated with a bridging SCN^- is much less favorable than with a bridging Br^-. It is difficult to visualize a reason for this entropy effect other than a more rigid activated complex when thiocyanate acts as a bridge. An increase in rigidity might be reasonable in terms of the model of the activated complex pictured in eq 11. Undoubtedly there is steric interaction between ammonias attached to the two platinum atoms; this interaction would reduce the rotational freedom of the ammonia molecules.

The rate data collected permit one to calculate the relative abilities of chloride and thiocyanate ions to

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TABLE VI

ACTIVATION PARAMETERS OF SOME REACTIONS OF THE TYPE *trans*-$Pt(NH_3)_4XY^{2+} + Cl^- \rightarrow$ *trans*-$Pt(NH_3)_4XCl^{2+} + Y^-$

Leaving ion (Y)	Bridging ion (X)	ΔH^*, kcal mole^{-1}	$\Delta(\Delta H^*)$, kcal mole^{-1}	ΔS^*, cal mole^{-1} deg^{-1}	$\Delta(\Delta S^*)$, cal mole^{-1} deg^{-1}
Br	Br	6[4]		−22[4]	
			−5		−2
Br	Cl	11[4]		−20[4]	
SCN	SCN	5		−30	
			−5		−10
SCN	Cl	10		−20	

function as bridging groups in the two-electron redox reactions between platinum(IV) and platinum(II). In reactions 4 and 5 the entering Cl^- and the leaving SCN^- are the same. The bridging groups are SCN and Cl, respectively. The relative rates are 32:1 (corrected for the higher symmetry of *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$). Thiocyanate ion in the bridging position produces considerably faster rates than chloride ion. Comparison of these rate data with previous kinetic data on related reactions shows these relative rates at 25° for a series of bridging groups:[20] $I^-:Br^-:-SCN^-:Cl^-$ as $4.7 \times 10^5:400:32:1$.

Data have been reported on the relative bridging ability of –SCN, –NCS, and –Cl in the one-electron redox process between $Cr(H_2O)_5X^{2+}$ ($X^- = -SCN^-$, $-NCS^-$, and Cl^-) and Cr^{2+}. The rate constants are 40 M^{-1} sec^{-1} (25°),[6] 1.4×10^{-4} M^{-1} sec^{-1} (25°),[21] and 10 M^{-1} sec^{-1} (0°),[21] respectively. In these reactions Cl and –SCN have similar bridging ability and –NCS is much less effective. The fact that $Cr–NCS^{2+}$ is appreciably more stable than $Cr–SCN^{2+}$ enhances the effectivensss of –SCN as a bridging group. In both cases it is probable that the predominant mode of bridging is through the remote atoms. In the platinum system the thiocyanate ion is clearly a much better bridging atom with respect to chloride than in the chromium reaction. This fact suggests that the bridging mechanism is different in the Pt and Cr reactions and supports the idea that bridging in the platinum reaction occurs through only the sulfur atom.

The leaving ability of SCN^- with respect to bromide can be assessed by comparison of the rate parameters of reaction 5 (k_3 (25°) = 2.7 M^{-2} sec^{-1}, $\Delta H^* = 10$ kcal/mole, $\Delta S^* = -20$ cal mole^{-1} deg^{-1}) with those of reaction 12[4] (k_3 (25°) = 6.3 M^{-2} sec^{-1}, $\Delta H^* = 11$ kcal/mole, $\Delta S^* = -20$ cal mole^{-1} deg^{-1}). The data show that bromide and thiocyanate ions have very similar leaving ability.

$$\textit{trans}\text{-}Pt(NH_3)_4BrCl^{2+} + Cl^- \longrightarrow \textit{trans}\text{-}Pt(NH_3)_4Cl_2^{2+} + Br^- \quad (12)$$

From the present work the entering ability of SCN^- cannot be so well characterized because activation parameters for reactions in which thiocyanate ion acts as an entering group were not determined. The rate of the reverse of reaction 5 (k_3 (35°) = 1.5×10^3 M^{-2} sec^{-1}) can be compared with the rate of reaction 13

$$\textit{trans}\text{-}Pt(NH_3)_4Cl_2^{2+} + Br^- \longrightarrow \textit{trans}\text{-}Pt(NH_3)_4ClBr^{2+} + Cl^- \quad (13)$$

(k_3 (35°) = 1.7×10^2).[4] The rates of these reactions, which differ only as to the nature of the entering group, show that thiocyanate reacts ten times more rapidly than bromide ion. This makes thiocyanate ion the best entering group for platinum(IV) complexes which we have studied. (It reacts more rapidly than Cl^-, Br^-, I^-, and NH_3.)

A comparison of the values of K_1 and K_2 for reactions 4 and 5, 0.084 and 0.0028, respectively (at 35°), with equilibrium constants reported[4] at 25° for the successive replacements of bromide ion in *trans*-$Pt(NH_3)_4Br_2^{2+}$ by chloride ion, 0.23 and 0.062, respectively, shows that the thiocyanate is coordinated in preference to both chloride and bromide ions. A surprising feature of the equilibrium measurements is that the ratio of K_1/K_2 is 30 which is considerably greater than the 4 expected on statistical grounds.

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