

Table IX. Thermodynamic Parameters for the Effect of Temperature on the Trans to Cis Equilibrium

	M in $[(\text{CH}_3)_2\text{MN}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2$		
	Al ^a	Ga	In
ΔH , kJ/mol	-4.47	+4.16	-1.94
ΔS , J/mol K	-1.74	+21.8	-10.3
$T\Delta S_{298}$, kJ/mol	-0.52	+6.50	-3.07
ΔG_{298} , kJ/mol	-3.95	-2.34	+1.13
r_b^2	0.9885	0.9676	0.9781

^a Reference 4. ^b Least-squares plot of $\ln K$ vs. $1/T$.

trans isomer is consistent with a stepwise dimerization reaction. Kinetic control in a concerted cycloaddition reaction would have led to the cis isomer.

The measurements of cis/trans ratios or equilibrium constants ($K = [\text{cis}]/[\text{trans}]$) at various temperatures permit the calculation of ΔH and ΔS for the trans to cis isomerization reaction. The results of these calculations are given in Table IX. The isomerization reaction is slow on the NMR time scale, but equilibrium was clearly established in 10-15 min at all temperatures studied. The calculated enthalpy and entropy changes are small. There are no simple, consistent changes in ΔH or ΔS from the aluminum- to gallium- to indium-nitrogen compounds. For the aluminum compound, as T decreases, the concentration of the cis isomer increases. Thus, the cis isomer is thermodynamically more stable and more readily formed by the concerted π -cycloaddition reaction, but there is an increase in entropy from the cis to the trans isomer. The situation is reversed for the gallium compound. The trans isomer is more stable, but the entropy change favors the more abundant cis isomer. The $T\Delta S$ term is responsible for the predominance of the cis isomer at all temperatures studied. These conclusions suggest that the ring of the cis

isomer might be bent in solution. In the case of the indium compound, the $T\Delta S$ term is also the most important factor for the temperatures studied, but it favors the trans isomer. The cis isomer is thermodynamically more stable, apparently being better solvated by the polar solvent CH_2Cl_2 . All of the conclusions suggest that very subtle factors influence the cis/trans isomer ratio. It is obvious that no one simple factor will give a periodic trend.

In conclusion, the experimental data are consistent with the hypothesis that the aluminum-nitrogen dimer is formed by a concerted π -cycloaddition reaction. Thus, polymers are precluded by the reaction mechanism. In the case of the gallium and indium derivatives, the dimers are most likely formed from the monomers by a series of metal-nitrogen bond-forming reactions. Concerted processes are inconsistent with the experimental data. Thus, inorganic polymers are potential products in gallium- and indium-nitrogen chemistry. However, the metal-nitrogen bonds must be strong enough to overcome the negative entropy change expected for polymer formation from the simple monomer. Consequently, small molecules are observed.

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Registry No. *trans*- $[(\text{CH}_3)_2\text{Ga}(\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5))_2]$, 77590-13-7; *cis*- $[(\text{CH}_3)_2\text{Ga}(\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5))_2]$, 77646-77-6; *trans*- $[(\text{CH}_3)_2\text{In}(\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5))_2]$, 77590-14-8; *cis*- $[(\text{CH}_3)_2\text{In}(\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5))_2]$, 77646-78-7; *trans*- $[(\text{CH}_3)_2\text{Al}(\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5))_2]$, 56604-60-5; *cis*- $[(\text{CH}_3)_2\text{Al}(\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5))_2]$, 56649-31-1; $\text{Ga}(\text{CH}_3)_3$, 1445-79-0; $\text{In}(\text{CH}_3)_3$, 3385-78-2.

Supplementary Material Available: Listings of data-processing formulas and observed and calculated structure factor amplitudes for $[(\text{CH}_3)_2\text{In}(\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5))_2]$ (14 pages). Ordering information is given on any current masthead page.

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Nucleophilic Substitution Reactions of Chloro-, Iodo-, and Aquo(1,5-diamino-3-methyl-3-azapentane)platinum(II) Cations. A New Nucleophilicity Scale for Cationic Platinum(II) Complexes and a Comparison of the Leaving Group Effects of Chloride and Iodide

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The kinetics of the replacement of X from $[\text{Pt}(\text{Medien})\text{X}]^{n+}$ (Medien = 1,5-diamino-3-methyl-3-azapentane; X = Cl or I ($n = 1$), H_2O ($n = 2$)) by a variety of nucleophiles (Cl^- , Br^- , N_3^- , SCN^- , I^- , SeCN^- , $(\text{NH}_2)_2\text{CS}$, H_2O) have been studied in water at 25.0 °C. There is a good linear relationship between $\log k_2^\circ$ for the 1+ cationic substrates (k_2° is the second-order rate constant at $\mu = 0$) and $\log k_2^\circ$ for the reaction of the same nucleophile with $[\text{Pt}(\text{NH}_3)(\text{en})\text{Cl}]^+$ (en = 1,2-diaminoethane) which is taken as a standard for a new nucleophilicity scale that is appropriate to the 1+ substrates. The slopes of these plots are 1.05 and 1.15 for the replacement of chloride and iodide, respectively, but lines cross and the rate constant for the aquation of the iodo complex is smaller than that for the chloro species. The factors causing the large difference in nucleophilic discrimination are discussed. The rate constants for the displacement of water from the corresponding dicationic species do not follow a similar linear relationship, but when they are plotted against $\log k_2^\circ$ for a standard 2+ cationic substrate $[\text{Pt}(\text{dien})\text{H}_2\text{O}]^{2+}$ (dien = 1,5-diamino-3-azapentane), the linearity returns. The behavior of the Medien complex is compared with that of the corresponding dien species.

Introduction

In a recent paper³ we observed that many of the departures from a linear relationship between the n_{Pt}° value of a particular

nucleophile and $\log k_2$ for its reaction with a particular substrate could be eliminated if we used as our standard a reference substrate of the same charge type as that being investigated. For a 1+ cation we used, as reference, $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+$ (en = 1,2-diaminoethane) in its reactions of the type $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+ + \text{Y}^- \rightarrow [\text{Pt}(\text{en})(\text{NH}_3)\text{Y}]^{(2-n)+} + \text{Cl}^-$ (in water at 25 °C). In that paper we were able to investigate the cis effect (relative to NH_3) of $(\text{CH}_3)_2\text{SO}$, and we have since

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(3) Bonivento, M.; Cattalini, L.; Marangoni, G.; Michelon, G.; Schwab, A. P.; Tobe, M. L. *Inorg. Chem.* 1980, 19, 1743.

Table I. Rate Constants for the Reaction $[\text{Pt}(\text{Medien})\text{X}]^+ + \text{Y}^- \rightarrow [\text{Pt}(\text{Medien})\text{Y}]^{(2-n)+} + \text{X}^-$

Y	X = Cl			X = I		
	$10^3 k_2, \text{M}^{-1} \text{s}^{-1}$	$10^3 k_2^\circ, \text{M}^{-1} \text{s}^{-1}$	$\log k_2^\circ$	$10^3 k_2, \text{M}^{-1} \text{s}^{-1}$	$10^3 k_2^\circ, \text{M}^{-1} \text{s}^{-1}$	$\log k_2^\circ$
H_2O^b	0.001062 ± 0.000006	0.001062	-5.97	0.00238 ± 0.00004	0.00238	-6.36
Cl^-				0.173 ^c	0.46	-3.34
Br^-	1.09 ± 0.08^d	3.52	-2.45	2.10 ± 0.1	5.48	-2.26
N_3^-	1.12 ± 0.05	2.96	-2.53	2.64 ± 0.04	7.0	-2.16
I^-	48.9 ± 0.7	129	-0.89			
SCN^-	84 ± 7^e	222	-0.65	331 ± 12^f	509	-0.29
$(\text{NH}_3)_2\text{CS}$	303 ± 15	303	-0.52	451 ± 9	451	-0.35
SeCN^-	1340 ± 13^g	2350	+0.37			

^a In H_2O at 25°C and $\mu = 0.50$ (NaClO_4). ^b $k_1/55.5$. ^c Calculated from the equilibrium constant. ^d $\mu = 1.0$. ^e $\mu = 0.50$ (Na_2SO_4). ^f $\mu = 0.05$ (Na_2SO_4). ^g $\mu = 0.1$.

shown it to be generally applicable to other complexes of the type $[\text{Pt}(\text{en})\text{LCl}]^+$ ($\text{L} = (\text{CH}_3)_2\text{S},^4 (\text{C}_2\text{H}_5)_3\text{P}^5$). We also made comparisons with data taken from the literature with $[\text{Pt}(\text{dien})\text{Cl}]^+$ ($\text{dien} = 1,5\text{-diamino-3-azapentane}$), but there was not full agreement between the values reported by different authors.^{6,7}

In this paper we report the kinetics of displacement of X^- ($\text{X} = \text{Cl}, \text{I}$) from $[\text{Pt}(\text{Medien})\text{Cl}]^+$ ($\text{Medien} = 1,5\text{-diamino-3-methyl-3-azapentane}$) by a series of nucleophiles, together with the kinetics of the displacement of H_2O from the dicationic $[\text{Pt}(\text{Medien})\text{H}_2\text{O}]^{2+}$.

Experimental Section

Materials. $[\text{Pt}(\text{Medien})\text{Cl}](\text{ClO}_4)^8$ and $[\text{Pt}(\text{Medien})\text{I}]^9$ were kindly provided by Dr. G. Albertin and were recrystallized before use.

The $[\text{Pt}(\text{Medien})\text{H}_2\text{O}]^{2+}$ cation was not isolated as a solid salt, but solutions were prepared by mixing an aqueous solution of $[\text{Pt}(\text{Medien})\text{Cl}](\text{ClO}_4)$ with slightly less than 1 molar equiv of AgClO_4 and leaving the mixture to stand at room temperature for 48 h in the dark. The solution was filtered from the precipitated AgCl , acidified to pH 4 with HClO_4 , and used as stock for the subsequent kinetics.

KSeCN was used as purchased, but, because of its deliquescence, it was always handled in a drybox under an atmosphere of nitrogen. Reagent grade NaI , NaBr , KSCN , and NaN_3 were dried over P_2O_5 in a vacuum dessicator and used without further purification.

Kinetics. All the reactions were followed spectrophotometrically. Where the reaction was slow enough, preliminary repetitive scan experiments were carried out to search for isosbestic points and to choose suitable wavelengths for evaluating the kinetics. When half-life was greater than 10 s, the absorbance change at a suitable wavelength was measured as a function of time with use of either a Perkin-Elmer Coleman 575 or Cary 17 D spectrophotometer. Reactions were initiated in the usual way by mixing two prethermostated solutions containing the complex and the other reagent, respectively. For half-lives shorter than 10 s the reactions were followed with a Durrum D 110 stopped-flow spectrophotometer equipped with a Gould 05-4100 digital storage oscilloscope and a Radiometer REC 61 potentiometric recorder. Care was taken to ensure that the ionic strengths of the reagents in both syringes were the same. In all cases the entering nucleophile was present in concentrations at least 10 times greater than that of the complex in order to ensure pseudo-first-order conditions.

Results and Discussion

The spectrophotometric changes observed in repetitive scanning of the spectrum of the reaction mixture are characteristic of a single chemical change with well maintained isosbestic points throughout. The change in spectrum followed

Table II. Equilibrium Constants for $[\text{Pt}(\text{Medien})\text{I}]^+ + \text{Cl}^- \rightleftharpoons [\text{Pt}(\text{Medien})\text{Cl}]^+ + \text{I}^-$ ^{a, b}

initial amt of $[\text{Pt}(\text{Medien})\text{I}] \times 10^4, \text{M}$	initial $[\text{NaCl}]_0, \text{M}$	$A_\infty^{315 \text{ nm}}$	$10^3 K$
9.97	0.40	0.267	3.39
9.97	0.30	0.290	3.38
4.98	0.30	0.115	3.58
9.97	0.20	0.317	3.55
4.98	0.20	0.130	3.69
9.97	0.10	0.363	3.51
4.98	0.10	0.157	3.69
		av	3.54 ± 0.13

^a In H_2O at 25°C . ^b $\epsilon_{[\text{Pt}(\text{Medien})\text{I}]^+} = 448$ and $\epsilon_{[\text{Pt}(\text{Medien})\text{Cl}]^+} = 71$ at 315 nm.

first-order kinetics, and plot of $\ln(A_t - A_\infty)$ against time (A_t and A_∞ being the absorbance at a given wavelength at time t and at the end of the reaction, respectively) were linear. The slopes of these plots (k_{obsd}) were determined by a nonlinear least-squares analysis of the data. Plots of k_{obsd} against $[\text{Y}]$ were linear, and the slopes of these plots, k_2 obtained by a linear least-squares analysis of the data are collected in Table I. The experimental conditions were chosen to give maximum accuracy in the determination of k_2 , and the error in the intercept (k_1) was too great for this to provide a reliable method for its determination. Consequently k_1 was obtained from a direct study of the aquation of $[\text{Pt}(\text{Medien})\text{X}]^+$ in the presence of sufficient hydroxide to fix the product as the stable $[\text{Pt}(\text{Medien})\text{OH}]^+$. The rate of this process is independent of $[\text{OH}^-]$. This procedure is only applicable if deprotonation of the amino groups is negligible under the conditions used or the reactivity of the amido species is not considerably greater than the original substrate, as it might be in the case of octahedral cobalt(III) complexes.¹⁰ Studies of the kinetics of proton exchange in complexes of this sort^{11,12} indicate that the $\text{p}K_a$ of the most acid proton would be in excess of 15. The lack of dependence of the rate of solvolysis on the concentration of the added hydroxide at concentrations in the range of 0.001–0.05 M in both the dien complex itself⁷ and the Medien complex demonstrates that amine deprotonation does not interfere with this measurement.

In order to facilitate the comparison of the rate constants for nucleophiles of different charge type, we corrected the observed values, where necessary, for primary salt effects and values of k_2° , defined by the expression $\log k_2 = \log k_2^\circ + 1.02z_a z_b \mu^{1/2} (1 + \mu^{1/2})^{-1}$ are also collected in Table I.

Because of the unfavorable position of the equilibrium $[\text{Pt}(\text{Medien})\text{I}]^+ + \text{Cl}^- \rightleftharpoons [\text{Pt}(\text{Medien})\text{Cl}]^+ + \text{I}^-$, it was not possible

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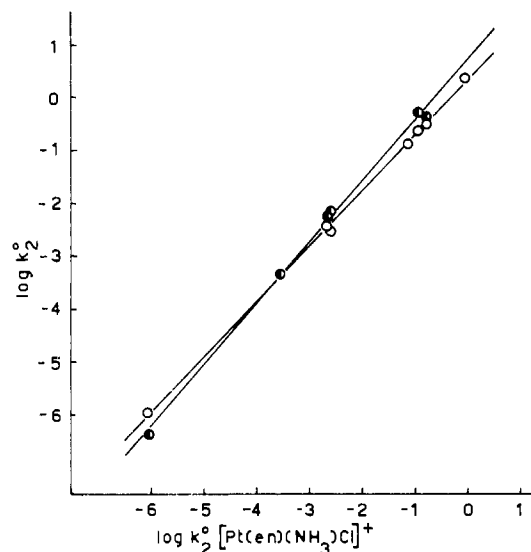


Figure 1. $\log k_2^\circ$ for the reactions of (O) $[\text{Pt}(\text{Medien})\text{Cl}]^+$ and (●) $[\text{Pt}(\text{Medien})\text{I}]^+$ plotted against $\log k_2^\circ$ for the reactions of $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+$.

to study the entry of chloride into the iodo complex under conditions where the reaction goes to completion. The equilibrium constant K was therefore determined directly by allowing solutions of $[\text{Pt}(\text{Medien})\text{I}]\text{I}$ and excess NaCl to come to equilibrium and then analyzing them spectrophotometrically with use of the expression $K = (C_0 - x)(2C_0 - x)/x[\text{Cl}^-]$, where $x = A - C_0\epsilon_2/\epsilon_1 - \epsilon_2$, A = absorbance at 315 nm using 10 mm cells, C_0 is the initial concentration of $[\text{Pt}(\text{Medien})\text{I}]\text{I}$, ϵ_1 and ϵ_2 are molar extinction coefficients of the iodo and the chloro cation, and $[\text{Cl}^-]$ is the initial concentration of NaCl . The information is reported in Table II. The value for $k_2^\circ(\text{Cl}^-)$ for entry of chloride into the iodo complex was then obtained from the relationship, $K = k_2^\circ(\text{Cl}^-)/k_2^\circ(\text{I}^-)$ where $k_2^\circ(\text{I}^-)$ is the second-order rate constant for entry of iodide into the chloro complex.

Plotting the values of $\log k_2^\circ$ in Table I against the corresponding values of $\log k_2^\circ$ for the standard 1^+ substrate $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+$ gives two good straight lines for the $[\text{Pt}(\text{Medien})\text{Cl}]^+$ and $[\text{Pt}(\text{Medien})\text{I}]^+$ complexes, respectively (Figure 1). It will be seen that the biphilic nucleophiles, especially thiourea, which do not lie on any line relating $\log k_2^\circ$ for these cationic complexes to n_{Pt}° , fit nicely on the line in Figure 1 which indicates that the π contribution of thiourea remains fairly constant in the rate-determining transition state of the substitution reactions of all the 1^+ cationic systems studied. It is of interest to note that, while the solvolysis of the $[\text{Pt}(\text{Medien})\text{I}]^+$ complex is slower than that of the chloro complex, most of the other displacements of iodide are faster than the displacement of chloride. This is the result of the significantly greater nucleophilic discrimination of the iodo complex (slope 1.15) as compared to that of the chloro complex (slope 1.05) and points out, once again, the danger of discussing relative reactivities without reference to the entering nucleophile.

Although we have a value for k_2° for the entry of Cl^- into $[\text{Pt}(\text{Medien})\text{I}]^+$, there is not data for the chloride exchange of $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+$ and so we cannot assign a nucleophilicity to Cl^- on our nucleophilicity scale. Nevertheless since the halide ions do not appear to show any biphilicity, we have assumed that the relative positions of these halides in any nucleophilicity scale will remain quantitatively the same. The point for chloride ($n_{\text{Pt}}^\circ = -3.53$) is therefore determined on this basis, and while (because of their speculative nature) these data are not included in the determination of the best-fit straight line, it is satisfying to see that the point lies very close

to it. These results can be compared to the values already in the literature for the structurally similar $[\text{Pt}(\text{dien})\text{X}]^+$ complexes.^{6,7} In searching for a consistent set of data we have to overcome the problem that, whereas Gray took particular care to obtain a precise value for k_1 by studying the solvolysis of $[\text{Pt}(\text{dien})\text{Cl}]^+$ in the presence of hydroxide, he did not maintain constant ionic strength in the other reactions, and so his values of k_2 (which do not agree with those of Belluco et al.⁹) are less reliable than those of the latter group, who did maintain constant ionic strength. However, the second group did not measure k_1 directly. We therefore combine the values of k_1 reported by Gray with those of k_2 of Belluco et al. In order to facilitate the comparison, we have estimated the values at 25 °C from the published data at 30 °C using the enthalpies of activation reported and then corrected for primary salt effects.¹³

An attempt was made to examine the leaving group effect in terms of the slopes of the plot of $\log k_2$ vs. n_{Pt}° ,¹⁴ but such a treatment is spoiled by the presence of the biphilic reagents in the sequence of nucleophiles examined. Plotting the data for $[\text{Pt}(\text{dien})\text{X}]^+$ against the cationic standard gives good linear relationships, and the slopes are essentially the same as those observed for $[\text{Pt}(\text{Medien})\text{X}]^+$ complexes. Nevertheless the dien complexes appear to be systematically somewhat more reactive than those of the analogous $[\text{Pt}(\text{Medien})\text{X}]^+$ complexes. The effect is small but probably outside the limits of the experimental error and may be ascribed to the greater inductive effect of the methyl substituent which, pushing charge toward the platinum, slightly reduces its electrophilicity. However, the change from H to CH_3 also will change the rigidity of the tridentate ligand and even the nature of the solvation about the middle nitrogens. These effects could also be sufficient to lead to the changes of the magnitude observed. It now appears that in the substitution reactions of the platinum(II) complexes two types of behavior can be observed in connection with the relationship between the nucleophilic discrimination factor and the nature of the leaving group. At the one extreme, for example, in the reactions of $[\text{Pt}(\text{bpy})(\text{NO}_2)\text{X}]$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{NO}_2, \text{N}_3$; $\text{bpy} = 2,2'$ -bipyridyl) in methanol at 30 °C,¹⁵ it was found that the slopes of all the plots of $\log k_2$ vs. n_{Pt}° were parallel (slopes between 0.87 and 0.94) even though for any particular nucleophile the reactivities cover a range of 3 orders of magnitude. Similar effects are noted for *trans*- $[\text{Pt}(\text{pip})_2(\text{NO}_2)\text{X}]$ ($\text{pip} = \text{piperidine}$).¹⁶ On the other hand, in the case of $[\text{Pt}(\text{dien})\text{X}]^+$ reported briefly by Belluco¹⁴ and confirmed with the cationic nucleophilicity scale plot and $[\text{Pt}(\text{Medien})\text{X}]^+$, the leaving group effect is characterized by a change in the nucleophilic discrimination ability of the substrate. It has been suggested that a lack of dependence of nucleophilic discrimination upon the nature of the leaving group is a sign that the bond-making and bond-breaking transition states are separated by a relatively deep potential well representing the 5-coordinated intermediate and a fully developed A mechanism and that as the depth of this well decreases, i.e., the process becoming less asynchronous (i.e., develops more I_d character) the leaving group has more influence on the nucleophilic discrimination until, in the limit as found in the reactions of $[\text{AuCl}_3(\text{am})]^{17}$ even the sequence of nucleophilicity was dependent upon the nature of the leaving group. If the extent to which the p_z orbital is brought into the bonding scheme to develop five equivalent bonds depends upon the effective nuclear charge on the central atom,¹⁸ it is

(13) The latter correction was unfortunately omitted from the data discussed in ref 3.

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Table III. Rate Constants for the Reaction $[\text{Pt}(\text{Medien})\text{H}_2\text{O}]^{2+} + \text{Y}^{n-} \rightarrow [\text{Pt}(\text{Medien})\text{Y}]^{(2-n)+} + \text{H}_2\text{O}^a$

Y	$k_2, \text{M}^{-1} \text{s}^{-1}$	$k_2^\circ, \text{M}^{-1} \text{s}^{-1}$	$\log k_2^\circ$	[Pt(dien)H ₂ O] ²⁺		$k_2^\circ(\text{dien})/k_2^\circ(\text{Medien})^d$
				$\log k_2^\circ, ^b$	$k_2^\circ, ^c \text{M}^{-1} \text{s}^{-1}$	
Cl ⁻	0.336 ± 0.004	1.04	0.02	0.29	1.44	1.4
Br ⁻	1.98 ± 0.03	6.1	0.79	1.16	10.7	1.8
(NH ₂) ₂ CS	23 ± 2.6	23	1.36	1.61	30.7	1.3
SCN ⁻	31.7 ± 0.3	98	1.99	2.23	125	1.3
I ⁻	57 ± 2.9	176	2.25	2.40	185	1.1

^a In H₂O at 25 °C, $\mu = 0.1$ (NaClO₄), pH 4 (HClO₄). ^b Data from ref 19 at 30 °C in H₂O. ^c Extrapolated to 25 °C with use of $\Delta H^\ddagger = 10$ kcal/mol. ^d Ratio of k_2° for [Pt(dien)H₂O]²⁺: [Pt(Medien)H₂O]²⁺ at 25 °C.

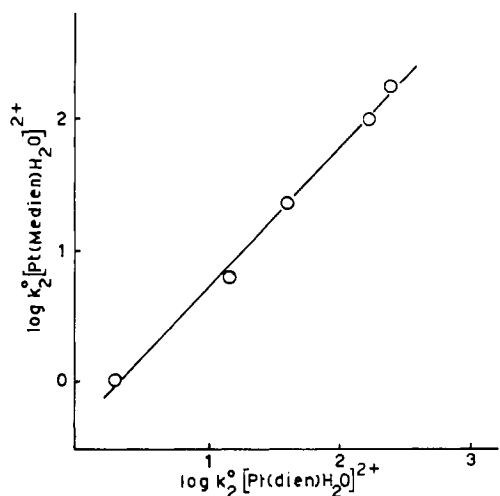


Figure 2. $\log k_2^\circ$ for $[\text{Pt}(\text{Medien})\text{H}_2\text{O}]^{2+} + \text{Y}^{n-} \rightarrow [\text{Pt}(\text{Medien})\text{Y}]^{(2-n)+} + \text{H}_2\text{O}$ at 25 °C in water plotted against data for analogous reactions of $[\text{Pt}(\text{dien})\text{H}_2\text{O}]^{2+}$ in water at 30 °C.¹⁹

not unreasonable to believe that the reactions of the cationic Pt complexes have more I_d character than those of the neutral ones and that this is reflected in the dependence of the nucleophilic discrimination upon the nature of the leaving group.

The reactions of the dicationic $[\text{Pt}(\text{Medien})\text{H}_2\text{O}]^{2+}$ species are, as expected, considerably faster than those involving the displacement of chloride and iodide. The most important observation is that thiourea, and to a smaller extent SCN⁻, are less reactive than predicted by the nucleophilicity with respect to the 1+ cation. This has been noted by Romeo in his recent definitive study of the substitution reactions of $[\text{Pt}(\text{dien})\text{H}_2\text{O}]^{2+}$,¹⁹ and it is clear that the biphilic contribution

of thiourea is not exhausted in the 1+ cation. Using Romeo's values for the $\log k_2^\circ$ at 30 °C in water as a standard for the 2+ cation, we found a reasonably good linear relationship between $\log k_2^\circ$ for reactions of $[\text{Pt}(\text{Medien})\text{H}_2\text{O}]^{2+}$ and $\log k_2^\circ$ for the standard at 30 °C (Figure 2). The value of $\log k_2^\circ$ for entry of chloride was determined from the relationship $K = k_1^a k_{-1}^b / k_1^b k_{-1}^a$, where K is the measured equilibrium constant for the reaction $[\text{Pt}(\text{Medien})\text{I}]^+ + \text{Cl}^- \rightleftharpoons [\text{Pt}(\text{Medien})\text{Cl}]^+ + \text{I}^-$, k_1^a and k_1^b are the solvolytic rate constants for the iodo and chloro complexes, k_{-1}^a is the rate constant for the replacement of water by iodide, and k_{-1}^b is the required rate constant for the replacement of water by chloride.

The slope of the line in Figure 2 is 1.05 ± 0.04 , but the range covered by the nucleophiles used is somewhat smaller, and so it is not possible to determine the slope with sufficient accuracy to comment on whether the departure from 1.00 is significant. For reaction with any specific nucleophile the Medien complex is somewhat more reactive (see Table III) than the dien analogue, repeating the behavior observed for the chloro and iodo species.

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Registry No. [Pt(Medien)Cl]⁺, 59538-45-3; [Pt(Medien)I]⁺, 77507-83-6; [Pt(Medien)H₂O]²⁺, 77507-84-7; H₂O, 7732-18-5; Cl⁻, 16887-00-6; Br⁻, 24959-67-9; N₃⁻, 14343-69-2; I⁻, 20461-54-5; SCN⁻, 302-04-5; (NH₂)₂CS, 62-56-6; SeCN⁻, 5749-48-4.

Supplementary Material Available: A listing of k_{obsd} values as a function of $[\text{Y}^{n-}]$ (2 pages). Ordering information is given on any current masthead page.

(18) (a) Nyholm, R. S. *Proc. Chem. Soc.* **1961**, 273. (b) Nyholm, R. S.; Tobe, M. L. *Experimentia, Suppl.* **1965**, No. 9, 112.

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