for $Ni_2C_{27}H_{54}S_{12}B_4F_{16}$: C, 26.41; H, 4.43; S, 31.33; Ni, 9.56. Found: C, 26.58; H, 4.35; S, 31.19; Ni, 9.92.

Preparation of $Ni_2(TTC)_3(BF_4)_4$.—To 0.43 g (1.39 mmol) of $Ni(BF_4)_2 \cdot 6H_2O$ in 10 ml of anhydrous nitromethane was added 0.87 g (8.55 mmol) of acetic anhydride. The mixture was stirred until the solid had dissolved, and then 0.50 g (2.08 mmol) of 1,4,7,10-tetrathiacyclododecane was added all at once. The solution immediately changed from green to blue. The mixture was allowed to stir for 0.5 hr and was then filtered into 100 ml of anhydrous ether. The blue precipitate was filtered, washed with ether, and dried *in vacuo*. This blue precipitate was placed in a Soxhlet extraction thimble and was extracted with 100 ml of dry acetone for a few hours. The volume of the resulting blue solution was reduced to approximately one-fourth and the complex was then precipitated with anhydrous ether. The blue solid was filtered, washed with ether, and dried *in vacuo;* yield, 0.71 g (84%). *Anal.* Calcd for $Ni_2C_{24}H_{48}S_{12}B_4F_{16}$: C, 24.30; H, 4.08; S, 32.44; Ni, 9.90. Found: C, 24.32; H, 3.74; S, 32.42; Ni, 9.99.

Preparation of $Ni(TTD)_2(BF_4)_2$.—To 245 mg (0.72 mmol) of $Ni(BF_4)_2 \cdot 6H_2O$ in 10 ml of dry nitromethane was added 440 mg of acetic anhydride. After the solid had dissolved 317 mg (1.43 mmol) of 1,5,9-trithiacyclododecane was added with stirring and the green color immediately turned to a red-brown. After stirring for 20 min the solution was filtered into 75 ml of anhydrous ether, and the precipitate which formed was filtered, washed with 100 ml of ether, and dried *in vacuo;* yield, 0.31 g (69%). *Anal.* Calcd for $NiC_{18}H_{36}S_6B_2F_8$: C, 31.93; H, 5.36; S, 28.41; Ni, 8.67. Found: C, 31.27; H, 4.98; S, 28.76; Ni, 8.28.

Preparation of $Ni(DTH)_3(BF_4)_2$.—This compound was prepared in an analogous way to that above in 85% yield, using the hexaacetic acid derivative of $Ni(BF_4)_2$ and 2,5-dithiahexane in nitromethane.

Acknowledgment.—We are indebted to the National Institutes of Health of the U. S. Public Health Service for support under Grant GM-10040 and Fellowship No. 5 FO2GM 28951-02. We also wish to thank Mr. Kent Travis for technical assistance and Dr. Howard D. Johnson, II, for running the ^{11}B nmr spectrum for us.

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Solvent Effects in Platinum(II)-Catalyzed Substitution Reactions of Platinum(IV) Complexes

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The rate of replacement of chloride ions in *trans*-$Pt(en)(NO_2)_2Cl_2$ and *trans*-$Pt(dien)NH_3Cl_2^{2+}$ by bromide ions has been studied in water, water–methanol, and water–dioxane solutions. The reaction rates are quite sensitive to solvent composition and increase in the case of the cationic complex and decrease in the case of $Pt(en)(NO_2)_2Cl_2$ as the solvent polarity is lowered. The reactions are catalyzed by the appropriate platinum(II) complex and a first-order rate dependence on catalyst was observed in all solvents used.

Introduction

A probable mechanism for a wide variety of substitution reactions of platinum(IV) complexes is presented in eq 1–3.[1] The mechanism is illustrated in terms

$$\mathrm{Pt(II)} + \mathrm{Br}^- \rightleftharpoons \mathrm{Pt(II)}\cdots\mathrm{Br}^- \qquad (1)$$

$$\mathrm{Cl{-}Pt^{IV}{-}Cl} + \mathrm{Pt(II)}\cdots\mathrm{Br}^- \longrightarrow \mathrm{Cl}\cdots\mathrm{Pt}\cdots\mathrm{Cl}\cdots\mathrm{Pt}\cdots\mathrm{Br}^- \qquad (2)$$

$$\mathrm{Cl}\cdots\mathrm{Pt}\cdots\mathrm{Cl}\cdots\mathrm{Pt}\cdots\mathrm{Br}^- \longrightarrow \mathrm{Cl}^- + \mathrm{Pt(II)} + \mathrm{Cl{-}Pt^{IV}{-}Br} \qquad (3)$$

of the reactions reported in this paper with the ligands in the platinum(II) complex and those *cis* to the reactive *trans*-dihalo axis of the platinum(IV) complex omitted for the sake of simplicity and generality.

No direct evidence for the intermediate postulated in step 1 has been presented for ammonia complexes. However, such species are known in both solution and solid states when the ligands in the square plane are good π acceptors.[2-4] It is possible that there are other preequilibria, for example, one involving association of the platinum(IV) and platinum(II) complexes. Since a variety of kinetic work in aqueous solution has failed to provide direct evidence for intermediates in reactions of ammonia complexes, it seemed appropriate to look for evidence in less polar solutions. If an appreciable fraction of the platinum(II) catalyst became associated with either bromide ion or the platinum(IV) complex, the rate law would deviate from the simple third-order behavior normally observed.

Although some rate studies on substitution reactions of platinum(IV) complexes have been made in nonaqueous solution (for example see ref 4), we are not aware of any in which a given reaction was studied in more than one solvent. This article provides such information on solvent effects in platinum(II)-catalyzed reactions of platinum(IV) complexes.

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(1) S. G. Bailey and R. C. Johnson, *Inorg. Chem.*, **8**, 2596 (1969), and references therein.

(2) C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960).

(3) A. D. Westland, *ibid.*, 3060 (1965).

(4) A. Peloso and G. Dolcetti, *Coord. Chem. Rev.*, **1**, 100 (1966).

TABLE I

RATE DATA

$$\textit{trans}\text{-}Pt(en)(NO_2)_2Cl_2 + Br^- \longrightarrow \textit{trans}\text{-}Pt(en)(NO_2)_2ClBr + Cl^-$$

$10^4[Pt(en)(NO_2)_2]$, M	$10^4 k_{obsd}$, sec^{-1}	k_3, M^{-2} sec^{-1}
	25.0° [a]	
0.25	4.4^{b}	176
0.50	8.0^{b}	160
1.00	15.7^{b}	157
1.00	8.3	166
1.00	4.5^{c}	180
1.00	$4.7^{c,d}$	192
1.00	$4.1^{c,e}$	164
	25.0° [f]	
0.50	1.28	25.6
1.00	2.56	25.6
2.00	5.2	26.0
2.00	2.56^{g}	25.6
2.00	1.23^{h}	24.6
2.00	1.35^{i}	27.0
	25.0° [j]	
0.25	0.123	4.7
0.50	0.22	4.4
1.00	0.44	4.4
	25.0° [m]	
0.50	0.23	4.6
1.00	0.48	4.8
2.00	1.04	5.2
	35.0° [a]	
0.25	3.3	264
0.50	5.9	236
1.00	10.9	218
	45.0° [a]	
0.25	4.1	328
0.50	8.5	340
1.00	16.7	334
	35.0° [f]	
0.50	2.0	40
1.00	3.6	36
2.00	7.4	37
	45.0° [f]	
0.50	2.7	54
1.00	4.9	49
2.00	9.8	49
	25.0° [j]	
1.00	0.20^{k}	4.0
1.00	0.116^{l}	4.6
	25.0° [m]	
2.00	0.50^{n}	5.0
2.00	0.22^{o}	4.4
2.00	0.24^{p}	4.8

[a] Solvent H_2O, $[Pt(en)(NO_2)_2Cl_2] = 5.0 \times 10^{-5}\ M$, $\mu = 0.10$, $[H^+] = 1.0 \times 10^{-3}\ M$, $[Br^-] = 0.050\ M$. [b] $[Br^-] = 0.100\ M$. [c] $[Br^-] = 0.025\ M$. [d] $[H^+] = 0.075\ M$. [e] $\mu = 0.025$. [f] Solvent 50% methanol–water by volume, $[Pt(en)(NO_2)_2Cl_2] = 5.0 \times 10^{-5}\ M$, $\mu = 0.10$, $[Br^-] = 0.10\ M$. [g] $[Br^-] = 0.050\ M$. [h] $[Br^-] = 0.025\ M$. [i] $[Br^-] = 0.025\ M$, $\mu = 0.025$. [j] Solvent 89% methanol–water by volume, $[Pt(en)(NO_2)_2] = 5.0 \times 10^{-5}\ M$, $[Br^-] = 0.10\ M$, $\mu = 0.10$. [k] $[Br^-] = 0.050\ M$, $\mu = 0.050$. [l] $[Br^-] = 0.025\ M$, $\mu = 0.025$. [m] Solvent 50% dioxane–water by volume, $[Pt(en)(NO_2)_2Cl_2] = 5.0 \times 10^{-5}\ M$, $[Br^-] = 0.10\ M$, $\mu = 0.10\ M$. [n] $[Br^-] = 0.050\ M$. [o] $[Br^-] = 0.025\ M$. [p] $[Br^-] = 0.025\ M$, $\mu = 0.025$.

Results and Discussion

Reactions 4 and 5 were chosen for study since the

$$\textit{trans}\text{-}Pt(en)(NO_2)_2Cl_2 + 2Br^- \longrightarrow \textit{trans}\text{-}Pt(en)(NO_2)_2Br_2 + 2Cl^- \quad (4)$$

$$\textit{trans}\text{-}Pt(dien)NH_3Cl_2^{2+} + 2Br^- \longrightarrow \textit{trans}\text{-}Pt(dien)NH_3Br_2^{2+} + 2Cl^- \quad (5)$$

complexes are relatively soluble in nonpolar solvents, illustrate two different charge types, and react cleanly, and the reactions are similar to those we have previously studied (en = ethylenediamine and dien = diethylenetriamine). On the basis of previous work it can be assumed that the rate-determining step in these reactions is the replacement of the first chloride, and this is proved by some limited rate studies on the reverse reactions cited later.

The kinetic behavior of reaction 4 was studied in water, water–methanol (50:50 and 11:89 by volume), and water–dioxane (50:50) solutions. The rate data are presented in Table I. The activation parameters in water are $\Delta H^* = 5.8 \pm 0.2$ kcal/mol and $\Delta S^* = -29.0 \pm 0.5$ cal/mol deg. In 50% methanol they are $\Delta H^* = 5.9 \pm 0.7$ kcal/mol and $\Delta S^* = -32 \pm 2$ cal/mol deg. The reaction exhibited third-order kinetics in all four solvents; the rate law is presented in eq 6. The

$$-d[Pt(en)(NO_2)_2Cl_2]/dt = k[Pt(en)(NO_2)_2Cl_2][Pt(en)(NO_2)_2][Br^-] \quad (6)$$

reaction rates were insensitive to changes in ionic strength over the range 0.025–0.10 M and to $[H^+]$ over the range 0.001–0.075 M. The reaction slowed down markedly as the concentration of nonaqueous solvent was increased. An attempt was made to study this reaction at 35 and 45° in 50% dioxane, but it was found that $Pt(en)(NO_2)_2Cl_2$ decomposes at a significant rate under these conditions.

The kinetic behavior of reaction 5 was studied in water and water–methanol (10:90 and 1:99 by volume) solutions. The data in aqueous solution are consistent with rate law 7. The k_3 term corresponds to the nor-

$$-d[Pt(dien)NH_3Cl_2^{2+}]/dt = (k_3 + k_4[Br^-]) \times [Pt(dien)NH_3Cl_2^{2+}][Pt(dien)NH_3^{2+}][Br^-] \quad (7)$$

mal platinum(II)-catalyzed mechanism. The fourth-order term may be due to reaction of $Pt(dien)NH_3Cl_2^{2+},Br^-$ ion pairs. A second-order dependence on entering halide has been reported for one related reaction (eq 8) and this was attributed to $Pt(NH_3)_4(SCN)_2^{2+},Cl^-$ ion pairs.[5] Ion pairs have been reported

$$\textit{trans}\text{-}Pt(NH_3)_4(SCN)_2^{2+} + Cl^- \longrightarrow \textit{trans}\text{-}Pt(NH_3)_4(SCN)Cl^{2+} + SCN^- \quad (8)$$

in other related systems, *trans*-$Pt(en)_2Cl_2^{2+},Cl^-$ and *trans*-$Pt(en)_2Br_2^{2+},Br^-$.[6] The form of the rate law in the methanol solutions is probably also like (7). The reaction is definitely first order in $Pt(dien)NH_3Cl_2^{2+}$ and $Pt(dien)NH_3^{2+}$. There is some uncertainty about the $[Br^-]$ dependence in the methanol solutions, since changing $[Br^-]$ also changes the ionic strength. It is not certain that replacement of NaBr with $NaBF_4$ does not produce specific ion effects. Increases in ionic strength cause increases in reaction rate in both water and methanol solutions. This is consistent with data on related systems and is expected for reactions of this charge type. The activation parameters for the k_3 term are $\Delta H^* = 4.2 \pm 0.8$ kcal/mol and $\Delta S^* = -33 \pm 2$ cal/mol deg. For the k_4 term they are $\Delta H^* = 5.9 \pm 0.7$ kcal/mol and $\Delta S^* = -24 \pm 2$ cal/mol deg. Activation parameters for the nonaqueous reaction were not determined due to the problems associated with rate law and ionic strength.

A few kinetic studies were carried out on the reverse of reaction 4 and on reactions 9 and 10. These studies

$$\textit{trans}\text{-}Pt(en)(NO_2)_2Br_2 + Cl^- \longrightarrow \textit{trans}\text{-}Pt(en)(NO_2)_2BrCl + Br^- \quad (9)$$

$$\textit{trans}\text{-}Pt(dien)NH_3Br_2^{2+} + Cl^- \longrightarrow \textit{trans}\text{-}Pt(dien)NH_3BrCl + Br^- \quad (10)$$

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[5] W. R. Mason, E. R. Berger, and R. C. Johnson, *Inorg. Chem.*, **6**, 248 (1967).

[6] A. J. Poë, *J. Chem. Soc.*, 183 (1963).

TABLE II

RATE DATA

trans-$Pt(dien)NH_3Cl_2^{2+} + Br^- \longrightarrow$ *trans*-$Pt(dien)NH_3ClBr^{2+} + Cl^-$

10^5[Pt-(dien)-NH_3^{2+}], M	[Br^-], M	10^3k_{obsd}, sec^{-1}
25.0° [a,c]		
2.5	0.100	1.20
5.0	0.100	2.4
10.0	0.100	4.6
5.0	0.050	0.97
5.0	0.025	0.43
5.0	0.025[b]	0.35
35.0° [a,d]		
1.25	0.100	0.84
2.5	0.100	1.70

10^5[Pt-(dien)-NH_3^{2+}], M	[Br^-], M	10^3k_{obsd}, sec^{-1}
35.0° [a,d]		
5.0	0.100	3.3
5.0	0.050	1.37
5.0	0.025	0.58
45.0° [a,e]		
1.25	0.100	1.10
2.5	0.100	2.2
5.0	0.100	4.2
5.0	0.050	1.68
5.0	0.025	0.73

[Br^-], M	μ	10^3k_{obsd}, sec^{-1}
25.0° [f]		
0.050	0.050	69
0.025	0.050	32
0.025	0.025	22

[Br^-], M	μ	10^3k_{obsd}, sec^{-1}
25.0° [f]		
0.0125	0.0375	8.4
0.0125	0.025	7.8
0.0125	0.0125	7.1

10^6[Pt(dien)-NH_3^{2+}], M	[Br^-], M	10^3k_{obsd}, sec^{-1}
25.0° [g]		
0.63	0.100	2.0
1.25	0.100	4.0
2.50	0.100	8.6
5.00	0.100	18.0
1.25	0.050	2.1
1.25	0.025	1.00

10^6[Pt(dien)-NH_3^{2+}], M	[Br^-], M	10^3k_{obsd}, sec^{-1}
35.0° [g]		
0.50	0.100	2.8
1.00	0.100	5.9
2.00	0.100	11.0
45.0° [g]		
0.50	0.100	3.7
1.00	0.100	7.4
2.00	0.100	14.9

[a] Solvent water, [$Pt(dien)NH_3Cl_2^{2+}$] = 2.00×10^{-5} M, μ = 0.10. [b] $\mu = 0.025$. [c] $k_3 = 3.0 \times 10^2$ M^{-2} sec^{-1}, $k_4 = 1.7 \times 10^3$ M^{-3} sec^{-1}. [d] $k_3 = 4.1 \times 10^2$ M^{-2} sec^{-1}, $k_4 = 2.5 \times 10^3$ M^{-3} sec^{-1}. [e] $k_3 = 5.0 \times 10^2$ M^{-2} sec^{-1}, $k_4 = 3.4 \times 10^3$ M^{-3} sec^{-1}. [f] Solvent 90% methanol–water by volume, [$Pt(dien)NH_3Cl_2^{2+}$] = 2.00×10^{-5} M; ionic strength was maintained with $NaBF_4$ which is only sparingly soluble in this solvent. $NaClO_4$ oxidizes $Pt(en)(NO_2)_2$ in this solvent. [g] Solvent 99% methanol–water by volume, [$Pt(dien)NH_3Cl_2^{2+}$] = 2.00×10^{-5} M, μ = [Br^-].

which are presented in Table III indicate that the solvent effects are similar for the forward and reverse reactions. The observed rate constants are about those which one would predict on the basis of previous studies on the effect on rate of changing, entering, leaving, or bridging groups.

The rates of both reactions 4 and 5 are very sensitive to the nature of the solvent. For reaction 4 the rate decreased and for reaction 5 the rate increased as the solution was made less polar. For some reactions linear relationships between the logarithm of the rate constants and the inverse of the solvent dielectric constant have been demonstrated.[7] This is not true for either of these reactions.

TABLE III

RATE DATA AT 25.0°

10^4[Pt(II)], M	Solvent	[Cl^-], M	10^4k_{obsd},[a] sec^{-1}	$10^{-2}k_3$, M^{-2} sec^{-1}
trans-$Pt(en)(NO_2)_2BrCl + Cl^- \longrightarrow$ *trans*-$Pt(en)(NO_2)_2Cl_2 + Br^-$				
1.00[b]	H_2O	0.100	0.88	0.088
1.00[b]	50% CH_3OH	0.100	0.20	0.020
trans-$Pt(en)(NO_2)_2Br_2 + Cl^- \longrightarrow$ *trans*-$Pt(en)(NO_2)_2BrCl + Br^-$				
0.050[b]	H_2O	0.0050	2.1	84
0.050[b]	50% CH_3OH	0.0050	0.32	12.8
trans-$Pt(dien)NH_3Br_2^{2+} + Cl^- \longrightarrow$ *trans*-$Pt(dien)NH_3BrCl^{2+} + Br^-$				
0.040[c]	H_2O	0.0025	1.40	140
0.010[c]	100% CH_3OH	0.00125	5.3	4200

[a] μ = [Cl^-], [$Pt(en)(NO_2)_2Br_2$] = 5.0×10^{-5} M, [$Pt(dien)NH_3Br_2^{2+}$] = 2.0×10^{-5} M. [b] Pt(II) = $Pt(en)(NO_2)_2$. [c] Pt(II) = $Pt(dien)NH_3^{2+}$.

The direction of the rate changes can be rationalized in terms of theories on solvent effects. Amis[8] stated that the rates of reactions between uncharged molecules and anions decrease as the solvent dielectric constant decreases. This could account for the solvent effects on reaction 4. For reaction 5 the preequilibrium association (eq 1) of a +2 and a −1 ion should be enhanced by a solvent of low dielectric constant. The postulated subsequent reaction between two positively charged ions, however, should be retarded under the same circumstances. If the proposed mechanism is correct, the observed marked rate enhancement in the nonpolar solvents suggests appreciably enhanced association in step 1.

The intent of this research was to find direct evidence for reaction intermediates in platinum(II)-catalyzed substitution reactions of platinum(IV)–amine complexes. No such direct evidence was obtained. Rate enhancement for reaction 5 in nonpolar solvents may be attributed to greater association between platinum(II) catalyst and bromide ion; however, even at 0.10 M bromide concentration in 99% methanol no appreciable fraction of platinum(II) is associated on the basis of the observed rate law. The results for reaction 4 suggest that association between $Pt(en)(NO_2)_2$ and bromide ion is actually reduced in solvents less polar than pure water.

Experimental Section

Preparation of Compounds.—Potassium tetrachloroplatinate(II)[9] and $Pt(en)Cl_2$[10] were prepared by published procedures. Diethylenetriamine complexes of platinum were obtained from Bailey.[1] The procedures used for preparing the dinitroethylenediamineplatinum compounds are modifications of those in the literature. Other materials used were reagent grade.

Dinitroethylenediamineplatinum(II) was prepared by adding solid $NaNO_2$ (0.30 g, 4.4 mmol) to 130 ml of a hot aqueous solution of 0.48 g (1.5 mmol) of $Pt(en)Cl_2$ and heating for 15 min. Cooling produces white crystals which were recrystallized from hot water and vacuum dried. The yield was 0.31 g (60%). *Anal.* Calcd for $Pt(C_2N_2H_8)(NO_2)_2$: Pt, 56.20. Found: Pt, 56.36.

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(7) E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press, New York, N. Y., 1966, pp 1–8.

(8) E. S. Amis, ref 7, p 40.

(9) W. E. Cooley and D. H. Busch, *Inorg. Syn.*, **5**, 208 (1957).

(10) F. Basolo, J. C. Bailar, Jr., and A. R. Tarr, *J. Am. Chem. Soc.*, **72**, 2433 (1950).

trans-Dichlorodinitroethylenediamineplatinum(IV) was prepared by passing Cl_2 gas for 2 hr through a suspension of 0.51 g (1.5 mmol) of $Pt(en)(NO_2)_2$ in 5 ml of water. The yellow crystals which formed were recrystallized from hot, very dilute hydrochloric acid and vacuum dried. The yield was 0.40 g (65%). *Anal.* Calcd for $Pt(C_2N_2H_8)(NO_2)_2Cl_2$: Pt, 46.66; Cl, 16.98. Found: Pt, 46.65; Cl, 16.77.

trans-Dibromodinitroethylenediamineplatinum(IV) was prepared by repeatedly contacting a 0.51-g (1.5-mmol) sample of $Pt(en)(NO_2)_2$ with 10 ml of an aqueous solution containing 1 drop of HBr (48%) which was kept saturated with bromine. The yellow crystalline product was recrystallized from a very dilute HBr solution and vacuum dried. The yield was 0.40 g (50%). *Anal.* Calcd for $Pt(C_2N_2H_8)(NO_2)_2Br_2$: Pt, 38.46; Br, 31.56. Found: Pt, 38.29; Br, 32.28. Platinum analyses were done by ignition; halide analyses, by a modified Volhard titration procedure.

Kinetic Measurements.—Kinetics were followed spectrophotometrically on a Beckman DU spectrophotometer modified with a Gilford 220 absorbance indicator. The cell compartment was thermostated to better than ±0.02°. The reactions were studied under pseudo-first-order conditions by using at least a 50:1 excess of entering anion. Unless otherwise indicated the ionic strength of the solutions was maintained with $NaClO_4$. Perchloric acid was used to adjust solution acidity. Bromide ion was provided as NaBr except in 90 and 99% methanol solution where $N(C_2H_5)_4Br$ was used. Chloride ion was provided as NaCl except in the runs in pure methanol where $N(C_2H_5)_4Cl$ was used. Fresh platinum(II) and -(IV) solutions were prepared each day kinetics were run. In many cases duplicate kinetic runs were carried out and average values are reported in Tables I–III. Duplicate runs reproduced quite well with deviations seldom being greater than ±3%. Infinite-time absorbances on kinetic solutions were consistent with those expected from the spectra of the reaction products.

The reactions were studied at wavelengths at which large absorbance changes were observed. In most cases the very intense ultraviolet maximum of the *trans*-dibromo compounds was used. Reaction 4 was studied at 233 mμ except for the dioxane solutions which were studied at 250 mμ. Reaction 9 was studied at 235 mμ and the reverse of reaction 4 was studied at 226 mμ, an isosbestic point for *trans*-$Pt(en)(NO_2)_2Br_2$ and *trans*-$Pt(en)(NO_2)_2ClBr$.

Rate data were analyzed by a Gauss–Newton nonlinear least-squares fit to the equation $A = A_0 + (A_0 - A_\infty)\exp(-kt)$. Absorbance *vs.* time data covering 4 half-lives were in general used and the fit to the equation was in general within the uncertainty of the absorbance measurements.

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Complexes of Thiazoles. I. Zinc(II), Cobalt(II), Copper(II), Nickel(II), and Platinum(II) Derivatives of Alkyl-Substituted Thiazoles

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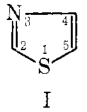
Nineteen complexes of 4- and 2,4-dialkyl-substituted thiazoles with copper(II), nickel(II), cobalt(II), zinc(II), and platinum(II) containing various anions have been synthesized and are generally of the form MX_2L_2. The electronic and far-infrared spectra and the temperature dependence of the magnetic moments are reported. All of the zinc and cobalt derivatives are tetrahedral, the 4-methyl copper and nickel species are octahedral, while the dialkyl complexes of copper and nickel, as well as the platinum complexes, are square planar. The four-coordinate dialkyl complexes follow the crystal field stabilization energy predictions as to the relative tendency to form tetrahedral as opposed to square-planar forms *i.e.*, Zn > Co > Cu > Ni. There was no evidence for ambidentate behavior; all of the complexes showed metal–nitrogen as opposed to metal–sulfur coordination.

Introduction

The general metal ion requirements noted in many thiamine-dependent enzyme systems[2,3] and the catalytic hydrogen wave produced by cobalt–ammonia buffer solutions of thiamine during polarography[4] lend support for some type of metal–thiamine interaction. Several studies have been carried out involving the thiamine analog thiazole (I). Metal complexes of thiazole,[5] benzothiazole,[6] and its 2-methyl derivative[7] have already been reported. Thiazole has both nitrogen and sulfur as possible donor sites, and whereas the majority of complexes have been found to be nitrogen bonded, a case of sulfur coordination has been postulated.[6]



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(2) T. P. Singer, "Methods in Enzymology," Vol. I, S. P. Colowick and N. O. Kaplan, Ed., Academic Press, New York, N. Y., 1955, p 465.

(3) A. Schellenberger, *Angew. Chem. Intern. Ed. Engl.*, 1024 (1967).

(4) O. H. Muller, "Methods of Biochemical Analysis," Vol. XI, D. Glick, Ed., Interscience Publishers, New York, N. Y., 1963, p 329.

(5) W. J. Eilbeck, F. Holmes, and A. E. Underhill, *J. Chem. Soc., A*, 757 (1967).

(6) E. J. Duff, M. N. Hughes, and K. J. Ruff, *ibid.*, 2354 (1968).

(7) M. Goodgame and M. J. Weeks, *ibid.*, 1156 (1966).