

than dialkyldithiocarbamates, which agrees with the fact that no Mo(VI) xanthate complexes are known.

Acknowledgments.—The authors gratefully acknowl-

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Isotopic Exchange of Bromide Ligands in Platinum(II) Complexes. The Bromo(diethylenetriamine)platinum(II)-Tetrabromoplatinate(II)-Bromide Systems¹

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The exchange rate of Pt(dien)Br⁺ with Br⁻ has been found to follow the rate law: $R_{\text{ex}} = \{k_1 + k_2[\text{Br}^-]\}[\text{Pt}(\text{dien})\text{Br}^+]$. The addition of PtBr₄²⁻ to the Pt(dien)Br⁺-Br⁻ solution has been shown to result in an increase in the exchange rate of both Pt(dien)Br⁺ and PtBr₄²⁻ by equal amounts. This mutually catalyzed exchange process is described by the expression: $R_{\text{excess}} = k_a[\text{Pt}(\text{dien})\text{Br}^+][\text{PtBr}_4^{2-}]$.

Introduction

We have recently² reported a study of bromide exchange in aqueous solutions of the PtBr₄²⁻ ion. The exchange rate between ligand bromide and bromide ion was described by a three-term expression. Two of the terms, first order, respectively, in PtBr₄²⁻ and PtBr₃(H₂O)⁻, probably describe the aquation of these species. A third term, which was predominant under some conditions, was second order, containing the product of concentrations, [PtBr₄²⁻][PtBr₃(H₂O)⁻]. The experimental evidence implied that this second-order rate term more likely described the formation of binuclear species or dimer containing a single bromide bridge rather than the doubly bridged Pt₂Br₆²⁻, characterized by Harris, *et al.*³

It was decided to investigate exchange in a system in which only a single bromide bridge would be expected. The Pt(dien)Br⁺-PtBr₄²⁻ system (where dien = diethylenetriamine) was an obvious choice because it appeared unlikely that Pt-N bonds would be broken in the course of any exchange reaction. To the best of our knowledge, the kinetics of bromide exchange between Pt(dien)Br⁺ and Br⁻ have not been previously reported; therefore, it was necessary first to investigate this reaction.

Experimental Section

Materials.—The [Pt(dien)Br]Br was prepared by allowing K₂[PtBr₄] to react with dien·2HBr in aqueous solution. Rb₂[PtBr₄]·H₂O was prepared and analyzed as described previously.² The platinum content of [Pt(dien)Br]Br was determined gravimetrically after hydrazine reduction, and bromide was estimated by a modified Volhard titration. *Anal.* Calcd for [Pt(dien)Br]Br: Pt, 42.6; Br, 34.9. Found: Pt, 42.1; Br, 34.5. Aqueous

solutions of the dien complex exhibited an absorption maximum at 275 mμ in agreement with the prior observations of Gray on the material.⁴ Bromine-82 was obtained by irradiating solid NH₄Br in the Ames Laboratory 5-Mw research reactor.

Water for exchange experiments was redistilled from alkaline KMnO₄ solution. All other materials were of Analytical reagent grade.

Procedures. A. Pt(dien)Br⁺-Br⁻ Exchange.—Solutions were prepared by dissolving weighed amounts of [Pt(dien)Br]Br and KBr in standardized NaNO₃ solutions in order to provide an over-all ionic strength of 0.318 M. The solutions were placed in flasks wrapped with opaque tape and permitted to stand for several hours in a thermostated water bath. Isotopic exchange was initiated by the addition of small volumes of solutions prepared from irradiated NH₄Br. Changes in volume were less than 1%. Except for solutions containing the lowest free bromide concentration (*i.e.*, 1.8 × 10⁻³ M), changes in bromide concentration were equally small. Known volumes of the reaction mixtures were withdrawn after measured time intervals; then all anions, including the free bromide ion, were replaced by the passage of these aliquots through columns containing large excesses of Amberlite IRA-400 anion-exchange resin in the nitrate form. Each effluent solution was diluted to 100 ml, and the 0.5-0.9-Mev γ activity was counted for a 25-ml aliquot in a plastic container placed over a 3-in. NaI crystal which formed the detector of a γ-ray scintillation spectrometer. After the application of a decay correction the fraction of exchange, F_i , at the separation time, t_i , was taken as

$$F_i = C_i/C_\infty \quad (1)$$

where C_i is the counting rate of sample collected at t_i and C_∞ is the average counting rate of at least two samples which were collected after isotopic equilibrium had been established.

Figure 1 is a typical plot of $\log(1 - F_i)$ vs. time. The excellent straight-line plot and the consistency of the experimental points indicated that the separation and counting procedures were most satisfactory. Half-lives of the reactions were determined from the plots of $\log(1 - F_i)$. Exchange rates (R_{ex}) were calculated by use of the usual McKay equation⁵

$$R_{\text{ex}} = \frac{\ln 2[\text{Pt}(\text{dien})\text{Br}^+][\text{Br}^-]}{([\text{Pt}(\text{dien})\text{Br}^+] + [\text{Br}^-])\tau_{1/2}} \quad (2)$$

(1) Work performed at the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1964.

(2) J. E. Teggin, D. R. Gano, M. A. Tucker, and D. S. Martin, Jr., *Inorg. Chem.*, **6**, 69 (1967).

(3) C. M. Harris, S. E. Livingstone, and N. C. Stephenson, *J. Chem. Soc.*, 3697 (1958).

(4) H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962).

(5) H. McKay, *Nature*, **142**, 997 (1938).

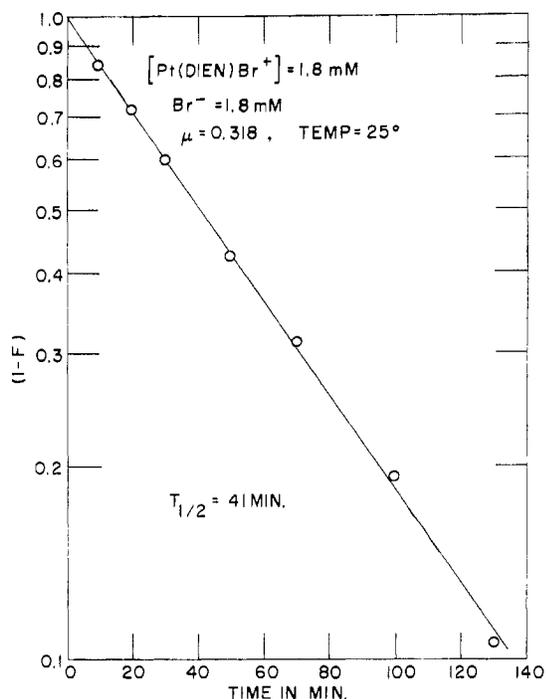


Figure 1.—Typical experiment for the exchange of Br^{82} between $\text{Pt}(\text{dien})\text{Br}^+$ and Br^- .

The experimental conditions, the observed half-time of exchange, and the indicated exchange rates are included in Table I.

TABLE I
 $\text{Pt}(\text{dien})\text{Br}^+ - \text{Br}^-$ EXCHANGE KINETICS

$[\text{Pt}(\text{dien})\text{Br}^+]$, mM	$[\text{Br}^-]$, mM	Half-time of exchange, min	$R_{\text{ex}}/[\text{Pt}(\text{dien})\text{Br}^+]$ $\times 10^3$, min^{-1}
25°, $\mu = 0.318$			
1.8	1.8	41	8.4
5.0	5.0	36	9.8
10.0	10.0	32	10.1
1.8	15.0	47	13.2
5.0	15.0	39	13.3
15.0	15.0	26	13.5
10.0	20.0	30	15
1.8	30.0	36	18
15.0	30.0	25	19
1.8	45.0	28	24
15°, $\mu = 0.318$			
1.8	1.95	141	2.6
1.8	2.10	136	2.8
0.9	30.0	102	6.6
1.8	30.0	100	6.6

B. $\text{Pt}(\text{dien})\text{Br}^+ - \text{Br}^-$ Exchange in the Presence of PtBr_4^{2-} .

For the majority of experiments, two solutions of equal volume were prepared. Both solutions had the same concentration for the components PtBr_4^{2-} , Br^- , and NaNO_3 , which, however, were not equal. The first solution contained the $\text{Pt}(\text{dien})\text{Br}^+$, the second, the tagged Br^- . Each solution was aged for several hours in the thermostated bath so that bromide in the PtBr_4^{2-} and in Br^- would have the same specific activity. The exchange was initiated by mixing the two solutions. The activity in $\text{Pt}(\text{dien})\text{Br}^+$ was determined as in section A, and the fraction of exchange was calculated in the same way by eq 1.

To describe the isotopic exchange between n chemically distinguishable components under steady-state conditions, the isotopic content of each component, which may be designated

by its specific activity, must be specified. These variables are related by a conservation condition since the total activity is fixed or decays at a known rate. Thus, in general, $n - 1$ first-order linear differential equations suffice to describe the kinetics. Such a set of equations has a general solution of $n - 1$ exponential functions in the time. For the familiar case of two components the function $1 - F$ follows a single exponential. For a three-component case the function $1 - F$ comprises two exponential functions. The present case is still more complex since the presence of $\text{PtBr}_3(\text{H}_2\text{O})^-$ requires the consideration of two more chemical components. However, in these present experiments the concentration of Br^- was much greater than the concentration of bromide in the $[\text{Pt}(\text{dien})\text{Br}^+]$. With this condition the coefficient of only one exponential function is significantly large. Therefore, good straight-line plots of $\log(1 - F)$ vs. time were obtained over the range $0 < F < 0.8$. A total rate of exchange between $\text{Pt}(\text{dien})\text{Br}^+$ and Br^- was then calculated from eq 2 with the $[\text{Br}^-]$ in the numerator virtually cancelling the [total Br^-] in the denominator.

The results have been tabulated in Table II. The presence of PtBr_4^{2-} materially shortened the half-time for the introduction of Br^{82} into the $\text{Pt}(\text{dien})\text{Br}^+$. For each experiment an exchange rate excess, R_{excess} , was calculated by

$$R_{\text{excess}} \text{ (for } \text{Pt}(\text{dien})\text{Br}^+) = R_{\text{ex}} \text{ (total)} - R_{\text{ex}} \text{ (without } \text{PtBr}_4^{2-}) \quad (3)$$

For the experiments marked with a "b" in the fourth column of Table II, the Br^- tracer was added to an aged solution containing the $\text{Pt}(\text{dien})\text{Br}^+$, PtBr_4^{2-} , and Br^- . For these experiments, therefore, the PtBr_4^{2-} was inactive at the beginning of the exchange experiment. The values of R_{ex} for these experiments were calculated from the initial slopes of the $\log(1 - F)$ plots. It is seen that for these experiments R_{ex} and, therefore, R_{excess} were, within the accuracy of the experiments, as high as for those in which the PtBr_4^{2-} was also tagged. Therefore, it must be concluded that the PtBr_4^{2-} catalyzes the direct introduction of free Br^- into the $\text{Pt}(\text{dien})\text{Br}^+$. There cannot be a significant trading of ligands between PtBr_4^{2-} and $\text{Pt}(\text{dien})\text{Br}^+$.

C. Exchange of PtBr_4^{2-} in the Presence of $\text{Pt}(\text{dien})\text{Br}^+$.—In these experiments weighed amounts of $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$ were added to the solution of $\text{Kb}_2[\text{PtBr}_4]$ and KBr before aging. The separation procedure involved the precipitation of the tetraphenylarsonium salts and the rate of exchange between PtBr_4^{2-} and Br^- was calculated by the same method used previously.²

In the absence of $\text{Pt}(\text{dien})\text{Br}^+$ the function $1 - F$ is represented by a single exponential function at the concentrations studied.² Since bromide introduced as the ligand of $\text{Pt}(\text{dien})\text{Br}^+$ was always a very minor component of total bromide, good linear plots were still obtained for the function $\log(1 - F)$. The presence of $\text{Pt}(\text{dien})\text{Br}^+$ increased the rate of exchange of PtBr_4^{2-} . Here again, an exchange rate excess, R_{excess} (for PtBr_4^{2-}), was calculated. Results are in Table III.

D. Aquation Equilibrium Quotient for $\text{Pt}(\text{dien})\text{Br}^+$.—An attempt was made to determine the extent of aquation in a $5 \times 10^{-3} M$ $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$ solution in a manner similar to that employed for the PtBr_4^{2-} ion, i.e., titration of the aquo protons with sodium hydroxide solution. In this case, the experiment indicated the presence of only small amounts of $\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}$ in the equilibrium mixture ($\sim 5 \times 10^{-5} M$) so the equilibrium quotient for the aquation process can be estimated as an order of magnitude of $5 \times 10^{-5} M$.

Results and Discussion

A plot of the results for the exchange rate between $\text{Pt}(\text{dien})\text{Br}^+$ and Br^- in Figure 2 shows that the exchange rate is given very accurately by the expression

$$R_{\text{ex}} = [\text{Pt}(\text{dien})\text{Br}^+]\{k_1 + k_2[\text{Br}^-]\} \quad (4)$$

This is the form of substitution rate law which has been found for a large number of replacement reactions for

TABLE II
 Pt(dien)Br⁺-Br⁻ EXCHANGE KINETICS IN PRESENCE OF ADDED Rb₂[PtBr₄]

[Pt(dien)Br ⁺], mM	[Br ⁻], mM	Added [Rb ₂ [PtBr ₄]], mM	Half-time of exchange, min	$R_{ex} \times 10^6$, M min ⁻¹	$R_{excess} \times 10^6$, M min ⁻¹	$R_{excess}/[Pt(dien)Br^+]$, M ⁻¹ min ⁻¹
25°, $\mu = 0.318$						
1.8	15	1.0	22	5.0	2.6	14
1.8	15	1.0	<i>b</i>	4.6	2.2	12
1.8	30	0.5	27.5	4.3	1.0	11
1.8	30	1.0	21	5.7	2.3	13
1.8	30	1.0	<i>b</i>	5.1	1.7	9.4
1.8	30	3.0	10.6	11.1	7.8	14
1.8	30	5.0	7.7	15.3	12.0	12
1.8	45	1.0	19	6.2	1.9	11
3.6	45	1.0	18	12.8	4.2	12
						Av 12.0
15°, $\mu = 0.318$						
0.9	30	2.5	33	1.83	1.1	4.8
1.8	30	5.0	<i>b</i>	5.5	4.1	4.5

^a Calculated by eq 3. ^b Species derived from PtBr₄²⁻ were inactive. Rates were derived from initial slopes of the exchange curves.

 TABLE III
 PtBr₄²⁻-Br⁻ EXCHANGE KINETICS IN PRESENCE OF ADDED Pt(dien)Br⁺ ([Br⁻] = 30 mM, $\mu = 0.318 M$)

[PtBr ₄ ²⁻] added, mM	[Pt(dien)Br ⁺], mM	Half-time of exchange, min	$R_{ex} \times 10^6$, M min ⁻¹	$R_{excess} \times 10^6$, M min ⁻¹	$R_{excess}/[PtBr_4^{2-}]$, M ⁻¹ min ⁻¹
25°					
5.0	0	90	9.0
5.0	1.8	41 ^a	19.9	11	12
5.0	1.8	43 ^a	19.0	10	11
5.0	1.8	38 ^b	21.5	12	13
5.0	1.8	39 ^b	20.9	12	13
15°					
5.0	0	250	3.3
5.0	1.8	105 ^a	8.1	4.8	5.3
2.5	0	357	1.43
2.5	0.9	173 ^a	2.95	1.52	6.8

^a PtBr₄²⁻ and Pt(dien)Br⁺ aged together prior to addition of activity. ^b PtBr₄²⁻ and Pt(dien)Br⁺ aged separately prior to addition of activity.

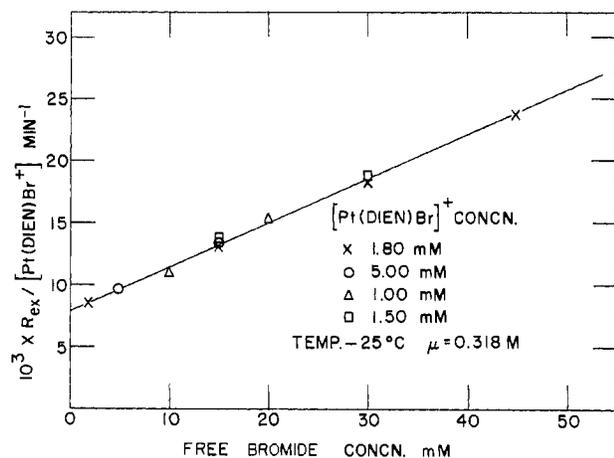


Figure 2.—Dependence of the exchange rate for the Pt(dien)-Br⁺-Br⁻ system upon bromide concentration.

the ligand X in the Pt(dien)X⁺ complexes.^{4,6} In particular, there is no evidence whatsoever for a contribution from a process which is higher than first order in concentrations of complexes as was found for the PtBr₄²⁻-

 TABLE IV
 RATE CONSTANTS FOR EXCHANGE PROCESSES

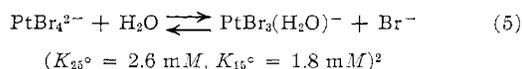
Temp, °C	k_1 (eq 4), sec ⁻¹	k_2 (eq 4), sec ⁻¹ M ⁻¹	k_a (eq 6), sec ⁻¹ M ⁻¹	k_a' (eq 7), sec ⁻¹ M ⁻¹
15	0.40×10^{-4}	2.3×10^{-3}	0.08	0.1
25	1.30×10^{-4}	5.9×10^{-3}	0.20	0.20
ΔH^\ddagger , kcal	20	16	15	(11)

Br⁻ system. Values of k_1 and k_2 obtained at 15 and 25° are tabulated in Table IV. The agreement of k_1 with the value of 1.32×10^{-4} sec⁻¹ reported by Gray⁴ for the corresponding term for hydroxide substitution indicates that the first-order term, k_1 , describes the aquation process for Pt(dien)Br⁺. The second-order term is surprisingly close to Gray's value of $k_2 = 53$ sec⁻¹ M⁻¹ at 25° for the replacement of Cl⁻ in Pt(dien)Cl⁺ by bromide. Thus, for replacement by bromide there appears to be little difference between bromide and chloride as the leaving group. Activation enthalpies of 20 and 16 kcal/mole for k_1 and k_2 appear normal for such systems.

It was apparent that the addition of Rb₂[PtBr₄] markedly increased the rate of exchange in the Pt-

(6) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

(dien)Br⁺-Br⁻ systems. The extent of aquation of PtBr₄²⁻ by the reaction



was not extensive with the amount of added bromide. However, the bromide liberated by reaction 5 was included in the evaluation of total free bromide. The range of concentration which could be tested was limited by the solubility of the compound, [Pt(dien)Br]₂[PtBr₄]. The plot of R_{ex} (for Pt(dien)Br⁺) in Figure 3 indicates a first-order process in PtBr₄²⁻. It is apparent from the last column in Table II that the quantity R_{excess} (for Pt(dien)Br⁺) is given satisfactorily by the expression

$$R_{\text{excess}}(\text{for Pt(dien)Br}^+) = k_a[\text{Pt(dien)Br}^+][\text{PtBr}_4^{2-}] \quad (6)$$

The average values for k_a are recorded in Table IV. It is to be noted from Table II that a change in the bromide concentration from 30 to 45 mM had no significant effect upon the excess exchange rate and, hence, presumably the predominant PtBr₄²⁻ ion is the effective agent rather than such minor species as PtBr₃(H₂O)⁻ or Pt₂Br₆²⁻ whose concentrations are strongly bromide dependent.

Only limited data could be obtained for the effect of the presence of Pt(dien)Br⁺ upon the exchange in the PtBr₄²⁻-Br⁻ system. As before, the solubility of [Pt(dien)Br]₂[PtBr₄] placed an upper limit on concentrations. Also the limitations of the [As(C₆H₅)₄]₂[PtBr₄] separation precluded using lower concentrations of PtBr₄²⁻. Since the complex must exchange four bromides, a comparable excess exchange rate produces a much smaller change in the exchange half-time than for the Pt(dien)Br⁺-Br⁻ system. However, the limited data from the experiments listed in Table III show that the exchange rate is definitely increased by the addition of Pt(dien)Br⁺. The rate constants for this excess exchange rate are given in Table IV if the following expression is assumed for this process

$$R_{\text{excess}}(\text{for PtBr}_4^{2-}) = k_a'[\text{Pt(dien)Br}^+][\text{PtBr}_4^{2-}] \quad (7)$$

Within the uncertainty of the experimental data, the R_{excess} for PtBr₄²⁻ is equal to the R_{excess} for Pt(dien)Br⁺. Each of the complex ions, therefore, mutually catalyzed the exchange of the other ion with free bromide by very nearly equal amounts.

The excess exchange rate may result from the formation of a single bromide bridge between the two complexes. For Pt(dien)Br⁺ the excess exchange may occur as a bromide ligand from PtBr₄²⁻ displaces the single bromide to form the bridge, as illustrated in Figure 4A. The reverse of this process then introduces the tagged bromide ion into the complex cation. The excess exchange for PtBr₄²⁻ can occur by the similar process illustrated in Figure 4B in which the bromide ligand from Pt(dien)Br⁺ forms the bridge to give the same binuclear intermediate. The experimental data require that the two processes in Figure 4A and B have identical rates at 25° and really within the experimental uncertainty the same activation energy.

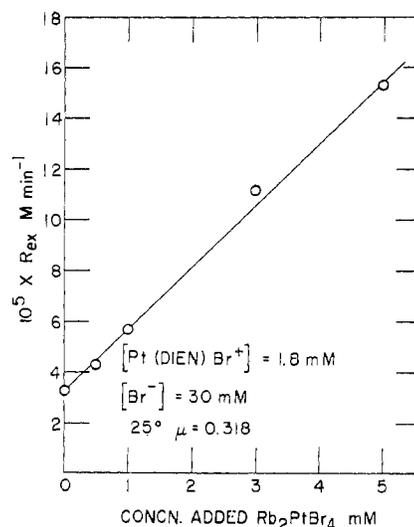


Figure 3.—Dependence of the exchange rate for the Pt(dien)-Br⁺-Br⁻ system upon the addition of PtBr₄²⁻.

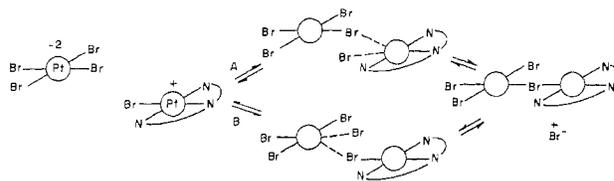


Figure 4.—Possible mechanisms for the mutually catalyzed exchange processes.

In addition, the second-order rate constants k_a and k_a' are very similar in magnitude to the value of 0.22 sec⁻¹ M⁻¹ for the term including the product of the concentrations [PtBr₄²⁻][PtBr₃(OH₂)⁻] for the PtBr₄²⁻-Br⁻ system A. If the two catalyzed exchange processes are independent, the identity in the rate constants and the activation energy is only a coincidence. With the approximate equality of k_a and k_a' there does appear to be the interesting possibility that the excess exchange of the two complexes occurs in a single process. If in the single bromide-bridged intermediate, formed exclusively by mechanism 4A, there was an exceedingly strong *trans* labilization caused by the -Br-Pt(dien) ligand, then the *trans*-bromide might be exchanged within the lifetime of the intermediate which must be very short. The result would be equal exchange of a bromide with free bromide from each of the two complexes. Current theories of the *trans* effect⁷ do not predict such an extreme *trans* labilization; however, they have not generally dealt with ligands of this nature. Still a third possibility to provide for equal excess exchange rates for the two complexes involves the formation of a Pt-Pt bond with a loss of a bromide ligand from each complex. It is not possible to choose between these various possible mechanisms from the present data, but the coincidence of identical rate constants for independent reactions appears per-

(7) (a) D. M. Adams, J. Chatt, J. Garratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964); (b) L. Oleari, L. DiSipio, and G. De Michelis, *Ric. Sci. Rend., Sez. A*, **8**, 413 (1965); (c) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955); (d) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

haps the most likely to the authors. It is planned to search for additional cases where such second-order substitution rate terms may be observed to obtain information which may permit discrimination between these different possibilities.

Grinberg and Shagisultanova⁸ reported that PtBr_4^{2-} and either the *cis*- or *trans*- $\text{Pt}(\text{NH}_3)_2\text{Br}_2$ "traded" bromide ligands. They based this result on the fact that the exchange between these species occurred more rapidly than the exchange of bromide ion with PtBr_4^{2-} . It seems possible in view of the present work that the exchange in these cases actually occurred by a mutually catalyzed exchange of the ligands in each

(8) A. A. Grinberg and G. A. Shagisultanova, *Radiokhimiya*, **2**, 592 (1960).

complex with free bromide ion. An attempt will be made to investigate this possibility.

The present work does emphasize that considerable care is needed in the preparation of platinum(II) compounds for kinetic studies, because the presence of one complex may catalyze the substitution reactions of another complex. In addition, it does provide a further indication that substitution reactions of platinum(II) compounds contain complications which have not been generally recognized previously.

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CONTRIBUTION FROM THE OLIN MATHIESON RESEARCH CENTER,
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Complexes Derived from 1,3-Diiminoisoindoline-Containing Ligands. III. The Divalent Nickel Complex with 2,6-Bis(1,3-diiminoisoindolin-1-yl)pyridine

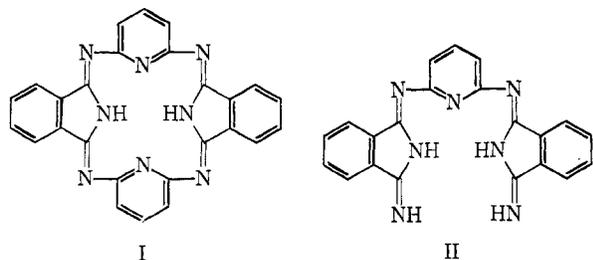
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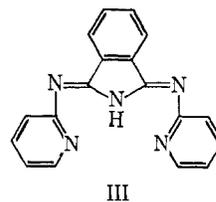
The divalent nickel ion coordinates with 2,6-bis(1,3-diiminoisoindolin-1-yl)pyridine in a bidentate fashion resulting in two types of complexes, (NiLX_2) and $(\text{NiL}_2)\text{X}_2$, where X is a univalent anion. This ligand contains five nitrogen atoms which are potential sites for coordination: the two terminal imino groups, the two isoindoline ring atoms, and, finally, the pyridine ring nitrogen. By utilization of a series of ligand reactions, it has been concluded that the points of attachment are one of the isoindoline ring nitrogens and the pyridine nitrogen.

Introduction

The formation of novel types of conjugated molecules by the condensation of 1,3-diiminoisoindoline with appropriate diimines was first described by Linstead and Elvidge.¹⁻³ They reported that the reaction between 1,3-diiminoisoindoline and 2,6-diaminopyridine could result in either the formation of a 16-membered macrocycle (I) or a related three-unit compound (II) depending on the stoichiometric ratio of the reactants. Robinson and co-workers⁴ reported on the transition metal complexes with molecules



similar to II. For example, 1,3-diiminobis(2-pyridyl)isoindoline (III) coordinates in a tridentate manner through the three ring nitrogens.



In this report, several varieties of divalent nickel complexes with II and some related molecules are described and characterized.

Experimental Section

Materials.—2,6-Diaminopyridine was obtained from the Aldrich Chemical Co. and purified before use. The other chemicals are standard inorganic reagents.

Synthesis.—1,3-Diiminoisoindoline was synthesized by the method of Elvidge and Linstead;¹ mp 194–196° (lit.¹ 194–195°).

2,6-Bis(1,3-diiminoisoindolin-1-yl)pyridine.—This compound was prepared by the method of Elvidge and Golden;² mp 241–243°.

[Dichloro-2,6-bis(1,3-diiminoisoindolin-1-yl)pyridine]nickel(II).—Nickel chloride hexahydrate (1.7 g, 0.0071 mole) was dissolved in butanol. To this, a butanol solution of 2,6-bis(1,3-diiminoisoindolin-1-yl)pyridine (2.6 g, 0.007 mole) was added rapidly, with stirring. A yellow crystalline material precipitated

(1) J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 5008 (1952).

(2) J. A. Elvidge and J. H. Golden, *ibid.*, 700 (1957).

(3) J. A. Elvidge and R. P. Linstead, *ibid.*, 5000 (1952).

(4) M. A. Robinson, S. I. Trotz, and T. J. Hurley, *Inorg. Chem.*, **6**, 392 (1967).