

H₂O molecule is presumably of the inner-sphere type. The same effectiveness order Li⁺ > K⁺ has been observed in almost all of those reactions between anions in which the nucleophilic reagent is OH⁻.¹⁹

The salt effect at low μ values appears much more complicated and is far from understood. A comparison can be made with analogous situations, although in a less pronounced fashion, already observed for other ionic reactions. In particular, the more effective acceleration of the tetralkylammonium cation compared with that of K⁺ at low concentrations on both k_1 and k_2 ²³ resembles the accelerating influence of R₄N⁺ ions

(23) This, *inter alia*, proves that the effect is not apparent and does not stem from the method employed to calculate k_1 and k_2 .

in the reactions of BrCH₂COO⁻ with S₂O₃²⁻^{19,24} and of IO₄⁴⁻ with I⁻.²⁵ In all likelihood, the observed behavior of R₄N⁺ ions results from a delicate balance of accelerating and retarding factors.

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The Reaction between 1,10-Phenanthroline and Platinum(II) Compounds. I. The Reaction in Aqueous Solution

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1,10-Phenanthroline reacts slowly and quantitatively with K₂PtCl₄ to give Pt(phen)Cl₂. Like most substitution reactions of platinum(II), this one proceeds by a direct path and also by a path that involves intermediate incorporation of a molecule of solvent. The respective rate constants at 45° in water are $3.74 \times 10^{-3} M^{-1} \text{sec}^{-1}$ ($\Delta H^\ddagger = 11.8 \text{ kcal/mol}$, $\Delta S^\ddagger = -24 \text{ eu/mol}$) and $11.5 \times 10^{-3} M^{-1} \text{sec}^{-1}$ ($\Delta H^\ddagger = 17.3 \text{ kcal/mol}$, $\Delta S^\ddagger = -16 \text{ eu/mol}$) at an ionic strength of 10.3×10^{-2} . Both paths are first order in phenanthroline and first order in platinum(II) concentrations. The reaction rate is sensitive to ionic strength and to the basicity of the phenanthroline but insensitive to pH in the range of 2.7–4.9. The slowness of the reaction and the unusual second-order solvent path appear to be the result of the inflexibility of the phenanthroline. The ratio of the rate of its reaction with K₂PtCl₄ to the rates of the more flexible ligands bipyridyl and ethylenediamine is 1:3:100, which is not explicable in terms of changes in nucleophilicity. The reactions of phenanthroline with *cis*- and *trans*-Pt(NH₃)₂Cl₂ are much slower than with PtCl₄²⁻, and its reaction with Pt(C₂H₄)Cl₂ is very much faster. The results are discussed in terms of a mechanism that is strongly dependent on dissociation of the platinum(II) complex.

Introduction

When Pt^{II}X₄ reacts with a flexible bidentate ligand, the first X group is substituted by one end of the ligand in a slow, rate-determining step. The other end of the ligand then displaces a second X group in a faster step.^{1,2} Both steps have the same mechanism as the substitution by a unidentate ligand: the interchange of a single coordinated group by another. The greater speed of the second step is merely the result of a sort of statistical advantage (anchimeric assistance) it has over the first. This stepwise process is probably impossible for 1,10-phenanthroline. The inflexibility of the molecule and the closeness of its donor nitrogens would seem to preclude its coordination though a single nitrogen.³ Unidentate phenanthrolines have been postulated as intermediates to explain the acid dependence of some dissociation reactions.^{4–6} These de-

pendences are often peculiar,^{4–7} and an alternative interpretation has been given, not involving a unidentate intermediate.^{8–10} The consequences of the closeness of the phenanthroline nitrogens can be seen in the structure of Zn(phen)Cl₂.¹¹ The N–Zn–N angle is only 80°, although the bond length is normal, whereas that in Zn(NH₃)₂Cl₂¹² is 108°. It was anticipated that these properties of the phenanthroline might cause its substitution reactions with metals of slight lability to exhibit some peculiarities, such as abnormal slowness. The kinetics of phenanthroline–metal dissociations have been examined for a number of metal ions.^{4–10} A few association reactions have also been studied, all using fairly labile metal ions.^{13,14} The association mechanism that has emerged involves the formation of an outer-sphere aggregate of phenanthro-

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line into the coordination sphere upon the loss of the first coordinated group.

We have studied the reaction of phenanthroline with some platinum(II) compounds, particularly K_2PtCl_4 , to find how phenanthroline substitutes a moderately inert metal ion. The consequences of its inflexibility are also examined by comparing its rate of substitution with that of bipyridyl and ethylenediamine.

Experimental Section

Chemicals.—Potassium tetrachloroplatinate(II) was synthesized by the method in ref 15 and 16. *Anal.* Calcd for K_2PtCl_4 : Cl, 34.16. Found: Cl, 34.13. The product of the reaction, dichloro(phenanthroline)platinum(II), was synthesized under the same conditions that were used in the kinetics runs. Potassium tetrachloroplatinate(II) (20.75 mg, 0.05 mmol), 1,10-phenanthroline (9.90 mg, 0.05 mmol), NaCl (67 mg), and aqueous HCl (0.1 ml) were dissolved in 100 ml of water. The solution was allowed to stand for several weeks at 45°. The product precipitated as yellow needles; yield 22.11 mg (99.1%). *Anal.* Calcd for $PtC_{12}H_8N_2Cl_2$: Pt, 43.7; Cl, 15.89. Found: Pt, 43.8; Cl, 15.99. Phenanthroline and bipyridyl were purchased from the J. T. Baker Chemical Co. All other chemicals were reagent grade materials.

Kinetics.—The reaction was initiated by adding the K_2PtCl_4 to a thermostated solution of all of the other ingredients (see above). Aliquots were withdrawn at intervals and pipetted into slightly acidic solutions of ferrous ammonium sulfate. The unreacted phenanthroline quickly complexed the iron, forming the dark red tris(phenanthroline)iron(II) ion. The color was allowed to develop for 40 min, during which period the solution was filtered to remove the insoluble $Pt(phen)Cl_2$. The product was well crystallized, and its removal by filtration presented no difficulties to following the progress of the reaction.

The absorbance of the solution was measured at 510 $m\mu$ on a Beckman Model DU spectrophotometer.

It was found by varying the development procedure over a considerable time that the presence of the iron(II) rapidly stopped the reaction but did not reverse it. Two or more reactions were measured at each set of conditions. The rates generally exhibited good reproducibility. The progress of most of the reactions was followed until the reagent concentrations had decreased to about half their original amounts. The reactions gave good second-order kinetics in this region and beyond, although when the phenanthroline concentration fell to too low a level, the red iron complex was not quantitatively formed.

When K_2PtCl_4 and phenanthroline were initially in equal concentrations, the rate constants for their reactions were calculated from a graph of the reciprocal of the concentration *vs.* time. When the initial concentrations were not equal, the rate expression was integrated for the particular set of initial conditions, and the appropriate function was plotted to determine the rate constant. The reactions of phenanthroline with $Pt(C_2H_4)Cl_3^-$ and *cis*- and *trans*- $Pt(NH_3)_2Cl_2$ were studied by the same method. Because perchlorate and nitrate ions gave insoluble precipitates with tris(phenanthroline)iron(II) ion, ammonium tetrafluoroborate was used to control the ionic strength.

The progress of the reaction between K_2PtCl_4 and ethylenediamine was followed by measuring the change in absorbance of the solution at 250 $m\mu$. The equilibrium constants and rates of aquation of K_2PtCl_4 were determined by the method of Martin.¹⁷

Reaction Products.— $Pt(phen)Cl_2$, as the product of reactions other than the one described above, was identified by comparing its infrared spectrum with that of an authentic sample. The product of the reaction between phenanthroline and *cis*- $Pt(py)_2Cl_2$ was tentatively identified as $Pt(phen)(py)Cl^+$. This identification was based on the observation that when equivalent amounts of the reactants were dissolved in boiling water, the conductivity of the solution rose to that of a 1:1 electrolyte as the phenanthroline disappeared, and no precipitate formed.

Results

Figure 1 shows a sample second-order graph for the reaction of 1,10-phenanthroline with tetrachloroplatinate(II) ion to give dichloro(phenanthroline)platinum(II). Table I lists the second-order rate

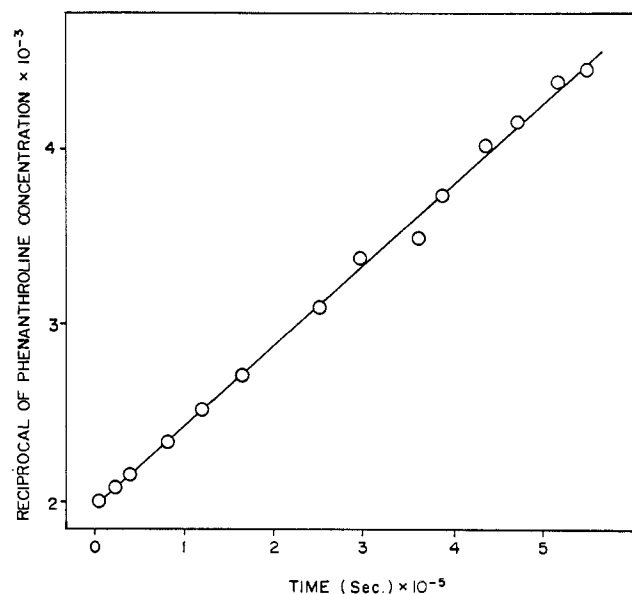


Figure 1.—Sample graph of the disappearance of 1,10-phenanthroline as a function of time. The conditions of the reaction are those given as the first entry in Table I.

TABLE I
SECOND-ORDER RATE CONSTANTS FOR THE REACTION BETWEEN K_2PtCl_4 AND 1,10-PHENANTHROLINE UNDER VARIOUS CONDITIONS

| $10^3[PtCl_4^{2-}]$, M | $10^3[phen]$, M | $10^2[Cl^-]$, M | pH | $10^2 \times$ ionic strength, M | $10^4 k_2$, $M^{-1} sec^{-1}$ |
|----------------------------|---------------------|---------------------|------|------------------------------------|-----------------------------------|
| 45° | | | | | |
| 0.50 | 0.50 | 2.2 | 2.7 | 2.3 | 4.5 ± 0.0 |
| 0.50 | 0.50 | 2.2 | 3.1 | 2.3 | 4.9 ± 0.6 |
| 0.50 | 0.50 | 2.2 | 3.5 | 2.3 | 4.6 ± 0.1 |
| 0.50 | 0.50 | 2.2 | 4.1 | 2.3 | 4.5 ± 0.1 |
| 0.50 | 0.50 | 2.2 | 4.9 | 2.3 | 4.5 ± 0.2 |
| 55° | | | | | |
| 1.00 | 1.00 | 2.0 | 2.01 | 2.3 | 11.4 ± 0.3 |
| 0.50 | 1.00 | 2.0 | 2.01 | 2.3 | 11.5 ± 0.3 |
| 1.00 | 0.50 | 2.0 | 2.01 | 2.3 | 11.9 ± 0.9 |
| 1.50 | 1.00 | 2.0 | 2.01 | 2.3 | 11.4 ± 0.1 |
| 1.00 | 1.50 | 2.0 | 2.01 | 2.3 | 11.4 ± 0.0 |
| 1.00 | 1.00 | 2.2 | 2.01 | 2.3 | 11.2 ± 0.0 |
| 1.00 | 1.00 | 0.10 | 3.28 | 10.3 | 11.2 ± 0.0 |
| 1.00 | 1.00 | 1.0 | 2.01 | 10.3 | 9.4 ± 0.0 |
| 1.00 | 1.00 | 4.0 | 2.01 | 10.3 | 6.8 ± 0.0 |
| 1.00 | 1.00 | 10.0 | 2.01 | 10.3 | 5.3 ± 0.0 |
| 1.00 | 1.00 | 2.0 | 2.01 | 4.3 | 10.2 ± 0.1 |
| 1.00 | 1.00 | 2.0 | 2.01 | 6.3 | 9.4 ± 0.4 |
| 65° | | | | | |
| 1.00 | 1.00 | 2.0 | 2.01 | 2.3 | 26.4 ± 0.1 |
| 1.00 | 1.00 | 2.2 | 2.01 | 2.3 | 24.6 ± 0.0 |
| 1.00 | 1.00 | 1.0 | 2.01 | 10.3 | 21.4 ± 0.1 |
| 1.00 | 1.00 | 10.0 | 2.01 | 10.3 | 11.0 ± 0.0 |

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constants for various reaction conditions. It may be seen from the experiments in which the concentrations of the reactants were varied that the form of the rate expression was

$$\text{rate} = k_2[\text{PtCl}_4^{2-}][\text{phen}]$$

No evidence was found for the first-order term, $k_1[\text{PtCl}_4^{2-}]$, which usually contributes to the rate of platinum(II) substitution reactions. The term is ordinarily evaluated from experiments in which the attacking ligand is present in much larger amounts than the platinum complex. In the research presented here, this approach was not used because the reaction was followed by measuring the concentration of the unreacted ligand. For a rate law with both first- and second-order terms, the first-order term will make the larger proportionate contribution to the rate when the ligand concentration is small. Thus, the reactions were run under very favorable conditions for the detection of a first-order contribution to the rate. The good second-order graphs for the data and the invariance of the second-order rate constants with changes in the reactant concentrations point to a first-order path that is either absent or abnormally ineffective in generating the product. This behavior can be explained. The first-order term arises from the "solvent path" to the product, involving a slow attack by the solvent followed by a rapid displacement of the solvent by the substituting ligand.¹⁸ Under our reaction conditions, the solvolysis of PtCl_4^{2-} did occur, but the attack of the solvolyzed species by the phenanthroline was slower than the solvolysis, giving a second-order solvent path. The data on the variation in observed rate constant with chloride concentration were consistent with this interpretation. In the subsequent discussion, PtCl_4^{2-} and the solvolysis product, presumably $\text{Pt}(\text{H}_2\text{O})\text{Cl}_3^-$, are denoted by PC and PS, respectively. Their sum, the total unreacted amount of platinum, is denoted by PT. The rate constant for the attack of PC by phenanthroline is k_o , that for the attack of PS is k_s , and the observed rate constant is k_o . The observed rate was

$$\text{rate} = k_o[\text{PT}][\text{phen}] \quad (1)$$

This was made up of two contributions

$$k_s[\text{PS}][\text{phen}] + k_o[\text{PC}][\text{phen}] = k_o[\text{PT}][\text{phen}] \quad (2)$$

Combining (1) and (2) and cancelling [phen] gives

$$k_o[\text{PT}] = k_s[\text{PS}] + k_o[\text{PC}] \quad (3)$$

The equilibrium between PS and PC was rapidly established, so we may write

$$K = \frac{[\text{PS}][\text{Cl}^-]}{[\text{PC}]} = \frac{([\text{PT}] - [\text{PC}])(\text{Cl}^-)}{[\text{PC}]} \quad (4)$$

Thus

$$[\text{PC}] = \frac{[\text{PT}][\text{Cl}^-]}{K + [\text{Cl}^-]} \quad (5)$$

and inserting (4) into (3) gives

$$[\text{PS}] = \frac{K[\text{PT}]}{K + [\text{Cl}^-]}$$

Now (3) becomes

$$k_o[\text{PT}] = \frac{k_s K[\text{PT}]}{K + [\text{Cl}^-]} + \frac{k_o[\text{PT}][\text{Cl}^-]}{K + [\text{Cl}^-]} \quad (6)$$

which simplifies to

$$k_o = \frac{k_s K + k_o[\text{Cl}^-]}{K + [\text{Cl}^-]} \quad (7)$$

Observed rate constants were measured at various concentrations of chloride, keeping all other conditions the same, and k_o and k_s at 55° were calculated from the data in Table I by using eq 7: $k_o = 3.74 (\pm 0.16) \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ ($\Delta H^\ddagger = 11.8 \text{ kcal/mol}$, $\Delta S^\ddagger = -24 \text{ eu}$) and $k_s = 11.5 (\pm 0.1) \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ ($\Delta H^\ddagger = 17.3 \text{ kcal/mol}$, $\Delta S^\ddagger = -16 \text{ eu}$). Figure 2 shows a graph of the data used for the calculation and a calculated curve. In order to justify this approach, it was necessary to show that equilibrium was established between PtCl_4^{2-} and the solvolysis product in a time that was short compared with the time of phenanthroline substitution. The solvolysis rate constant at 55° was found to be $1.5 \times 10^{-3} \text{ sec}^{-1}$, so that equilibrium would have nearly been reached after the other reaction had progressed only a short way. This is consistent with the observation that the reaction had a short induction period, although not one so serious as to hinder the evaluation of the rate constants. That the induction period corresponded to homogeneous reaction and the faster reaction thereafter to heterogeneous catalysis by the precipitated product can be shown not to be the case. The period of induction was the time expected for the solvolysis reaction to approach equilibrium and not the time before appearance of the precipitate. Further, the induction period did not occur when K_2PtCl_4 was dissolved in water a few thousand seconds before the phen-

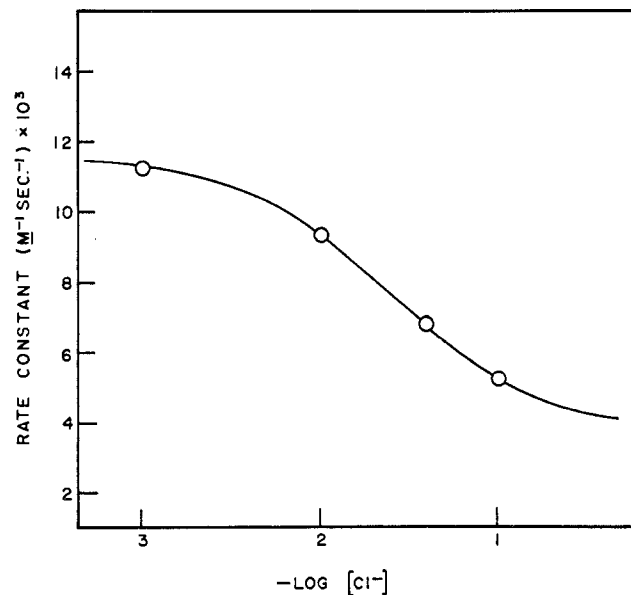


Figure 2.—Second-order rate constants as a function of $\log [\text{Cl}^-]$. The points are experimental, and the curve is calculated from eq 7.

(18) See ref 2, p 337.

anthroline was added, so that solvolysis was at equilibrium when the substitution reaction began. Finally, second-order kinetics would be inconsistent with heterogeneous catalysis by the product.¹⁹ The equilibrium constant (K in eq 4) was $2.52 \times 10^{-2} M$ at 55°.

The rate constants were measured at various pH's to determine whether the reaction was occurring through free phenanthroline or the phenanthroline ion. As the pH increased from 2.7 to 4.9, the concentration of phenanthroline ion decreased by factor of 2 and the concentration of free phenanthroline rose by a factor of about 200. Although the decrease in phenanthroline ion concentration was not large, the precision of the rate measurements was easily adequate to show that the rate did not decrease correspondingly. The invariance of the rate constant within this pH range was consistent with an absence of selectivity between the two forms of the ligand. Other explanations of this phenomenon are possible, but in view of the variety of pH dependences in phenanthroline reactions mentioned in the Introduction, more detailed speculation would be fruitless. The reaction rate was sensitive to changes in the nucleophilic character of the phenanthroline. Table II lists the rate constants for a variety of reactions related to the principal one being studied, and the first three entries illustrate this point. The 5,6-dimethyl and the 4,7-dimethyl derivatives are, respectively, about one-tenth and ten times as basic as the unsubstituted phenanthroline,²⁰ and they produced reactions that are about one-half and three-halves times as rapid, respectively.

TABLE II
RATE CONSTANTS FOR THE REACTIONS OF VARIOUS PLATINUM(II)
COMPOUNDS AND BIDENTATE LIGANDS^a

| Complex | Ligand | $k_2, M^{-1} \text{sec}^{-1}$ | Temp, °C |
|---|----------------------------------|-------------------------------|----------|
| PtCl ₄ ²⁻ | Phenanthroline | 0.0045 | 45 |
| | 4,7-Dimethyl-1,10-phenanthroline | 0.0059 | 45 |
| | 5,6-Dimethyl-1,10-phenanthroline | 0.0020 | 45 |
| Pt(C ₂ H ₄)Cl ₃ ⁻ | 2,2'-Bipyridyl | 0.012 | 45 |
| | Ethylenediamine | 0.094 | 25 |
| Pt(C ₂ H ₄)Cl ₃ ⁻ | Phenanthroline | >40 | 45 |
| <i>cis</i> -Pt(NH ₃) ₂ Cl ₂ | | 0.00012 | 65 |
| <i>trans</i> -Pt(NH ₃) ₂ Cl ₂ | | <0.00001 | 65 |

^a Reaction conditions: [platinum(II)] = [ligand] = $5 \times 10^{-4} M$, [Cl⁻] = $2.2 \times 10^{-2} M$, ionic strength 2.3×10^{-2} , and pH 2.7, except for ethylenediamine, where the pH was 6.0, in order to make the extent of ligand protonation approximately comparable.

Table I also shows that the rate increased as the ionic strength decreased, denoting reactants of opposite charge. This was the expected result, because at the pH of the reaction nearly all of the phenanthroline was in the form of the phenanthroline ion. The charge product of the reactants was calculated by the Brøn-

sted-Bjerrum-Christiansen equation²¹ (the kinetic analogy of the Debye-Hückel limiting law) to be nearly 2. This was consistent with PtCl₄²⁻ as a reactant, but not with Pt(H₂O)Cl₃⁻ (which made a substantial contribution to the rate). Pt(OH)Cl₃²⁻ was not the reactant, because the aquo complex is a very weak acid, and the rate was pH independent at moderate acidities. However, the Brønsted-Bjerrum-Christiansen relation is often not a reliable quantitative indicator of the charges of the reactants. At these high ionic strengths, the assumptions under which it was derived are not strictly valid, and, furthermore, nonreacting ions are known to play a special role in some substitution reactions of phenanthroline.⁸⁻¹⁰

The importance of flexibility in a bidentate ligand to its attack of PtCl₄²⁻ was demonstrated by comparing rates of phenanthrolines with those of bipyridyl and ethylenediamine. Bipyridyl has the same basicity as 5,6-dimethyl-1,10-phenanthroline,²² but its reaction was about five times faster.

An examination of molecular models indicated that when its two rings are perpendicular to each other, bipyridyl can occupy a single coordination position on a metal ion. There was, however, extreme crowding in the model, and this probably accounts for the absence of a more pronounced increase in the rate. The high rate of ethylenediamine attack may have been due to increased nucleophilicity (although pyridine is more nucleophilic than aniline toward platinum(II)),²³ but very likely it was mostly because ethylenediamine can form an uncrowded unidentate complex with the metal.

Phenanthroline reacted with other platinum(II) compounds at a wide variety of rates. It has already been shown that it reacted more rapidly with Pt(H₂O)Cl₃⁻ than with PtCl₄²⁻. This is usually explained by saying that the water is more quickly replaced by an attacking ligand than is a chloride ion. A different explanation seems necessary for the extremely fast reaction of Pt(C₂H₄)Cl₃⁻. The ethylene must have assisted the phenanthroline in displacing the *trans* chloride. By whatever mechanism the platinum resumed its square-planar geometry, the initial product would have been Pt(C₂H₄)(phen)Cl⁻. The compound that rapidly precipitated, however, was Pt(phen)Cl₂, so there must have been another rapid step in which the ethylene, labilized by the phenanthroline, was replaced by a chloride. The great insolubility of the product would have driven the reaction to completion. The rates of the two diammine complexes were interesting, when compared with that of PtCl₄²⁻. Charge usually has little to do with platinum(II) reaction rates, because bond making and bond breaking are of comparable importance.²⁴ In this case, however, dissociation seems to be more important to the reaction rate.

(21) See ref 19, pp 142-155.

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(24) See ref 2, p 385.

The introduction of the bulky phenanthroline was strongly affected by the greater ease with which a ligand could dissociate from the negatively charged complex than from a neutral complex when the incoming ligand was not providing much assistance.

Conclusion

Compared with the platinum(II) substitution reactions by unidentate and flexible bidentate ligands, those by phenanthrolines are slow. As with the other ligands, there are both direct and solvent paths to the prod-

uct. The latter path, however, is unusual in being second order, the result of the slower attack on the platinum by phenanthroline than by water. The reaction is unusually sensitive to the charge of the complex, with more negative charges giving faster rates. It is true that $\text{Pt}(\text{H}_2\text{O})\text{Cl}_3^-$ reacts a little faster than PtCl_4^{2-} , but not nearly as much faster as anticipated, considering that water is being replaced.²⁵ These facts seem to indicate that the character of the substitution is more dissociative than it is with other ligands.

(25) See ref 2, pp 379, 383.

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Medium-Ring Complexes. III. A Comparison of Planar and Pyramidal Copper(II) and Planar Nickel(II) Complexes Containing Seven- and Eight-Membered-Ring Diamines¹

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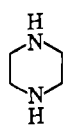
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The spectral properties of planar complexes of copper(II) and nickel(II) with 1,5-diazacyclooctane (daco) are compared to planar nickel(II) and planar and pyramidal copper(II) complexes with 1,4-diazacycloheptane (dach). The geometry of the chelate rings in the bis-dach complexes is discussed and the effects of conversion of $\text{Cu}(\text{dach})_2^{2+}$ complexes from four- to five-coordinated species are analyzed. The planar $[\text{Cu}(\text{dach})_2](\text{ClO}_4)_2$ has a λ_{max} in the visible spectrum at 505 m μ whereas the pyramidal $[\text{Cu}(\text{dach})_2\text{Cl}]\text{ClO}_4$ has a λ_{max} near 610 m μ . When other ligands occupy the apical position of the pyramidal complex, the maximum lies between these extremes. A spectrochemical series may be established based on the shift of the absorption maxima to lower energy as various ligands are added to the apical position: $\text{ClO}_4^- \sim \text{CH}_3\text{NO}_2 < (\text{CH}_3)_2\text{CO} < \text{CH}_3\text{CN} < \text{DMSO} \sim \text{NO}_3^- < \text{H}_2\text{O} < \text{HCONH}_2 \ll \text{SCN}^- \sim \text{Br}^- \sim \text{Cl}^-$.

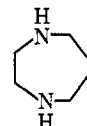
Introduction

Acyclic molecules containing the grouping $\text{N}(\text{CH}_2)_n\text{N}$ in their structures are among the best characterized chelating agents for transition metal ions.²⁻⁹ However, the related cyclic diamines have not been studied extensively. Piperazine, the six-membered-ring diamine, does not form chelated bicyclic complexes with the smaller transition metal ions such as copper(II) and nickel(II) although complexes of palladium(II) and iridium(II) can be prepared.^{10,11} Assuming that the strain induced in the chelated structure would be reduced if additional methylene groups was introduced between the amine functions, the eight-membered-ring diamine 1,5-diazacyclooctane (daco)¹² and the seven-membered-ring diamine 1,4-diazacycloheptane

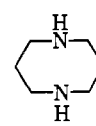
(dach) were examined as chelating agents for nickel(II) and copper(II).



piperazine



1,4-diazacycloheptane
homopiperazine
(dach)



1,5-diazacyclooctane
(daco)

When nickel(II) and copper(II) salts were treated with daco, planar complexes were obtained regardless of the anion or solvent present.¹² Nickel(II) complexes of dach were also planar. However, the geometry of the dach complexes of copper(II) was dependent on the solvent and the anions present, for both tetra- and pentacoordinated complexes could be prepared.¹³ Thus, a comparison of daco and dach complexes is advantageous since the local environment of the metal ions in the planar, four-coordinated bis complexes is similar, and variations in the physical and chemical properties of the two complexes can be attributed to

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