

assigning the vibrational spectrum of the  $\text{Sn}(\text{N}_3)_6^{2-}$  ion on the basis of  $D_{3d}$  or  $S_6$  symmetry. Since both structures have a center of symmetry, the rule of mutual exclusion should apply. However, it can be seen that three of the infrared fundamentals—2112, 2080, and  $335\text{ cm}^{-1}$ —appear to have Raman counterparts at 2113, 2078, and  $335\text{ cm}^{-1}$ . The 2112–2113- $\text{cm}^{-1}$  coincidence can be dismissed as accidental since, even if the anion loses its center of symmetry and has the point group  $D_3$ , the  $A_1$  modes do not become infrared active and the  $2113\text{-cm}^{-1}$  Raman band is polarized. An accidental coincidence of the 2080 and  $2078\text{ cm}^{-1}$  modes is also possible since differences in these modes depend upon coupling of the azide vibrations *via* several bonds and the heavy central metal atom which may be weak. The occurrence of a band at  $335\text{ cm}^{-1}$  in both the Raman and infrared spectra cannot be so readily

dismissed as accidental. This coincidence could indicate a  $D_3$  point group for the anion in which case 21 infrared-active fundamentals are allowed above  $200\text{ cm}^{-1}$  whereas only eight or nine are observed. Many of the 21 infrared-active fundamentals of  $D_3$  would be expected to have very low intensity, and thus it is not possible to rule out this structure entirely. If there were relatively free rotation about the Sn–N bonds, there is a possibility of population of some low-symmetry forms. However, the Raman polarization data militate against this. The best explanation of the observed spectrum is to assume that the  $335\text{-cm}^{-1}$  coincidence is accidental and therefore the frequencies have been tentatively assigned on the basis of  $D_{3d}$  symmetry, although a decision between  $D_{3d}$  and  $S_6$  symmetry on the basis of the vibrational spectrum is virtually impossible.

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## Peroxo Complexes of Cobalt(III) with a Cyclic Quadridentate Secondary Amine

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A number of complex cobalt(III) cations, having the stoichiometry  $[\text{Co}(\text{cyclam})\text{XO}]^{n+}$  (where cyclam = 1,4,8,11-tetraazacyclotetradecane and  $\text{X} = \text{Cl}, \text{N}_3, \text{H}_2\text{O}, \text{NCS}, \text{or } \text{NO}_2$ ), have been isolated and their chemical and physical properties examined. These complexes are the first stable species that can be isolated during the aerial oxidation of aqueous solutions containing cobaltous salts and the tetramine. The properties indicate that the complexes are dimeric, with a peroxo bridge between two trivalent cobalt atoms and a *trans* disposition of the cyclic ligand. In the presence of acid (HY), the peroxo bridge is broken and mixed complex cations of the type *trans*- $[\text{Co}(\text{cyclam})\text{XY}]^{n+}$  can be obtained.

### Introduction

The ability of ammoniacal solutions of cobaltous salts to absorb atmospheric oxygen has been known for many years.<sup>1</sup> Except for a few cases,<sup>2</sup> this process is irreversible and leads to the formation of the relatively unstable peroxo complexes<sup>1</sup> that probably exist in the deep brown solutions formed in the preparation of cobalt(III) complexes by aerial oxidation.

In the course of the study of the properties and the chemical kinetics of complexes containing the cyclic quadridentate ligand 1,4,8,11-tetraazacyclotetradecane (cyclam), it was found that the brown species formed during the preparation of the cobalt(III) complexes<sup>3</sup> were relatively stable, and, furthermore, provided us with suitable intermediates for the preparation of complex cations of the type *trans*- $[\text{Co}(\text{cyclam})\text{XY}]^{n+}$ , which were required for the kinetic investigations and which were difficult to prepare in adequate amounts by other methods. This paper describes the preparation

of these peroxo complexes and their physical and chemical properties.

### Results and Discussion

Two methods have been used in order to synthesize these complexes. In the first, which is suitable for  $\text{X} = \text{Cl}, \text{NO}_2$ , and  $\text{NCS}$ , a solution of cobaltous perchlorate was slowly added to an aqueous solution of cyclam and a suitable salt of the appropriate anion. The color immediately changed to dark brown, indicating an extremely rapid uptake of dissolved oxygen, and the appropriate complexes slowly crystallized out on standing. In the absence of coordinating anions the aquo complex, *trans*- $[\text{H}_2\text{OCo}(\text{cyclam})\text{O}_2(\text{cyclam})\text{CoH}_2\text{O}](\text{ClO}_4)_4$ , was obtained and the coordinated water could be replaced readily by other ligands. This formed the basis of the second method of preparation, which could be used to obtain all the complexes listed above as well as the azido complex, which could not be obtained by the first method.

These compounds are insoluble in most common organic solvents and are sparingly soluble in water where they slowly decompose to produce the *trans*- $[\text{Co}(\text{cyclam})\text{XH}_2\text{O}]^{2+}$  cations; they are, however, quite stable

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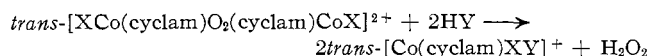
(3) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

TABLE I  
 PHYSICAL PROPERTIES OF THE PEROXO-BRIDGED COBALT(III) CYCLAM COMPLEXES

Complex	Color	Diffuse reflectance spectrum ( $\lambda_{\max}$ ), m $\mu$	Aqueous soln spectrum ( $\lambda_{\max}$ ), m $\mu$	Specific molar conductivity, mhos cm <sup>2</sup> mole <sup>-1</sup> (24.0°)	10% $\chi$ , cgs units. (20.0°)
<i>trans</i> -[SCNCo(cyclam)O <sub>2</sub> (cyclam)CoNCS](NCS) <sub>2</sub>	Brown	540 425	530 (246) <sup>a</sup> ~420 (703)	228	-102
<i>trans</i> -[N <sub>3</sub> Co(cyclam)O <sub>2</sub> (cyclam)CoN <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Dark brown	565 440	550 (390) ~440 (1000)	233	-76
<i>trans</i> -[O <sub>2</sub> NCo(cyclam)O <sub>2</sub> (cyclam)CoNO <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Brown	500	~500 (270)	233	-92
<i>trans</i> -[H <sub>2</sub> OCo(cyclam)O <sub>2</sub> (cyclam)CoOH <sub>2</sub> ](ClO <sub>4</sub> ) <sub>4</sub>	Brown	550 450	530 (170) ~430 (470)	460	-120
<i>trans</i> -[ClCo(cyclam)O <sub>2</sub> (cyclam)CoCl](ClO <sub>4</sub> ) <sub>2</sub>	Brown	570 445	<i>b</i>	330	-103

<sup>a</sup> Molar extinction coefficients (1. mole<sup>-1</sup> cm<sup>1</sup>) given in parentheses. <sup>b</sup> The spectrum of this complex is poorly resolved in aqueous solution.

in the solid state. In acid solution they decompose at a rate which is critically dependent upon the concentration of acid and form, initially, the relatively labile aquo complex, whose coordinated water is readily replaced by other ligands.



Thus, for example, we have been able to prepare the *trans*-[Co(cyclam)NO<sub>2</sub>Cl]<sup>+</sup>, *trans*-[Co(cyclam)NO<sub>2</sub>Br]<sup>+</sup>, *trans*-[Co(cyclam)NCSCl]<sup>+</sup>, and *trans*-[Co(cyclam)N<sub>3</sub>Cl]<sup>+</sup> cations, all of which we have found either difficult or impossible to prepare by conventional methods.<sup>3</sup> Complete cleavage of the peroxo group in the *trans*-[SCNCo(cyclam)O<sub>2</sub>(cyclam)CoNCS]<sup>2+</sup> cation, provided as the thiocyanate salt, was achieved by warming a solution of the complex in dilute nitric acid. In the presence of excess potassium thiocyanate it was shown, spectrophotometrically, that all the cobalt in the original complex was quantitatively converted to the *trans*-[Co(cyclam)(NCS)<sub>2</sub>]<sup>+</sup> cation. A kinetic investigation of these cleavage reactions has been started and we wish to postpone further discussion to a later paper.

The reactions in acid solution suggest that hydrogen peroxide, rather than oxygen,<sup>4</sup> is released during the reaction. We have been able to detect hydrogen peroxide in a semiquantitative way, using either potassium iodide or potassium permanganate, but until now it has not been possible to devise conditions that will determine the amount of peroxide quantitatively.<sup>4,5</sup> Titration only indicated about 70% of the expected amount of hydrogen peroxide under the most favorable conditions, and the titer required decreased rapidly if the solution was allowed to stand after acidification. Apart from the quantitative analysis of the oxygen present in the thiocyanato complex, other evidence for the existence of the peroxo bridge in these complexes comes mainly from inferences based upon chemical analogies with the known peroxo complexes of established structure<sup>6</sup> and upon the physical properties which are described and discussed below.

(4) A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

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(6) W. P. Schaefer and R. E. Marsh, *J. Am. Chem. Soc.*, **88**, 178 (1966).

**Physical Properties.**—These are summarized in Table I. All the complexes are essentially diamagnetic in the solid state and the molar susceptibilities, given in the table, after correction for the diamagnetic properties of the ligands and the anions, lead to magnetic moments of about 0.5 BM per cobalt ion. This is the value usually found for the temperature-independent paramagnetism of spin-paired cobalt(III) complexes. The conductivities of aqueous solutions of all the complexes, with the exception of the chloro compound, are consistent with their formulation as 2:1 electrolytes (4:1 in the case of the aquo species) based upon the proposed dimeric formulation, and the spectra of these complexes in aqueous solution are very similar to their diffuse reflectance spectra. The chloro complex, however, has a molar conductivity in 10<sup>-3</sup> M solution approaching that of a 3:1 electrolyte, and the absorption spectrum of the aqueous solution differs markedly from that of the solid. Closer study indicates that the chloro complex rapidly releases one chlorine on dissolving in water and that the process is complete before the above measurements can be made. The solution spectrum, in some respects, resembles that of a mixture of the solid dichloro and diaquo peroxy complexes. The spectra of the aqueous solutions of all the complexes change slowly with time and it is likely that this is due to a slow solvolytic breaking of the peroxo bridge.

The question as to whether these complexes should be looked upon as oxygen-containing complexes of cobalt(II) or peroxo complexes of cobalt(III) is to some extent answered by an examination of the visible absorption spectra of the solids (Figure 1). These spectra are remarkably similar to those of the *trans*-diacidotetramine complexes of cobalt(III) which are generally regarded as containing a perturbed spin-paired d<sup>6</sup> Co<sup>3+</sup> ion. However, the d → d bands tend to be overlaid by a rather intense band which intrudes into the visible region to give the peroxo complexes their characteristic brown color. The consistent association of the peroxo group with the appearance of this band suggests that the transition is due to an excitation that involves both the peroxo group and the cobalt atom. The donor group microsymmetry of each cobalt atom is C<sub>4v</sub> and thus the first spin-allowed excited state <sup>1</sup>T<sub>1g</sub> (in O<sub>h</sub>) will

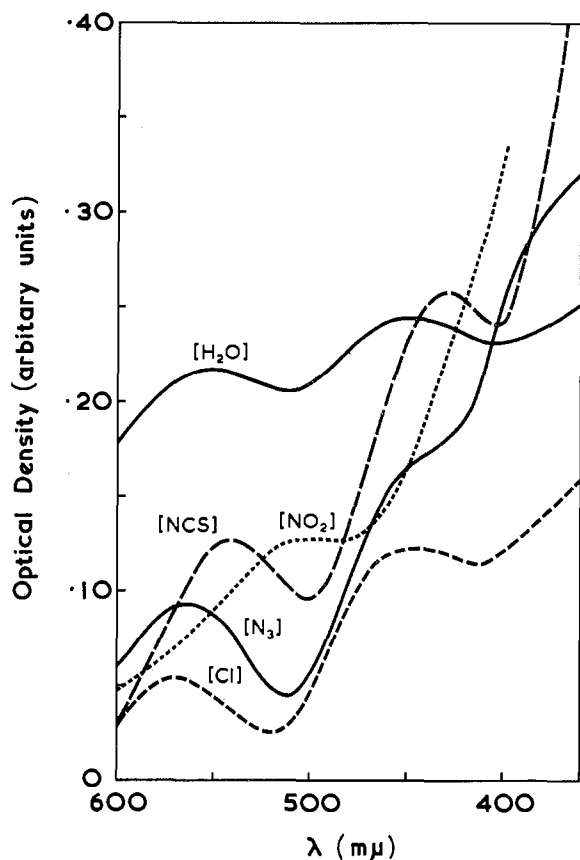


Figure 1.—Diffuse reflectance spectra of  $\text{MgCO}_3$  mulls of the peroxo-bridged complexes. The curves are labeled according to the *trans* monodentate ligand.

be split into a singly degenerate  ${}^1A_2$  and a doubly degenerate  ${}^1E$  state. Depending upon whether the average ligand field of the atoms in the tetragonal positions is greater or less than that of the atoms in the tetragonal plane, the  ${}^1E$  state will be displaced to higher or lower energies, respectively, compared to the center of gravity of the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition of the ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (at 478  $m\mu$ ) while the  ${}^1A_2$  component will remain approximately at that position throughout.<sup>7</sup> If it is assumed that the peroxo group has roughly the same ligand field as the hydroxo ligand, then all the complexes described here should have the  ${}^1E$  component displaced to lower energies compared with the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation. We thus assign the low-energy bands in these complexes as  ${}^1A_1 \rightarrow {}^1E$  and the next transition, which is in about the same position as the first band in the hexamine, as  ${}^1A_1 \rightarrow {}^1A_2$ . The components ( ${}^1B_2$  and  ${}^1E$ ) of the second band,  ${}^1A_{1g} \rightarrow {}^1T_{2g}$ , which should occur at about 360  $m\mu$  and would be expected to exhibit less splitting<sup>7</sup> than the first, are masked by the strong "brown band" of the cobalt peroxo system.

The infrared spectra of the complexes in the solid state measured in the region 400–4000  $\text{cm}^{-1}$  show a very close similarity to those of the known *trans* mononuclear cyclam complexes<sup>8,9</sup> and are distinctly

different from the spectra of the *cis* isomers.<sup>10,11</sup> However, many of the pertinent features are masked by the broad absorption band of the perchlorate ion at about 1100  $\text{cm}^{-1}$  which in all cases is not split any appreciable extent and indicates the absence of any coordination to the metal. The appearance of a band at 2103  $\text{cm}^{-1}$  in the *trans*- $[\text{NCSCo}(\text{cyclam})\text{O}_2(\text{cyclam})\text{CoNCS}](\text{SCN})_2$  complex is consistent with the presence of a nitrogen-bonded coordinated thiocyanate ligand.<sup>12</sup> We have been unable to observe any band which can be assigned to the peroxo group in any of the complexes. This is in accord with the supposition that the  $\text{Co}-\text{O}_2-\text{Co}$  grouping has  $C_{2h}$  local symmetry,<sup>6</sup> in which case the  $\text{O}-\text{O}$  stretch would transform as  $A_g$  and therefore be infrared inactive in the fundamental.

### Experimental Section

1,4,8,11-Tetraazacyclotetradecane was prepared by the method of Bosnich, *et al.*<sup>3</sup>

***trans*-Chloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III)-*u*-peroxo-*trans*-chloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate.**—A filtered solution of cobaltous perchlorate (0.9 g) in water (3 ml) was added drop by drop to a stirred solution of the ligand (0.5 g) and lithium chloride (1.0 g) in water (15 ml). Brown crystals soon started to come down and the mixture was placed in the refrigerator for 15 min. The greenish brown crystals were then filtered off, washed with dry ethanol and ether, and dried over phosphorus pentoxide; yield 0.33 g. Because of their lability in water, recrystallization of this and many of the other complexes described in this paper served only to decrease the yield and the purity. Consequently, care was taken to ensure that the complexes, when first deposited, were as pure as possible. *Anal.* Calcd for  $[\text{C}_{20}\text{H}_{48}\text{N}_4\text{Cl}_2\text{O}_2\text{Co}_2](\text{ClO}_4)_2$ : C, 29.3; H, 5.9; coordinated Cl, 8.6. Found: C, 29.4; H, 5.9; coordinated Cl, 8.3.

***trans*-Isothiocyanato(1,4,8,11-tetraazacyclotetradecane)cobalt(III)-*u*-peroxo-*trans*-isothiocyanato(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Thiocyanate.**—A clear solution of cobaltous thiocyanate (0.44 g) in water (15 ml) was added drop by drop to a stirred solution of the ligand (0.5 g) in water (15 ml). After standing for 30 min in the refrigerator the brown crystals were filtered off, washed with dry acetone and ether, and dried over phosphorus pentoxide; yield 0.3 g. *Anal.* Calcd for  $\text{C}_{24}\text{H}_{48}\text{N}_{12}\text{O}_2\text{S}_4\text{Co}_2$ : C, 36.8; H, 6.2; N, 21.5; S, 16.4; O, 4.1. Found: C, 36.8; H, 6.3; N, 21.2; S, 16.1; O, 4.2.

The perchlorate salt was prepared by adding a strong solution of sodium perchlorate to a filtered aqueous solution of the thiocyanate.

***trans*-Nitro(1,4,8,11-tetraazacyclotetradecane)cobalt(III)-*u*-peroxo-*trans*-nitro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate.**—A filtered solution of cobaltous perchlorate (1.8 g) in water (8 ml) was added drop by drop to a stirred solution of the ligand (1.0 g) and sodium nitrite (1.5 g) in water (30 ml). The brown crystals were filtered off after the mixture had been allowed to stand in the refrigerator for 30 min and were washed with dry ethanol and ether and dried. More crystals could be obtained if sodium perchlorate was added to the filtrate. This complex could be recrystallized satisfactorily by adding solid sodium perchlorate to a filtered aqueous solution; yield 0.8 g. *Anal.* Calcd for  $\text{C}_{20}\text{H}_{48}\text{N}_{10}\text{O}_4\text{Cl}_2\text{Co}_2$ : C, 28.6; H, 5.8; Cl, 8.4; N, 16.7. Found: C, 28.7; H, 5.8; Cl, 8.3; N, 16.6.

***trans*-Aquo(1,4,8,11-tetraazacyclotetradecane)cobalt(III)-*u*-peroxo-*trans*-aquo(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate.**—This was prepared by adding a solution of

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cobaltous perchlorate (1.8 g) in water (5 ml) to a solution of the ligand (1.0 g) in water (20 ml) in the manner previously described, and the crystals were isolated and treated in the way described; yield 2.0 g. *Anal.* Calcd for  $C_{20}H_{62}N_8O_{20}Cl_4Co_2$ : C, 24.4; H, 5.3; N, 11.4; Cl, 14.4. Found: C, 25.4; H, 5.67; N, 11.5; Cl, 14.2.

*trans*-Azido(1,4,8,11-tetraazacyclotetradecane)cobalt(III)- $\mu$ -peroxo-*trans*-azido(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate.—A saturated solution of sodium azide (40 ml) was added to a solution of  $[H_2OCo(cyclam)O_2(cyclam)CoH_2O](ClO_4)_4$  (2.5 g) in water (200 ml), and the mixture was stirred for 1 hr. Saturated sodium perchlorate solution (5 ml) was then slowly added and brown crystals separated. The mixture was allowed to stand for 30 min in the refrigerator, and the crystals were filtered off, washed with dry ethanol and ether, and recrystallized by adding concentrated sodium perchlorate solution to a saturated aqueous solution; yield 0.8 g. *Anal.* Calcd for  $C_{20}H_{48}N_{14}O_{10}Cl_2Co_2$ : C, 28.8; H, 5.8; N, 23.5; Cl, 8.5. Found: C, 28.7; H, 5.8; N, 23.4; Cl, 8.5.

*trans*-Chloronitro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate.—Purified  $[O_2NCo(cyclam)O_2(cyclam)CoNO_2](ClO_4)_2$  (0.2 g) was added little by little to stirred concentrated hydrochloric acid (30 ml), and the mixture was allowed to stand with further stirring for 1.5 hr. The pinkish red solution was filtered and concentrated perchloric acid (20 ml) was added.

Pinkish red crystals started to separate, and the mixture was placed in the refrigerator for 1 hr. The solid was filtered off, washed with water, anhydrous ethanol, and ether, and recrystallized as rapidly as possible from hot water. The complex aquates rapidly under these conditions and may be lost if sufficient care is not taken. *Anal.* Calcd for  $C_{10}H_{24}N_8O_6Cl_2Co$ : C, 27.3; H, 5.5; N, 15.9; Cl, 16.1. Found: C, 27.3; H, 5.4; N, 15.8; Cl, 16.3.

*trans*-Bromonitro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) perchlorate trihydrate was prepared in an analogous way by adding the nitro-peroxo complex (0.8 g) to bromine-free, 48% hydrobromic acid (300 ml), which was then stirred for 1.5 hr. The pinkish brown product was recrystallized rapidly from hot water. *Anal.* Calcd for  $C_{10}H_{20}N_8O_6ClBrCo$ : C, 22.4; H, 5.5; N, 13.0; Br, 14.8; Cl, 6.7. Found: C, 24.5; H, 4.9; N, 12.8; Br, 14.6; Cl, 6.5.

The diffuse reflectance spectra of  $MgCO_3$  mulls of the solids were measured with a Unicam SP 500 spectrophotometer. The infrared absorption spectra of Nujol and hexachlorobutadiene mulls between KBr plates were measured with a Perkin-Elmer 337 spectrophotometer. Conductivities were measured with a Wayne-Kerr Universal bridge.

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## Reactivity of Amines toward a Neutral Platinum(II) Complex

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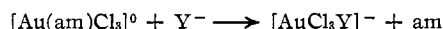
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The displacement by amines of one chloride in  $[Pt(bipy)Cl_2]$  has been studied in methanol at 25°. A linear relationship is observed between the logarithm of rate constants and the basicity of the entering groups. Three groups of amines have different reactivity owing to the different steric hindrance effects, and the results show that the steric influence of methyl groups in the  $\alpha$  position to the nitrogen in the entering amine is additive. However, apart from the marked steric hindrance effect, variations of the structure, size, and basicity of the amine molecule have little effect on the rate of these reactions.

### Introduction

Polarizability rather than basicity seems to have the most important role in determining the nucleophilic reactivity toward square-planar platinum(II) complexes.<sup>1</sup> For example, olefins and phosphines are good nucleophiles in reactions with complexes of platinum(II), whereas hydroxide and ethoxide ions are very poor nucleophiles<sup>2</sup> and the reactivity order of halide ions is  $I^- > Br^- > Cl^-$ .<sup>3</sup>

The dependence of reactivity on the basicity of the leaving group has been studied in reactions of gold(III) complexes<sup>4</sup>



(am = heterocyclic nitrogen base), and a linear free energy relationship was found in the case in which  $Y^-$

was essentially a pure nucleophile, e.g.,  $Cl^-$ , whereas this simple behavior was not followed by "biphilic" reagents such as azide and nitrito ions. At the present time, there is no information about the influence of the basicity of a series of entering groups with the same donor atom upon the reactivity of planar complexes with  $d^8$  electronic configuration. On the other hand, a considerable amount of information is available about the relation between basicity and reactivity in organic reactions. Hudson and Withey<sup>5</sup> have shown that the rate constants for the reaction between substituted pyridines and ethyl methanesulfonate follow a linear free energy dependence upon basicity when steric effects are similar. Thus,  $\alpha$  and  $\alpha,\alpha'$  substitutions decrease the magnitude of the rate constant considerably, but the slopes of the linear  $\log k$  vs.  $pK_a$  relationships are the same if only molecules with similar steric properties are compared. Similar retardation effects by  $\alpha$  substitution in heterocyclic

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