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A Study of the Trans Effect in Pyridinato(methyl)bis(dimethylglyoximato)cobalt and Related Complexes

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The trans effect in certain cobalt complexes has been studied by comparing the chemical shifts of the methyl protons for a series of substituted pyridinato(methyl)bis(dimethylglyoximato)cobalt complexes and the related substituted pyridinato(methyl)-1,3-bis(diacetyl monoxime)iminopropanatocobalt(III) complexes with the chemical shifts of the methyl protons for the corresponding *N*-methylpyridinium iodides. The slope of the dependence of the chemical shift of the methyl protons on Hammett's σ constants for the substituent on the pyridine is about two-thirds of that observed for the chemical shift of the methyl protons on Hammett's σ constants for a substituent in the *N*-methylpyridinium salts thus demonstrating that a cobalt atom will conduct about two-thirds of the electronic effect of a substituent.

The trans effect in the bis(dimethylglyoximato)cobalt complexes, cobalamins, and related cobalt(III) complexes has been studied by the effect of various ligands on the equilibrium[3] and kinetic properties[4-6] as well as the stretching frequency of a trans cyano group[7] and the nmr shifts of a trans methyl group.[8] A separation of the trans effect of σ- and π-donor properties of ligands has been measured by means of ^{19}F nmr.[9]

All of these studies show a trans effect but often it is difficult to assess quantitatively. We report here a more quantitative measure of the trans effect in the $CH_3Co(DH)_2L$ complexes. The nmr shifts of a series of $CH_3Co(DH)_2$ complexes containing various substituted pyridines were compared with the corresponding methylpyridinium salts. The equilibrium constants for the formation of the substituted $CH_3Co(DH)_2pyX$ complexes were also measured. The abbreviations used are as follows: $CH_3Co(DH)_2L$ for methylbis(dimethylglyoximato)cobalt complexes; $[CH_3Co[(DOH)(DO)pn]OH_2]^+$ for methyl-1,3-bis(diacetyl monoxime)iminopropanatocobalt complexes; py for pyridine and pyX for substituted pyridines.

Experimental Section

Preparation of Compounds.—$CH_3Co(DH)_2py$, $CH_3Co(DH)_2py$-4-CH_3, and $CH_3Co(DH)_2py$-4-NH_2 were prepared by the method of Schrauzer and Windgassen.[8]

$CH_3Co(DH)_2OH_2$ was prepared by warming a methanolic solution of the pyridinato complex with dimethyl sulfate.[8]

$CH_3Co(DH)_2py$-4-CN was prepared by addition of a tenfold excess of 4-cyanopyridine to a methanolic solution of $CH_3Co(DH)_2OH_2$. The compound was crystallized by evaporation of methanol and addition of water.

Diacetyl monoxime was prepared by reaction of ethyl nitrite with methyl ethyl ketone.[10]

1,3-Bis(diacetyl monoxime)aminopropane was prepared from diacetyl monoxime and 1,3-diaminopropane.[11]

$Co[(DOH)(DO)pn]Br_2$.—To a stirred suspension of 24 g (0.1 mol) of 1,3-bis(diacetyl monoxime)aminopropane in 40 ml of water–acetone there was added 21.9 g (0.1 mol) of $CoBr_2$. The mixture was stirred for 1 hr and the dark green crystals were filtered, washed with water and ether, and air-dried; yield 9 g (20%).

$[CH_3Co[(DOH)(DO)pn]OH_2]ClO_4$ was prepared by reaction of $Co[(DOH)(DO)pn]Br_2$ with methylmagnesium chloride in tetrahydrofuran.[12]

***N*-Methylpyridinium Salts.**—These were prepared by well-known procedures.[13-16] Each pyridine was dissolved in 25 parts of absolute ethanol and a 0.5 molar excess of methyl iodide was added at room temperature. The 3-bromo and 3-chloro derivatives were prepared at 0° in the dark by the method of Liveris and Miller.[16]

Nuclear Magnetic Resonance Spectra.—^1H nmr spectra were obtained using a Varian A-60A (60 MHz) spectrometer at 35 ± 2°. The concentration of compounds was in the range of 0.2–0.3 *M*. Samples contained TMS as an internal standard for the organic solvents and sodium 3-(trimethylsilyl)propylsulfonate as an internal standard in the aqueous solvents.

Formation Constants.—Formation constants, K_f, were estimated from the slope of a straight line calculated from a least-squares fit of experimental data for a plot of $\Delta A/(\Delta A_{max} - \Delta A)$ against pyridine concentration. The absorbance difference, ΔA, at 445 nm between solutions containing methyl(aquo)bis(dimethylglyoximato)cobalt(III) and pyridine were recorded against a reference containing an equivalent concentration of the methyl(aquo) complex using a Cary Model 14 recording spectrophotometer. The absorbance difference was then plotted against the pyridine concentration to determine the maximum absorbance difference, ΔA_{max}. The formation constants for methyl(4-X-pyridinato)bis(dimethylglyoximato)cobalt(III) in 50% dimethyl sulfoxide–H_2O (v/v) were determined at ambient temperature (23 ± 2°). The concentration of $CH_3Co(DH)_2OH_2$ was 6.0×10^{-4} *M* and the pyridine concentration varied from 10^{-6} to 1 *M*. Experimental data included at least five values of ΔA against pyridine concentration for which $\Delta A/\Delta A_{max}$ was in the range 0.1–0.9.

Discussion

The ^1H nmr spectrum of $CH_3Co(DH)_2OH$ is shown in Figure 1. The broadness of the signals at τ 6.72 and 9.60, which are assigned to the H_2O and cobalt

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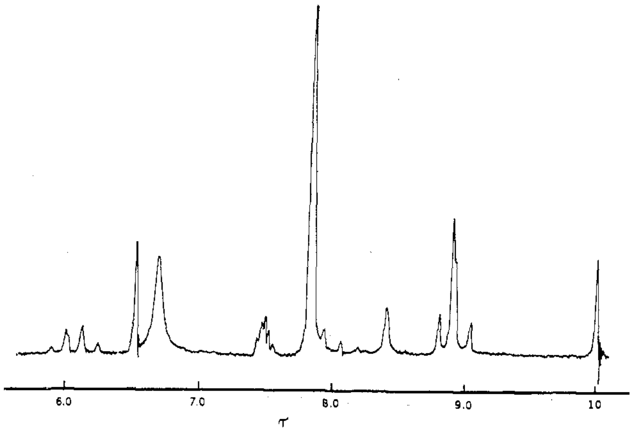

Figure 1.—^{1}H nmr spectrum of methyl(aquo)bis(dimethylglyoximato)cobalt(III) (0.3 M in DMSO-d_6 with TMS added as an internal standard).

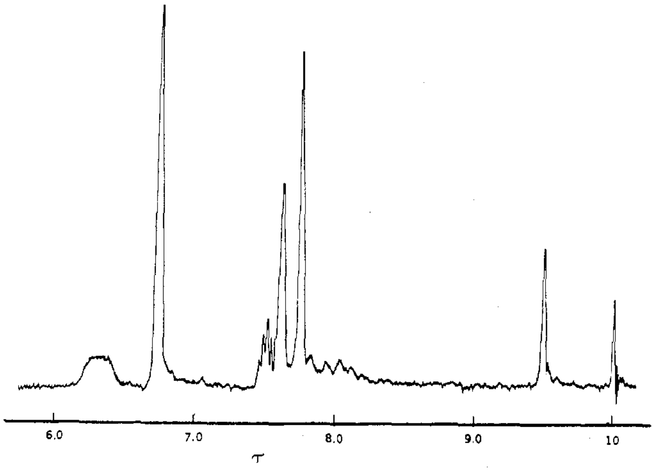

Figure 2.—^{1}H nmr spectrum of methyl(aquo)-1,3-bis(diacetyl monoxime)iminopropanatocobalt(III) perchlorate (0.25 M in DMSO-d_6 with TMS added as an internal standard).

CH_3 protons, respectively, may indicate that exchange between coordinated water and the solvent (DMSO-d_6) or bulk phase water, which is an impurity in the solvent, occurs under these conditions. The spectrum was not observed below τ −6. The signal due to the O- - -H–O protons for cobalt complexes of dimethylglyoxime has been reported[17] to occur at approximately τ −8.

The ^{1}H nmr spectrum of $[CH_3Co[(DOH)(DO)pn]OH_2]ClO_4$ is shown in Figure 2. The spectrum was not observed below τ 1.8. The broad signal at τ 6.30 was difficult to assign. However, broadening of this signal might also be caused by existence of a rapid equilibrium between two different conformations of the methylene bridge. The angle between the cobalt–nitrogen plane and the N–C$_{1'}$–C$_{2'}$ bond may be directed toward either the fifth ligand (CH_3) or the sixth ligand. This signal appeared as a poorly resolved triplet at τ 6.28 and 6.25 for samples containing 4-aminopyridine and 4-methylpyridine, respectively. Bulky ligands occupying the sixth coordination position would sterically hinder the methylene group. The assignments for $[CH_3Co[(DOH)(DO)pn]OH_2]ClO_4$ are presented in Table I.

Table I

Assignment of the ^{1}H Nmr Spectra of $CH_3Co(DH)_2OH_2$ and $[CH_3Co[(DOH)(DO)pn]OH_2]ClO_4$

Compd	Chem shift	Multiplicity	Assignment
$CH_3Co(DH)_2OH_2$[a]	9.60	Singlet (broad)	CH_3Co
	7.87	Singlet	$CH_3—C{=}N$
	6.72	Singlet (broad)	$Co—OH_2$ and H_2O
$[CH_3Co[(DOH)$-$(DO)pn]OH_2]ClO_4$[b]	9.49	Singlet	CH_3Co
	7.7–8.2	Multiplet	$-CH_2-$
	7.73	Singlet	$CH_3—C{=}N—CH_2$
	7.62	Singlet	$CH_3—C{=}N—O$
	6.75	Singlet	$Co—OH_2$ and H_2O
	6.30	Undefined (broad)	$-CH_2—N{=}$

[a] The concentration of $CH_3Co(DH)_2OH_2$ was 0.3 M in DMSO-d_6 with TMS as an internal standard. [b] The concentration of $[CH_3Co[(DOH)(DO)pn]OH_2]ClO_4$ was 0125 M in DMSO-d_6 with TMS as an internal standard.

The effect of substituents (X) on the chemical shift of the methyl groups of $CH_3Co(DH)_2py$-4-X and of $[CH_3Co[(DOH)(DO)pn]py\text{-}4\text{-}X]^+$ is summarized in Table II. The ^{1}H nmr spectra of the 4-substituted-pyridinato(methyl)bis(dimethylglyoximato)cobalt(III) compounds were observed in DMSO-d_6 and CH_2Cl_2. The 4-cyanopyridinato complex exhibited a single signal for the cobalt CH_3 protons at τ 9.37 in DMSO-d_6. However, two signals at τ 9.48 and 9.12 were observed for $[CH_3Co[(DOH)(DO)pn]OH_2]^+$ in the presence of 3 equiv of 4-cyanopyridine in DMSO-d_6. Observation of two signals was attributed to the existence of an equilibrium between the aquo- and 4-cyanopyridinato complexes. Similar equilibrium mixtures were observed for $[CH_3Co[(DOH)(DO)pn]OH_2]^+$ in the presence of 1 equiv of pyridine or 3 equiv of 3-cyanopyridine. However, only a single signal in the region τ 9–10 was observed for $[CH_3Co[(DOH)(DO)pn]OH_2]^+$ in the presence of an equivalent amount of 3-methylpyridine, 4-methylpyridine, 8-aminopyridine, or 4-aminopyridine. Although the concentration of water was not determined in these samples, the results indi-

Table II

Effect of Substituents on the Chemical Shifts in $CH_3Co(DH)_2py$-4-X and $[CH_3Co[(DOH)(DO)pn]pyX]^+$

Substituent	$\tau(CH_3Co)$	$\tau(CH_3—C{=}N)$	Log K_f[c]
	$CH_3Co(DH)_2py$-4-X[a]		
NC	9.22	7.92	
H	9.32	7.93	
CH_3	9.35	7.93	
	$CH_3Co(DH)_2py$-4-X[b]		
NC	9.37	7.89	2.03
H	9.45	7.90	3.16
CH_3	9.48	7.91	3.40
H_2N	9.60	7.91	4.14
	$[CH_3Co[(DOH)(DO)pn]pyX]^+$[b]		
4-CN	9.12		
3-CN	9.12		
H	9.18		
4-CH_3	9.21		
3-CH_3	9.19		
4-NH_2	9.35		
3-NH_2	9.25		

[a] Solvent is CH_2Cl_2 with TMS as an internal standard. [b] Solvent is DMSO-d_6 with TMS as an internal standard. [c] Solvent is 50% DMSO–H_2O (v/v). The error in K_f has been estimated to be ±5%.

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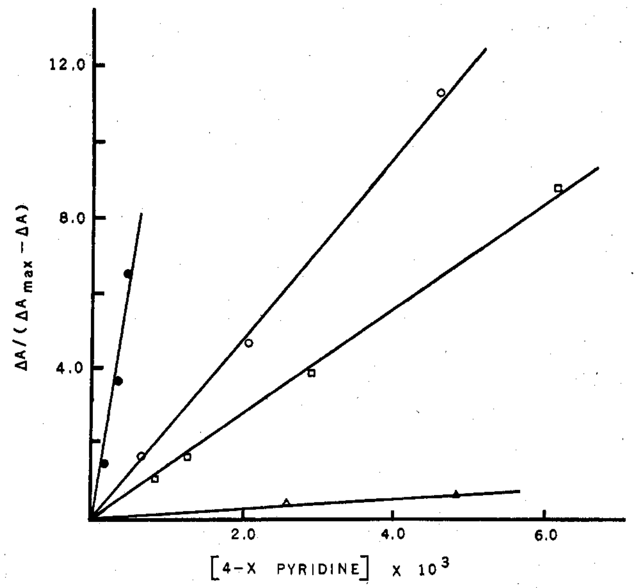

Figure 3.—Plot of $\Delta A/(\Delta A_{\max} - \Delta A)$ at 445 nm in 50% DMSO–H_2O (v/v) *vs.* the concentration of 4-X-pyridine: ●, X = amino; ○, X = methyl; □, X = hydrogen; Δ, X = cyano.

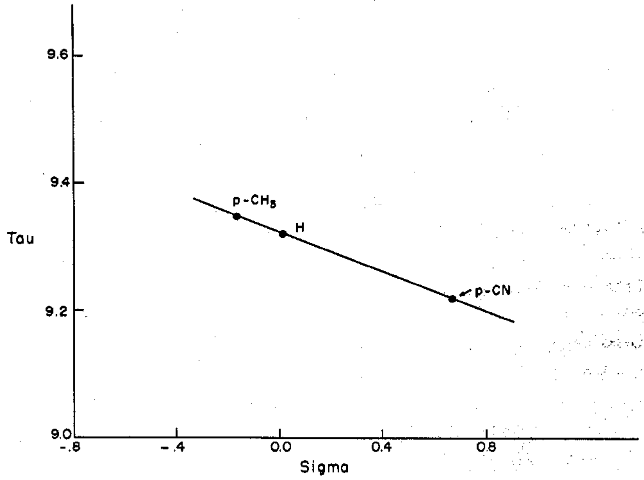

Figure 4.—Chemical shift of the methyl group of $CH_3Co(DH)_2py$-4-X measured in methylene dichloride *vs.* Hammett's σ constant for X.

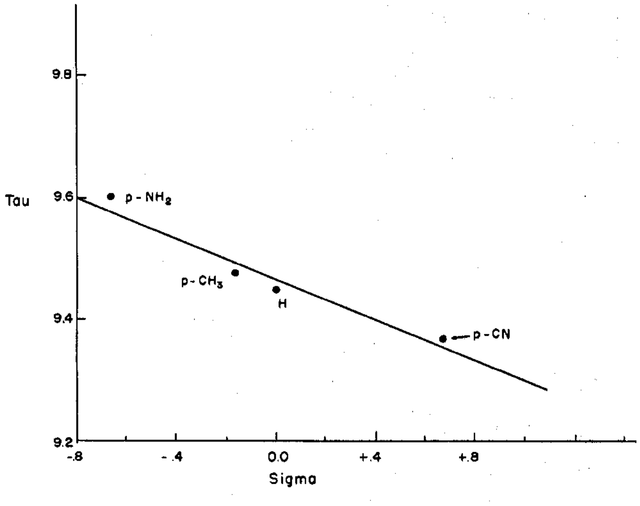

Figure 5.—Chemical shift of the methyl group of $CH_3Co(DH)_2py$-4-X measured in dimethyl sulfoxide *vs.* Hammett's σ constant for X.

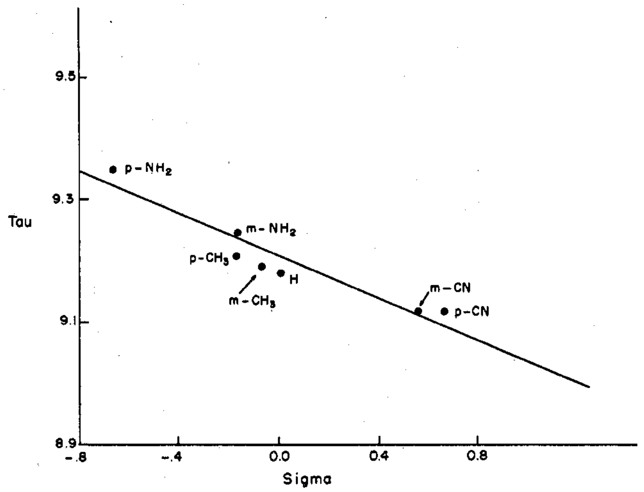

Figure 6.—Chemical shift for the methyl group of $CH_3Co(DO)(DOH)pyX$ measured in dimethyl sulfoxide *vs.* Hammett's σ constant for X.

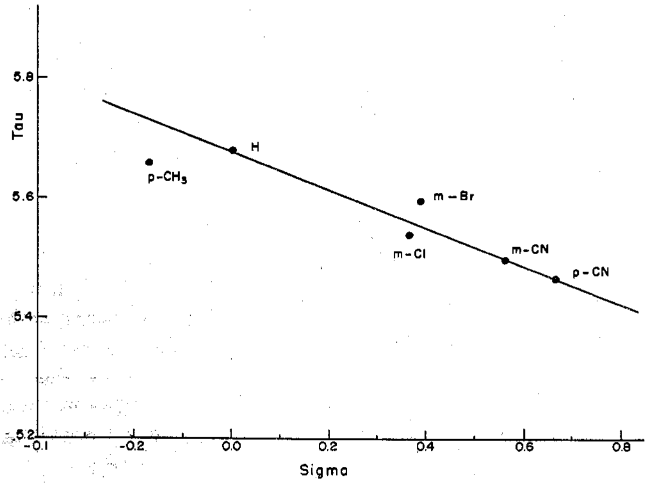

Figure 7.—Chemical shift for the methyl group of *N*-methylpyridinium salts measured in deuterium oxide *vs.* Hammett's σ constants.

cate that formation constants for $[CH_3Co[(DOH)(DO)pn]pyX]^+$ may be less than the corresponding formation constants for $CH_3Co(DH)_2pyX$. The signals in the region τ 1–2.5 assigned to the pyridine protons were not analyzed.

The formation constants, as listed in Table II, were estimated from the slopes of plots of $\Delta A/(\Delta A_{\max} - \Delta A)$ at 445 nm *vs.* pyridine concentration calculated by a least-squares fit of data to an equation for a straight line as shown in Figure 3.

The chemical shifts of the cobalt CH_3 protons for both $CH_3Co(DH)_2py$-4-X and $[CH_3Co[(DOH)(DO)pn]py\text{-}4\text{-}X]^+$ were correlated with the Hammett σ function[18] for the substituent. The correlation depended upon both the compound and the solvent. Plots of chemical shift *vs.* σ constant are shown in Figures 4–6.

In order to be able to assess the magnitude expected for the variation of the chemical shift of the methyl protons with substituent constant, the chemical shifts at the methyl protons for a series of substituted *N*-methylpyridinium salts were also measured. Figure

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7 is a plot of chemical shift *vs.* σ constant for the *N*-methylpyridinium compounds.

Table III lists slopes and intercepts calculated by a least-squares fit of the dependence of the chemical shift on Hammett's σ constants. The electronic effect of the pyridine ring substituent upon the chemical shift of the methyl group is reduced from a slope of −0.245 to a slope of −0.155 or −0.171 upon interposition of a cobalt(III) ion. Therefore, about two-thirds of the electronic effect is transmitted through the cobalt to the methyl group. This ratio is surprisingly high. It can be compared with a corresponding value for an sp^3 carbon, commonly one-third but with estimates as high as half.[19] Since the electronic effect must depend on the overlap between the methyl and cobalt orbitals, we expected to find a larger conduction in the more negatively charged (and hence more extended orbitals) dimethylglyoximato complexes than in the diacetyl monoxime iminopropanato complexes, but this appears not to be true. The total charge is larger on the dimethylglyoximato complex but there are two oxygens to carry the charge compared to only one in the diacetyl monoxime iminopropanato complexes.

TABLE III

CORRELATION OF CHEMICAL SHIFTS WITH HAMMETT'S σ CONSTANTS BY A LEAST-SQUARES FIT TO A STRAIGHT LINE

Ordinate	Intercept	Slope	Correlation coefficient	Per cent conduction
$\tau(\mathrm{C}H_3\text{–Co})^a$	9.32	−0.155	−1.00	63
$\tau(\mathrm{C}H_3\text{–Co})^b$	9.47	−0.171	−0.98	70
$\tau(\mathrm{C}H_3\text{–Co})^c$	9.21	−0.166	−0.95	68
$\tau(\mathrm{C}H_3\text{–N}^+)^d$	5.65	−0.245	−0.94	100

[a] For $CH_3Co(DH)_2$py-4-X in CH_2Cl_2. [b] For $CH_3Co(DH)_2$py-4-X in DMSO-d_6. [c] For $[CH_3Co[(DOH)(DO)pn]pyX]^-$ in DMSO-d_6. [d] For CH_3py^+ in D_2O.

Clearly, the trans effect is large. The conduction through the cobalt atom is highly efficient. These results do not answer the question of what orbitals are responsible for the trans effect, σ or π orbitals.

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Aquation of Nitritopentaamminecobalt(III) Catalyzed by Hydrogen, Halide, and Thiocyanate Ions[1]

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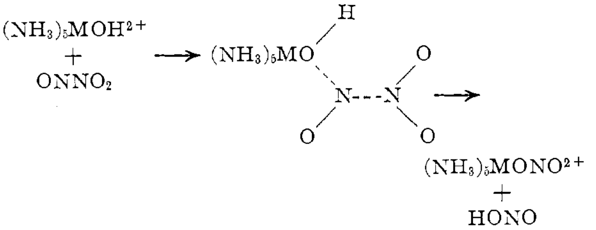
The reaction $Co(NH_3)_5ONO^{2+} + H_2O + H^+ = Co(NH_3)_5OH_2^{3+} + HNO_2$ has been studied kinetically at 25° and $\mu = 1.00$ *M*. With $HClO_4$–$LiClO_4$ mixtures to adjust μ, the rate law is $d \ln [Co(NH_3)_5ONO^{2+}]/dt = k_1[H^+] + k_2[H^+]^2$, where $k_1 = 1.32 \times 10^{-3}\ M^{-1}\ sec^{-1}$ and $k_2 = 1.37 \times 10^{-3}\ M^{-2}\ sec^{-1}$. Halide and thiocyanate ions catalyze the reaction, and the dominant additional terms in the above rate law are $k_3^X[H^+][X^-]$ where k_3^X has the values 8.47×10^{-2}, 1.04, 15.8, and 6.53 $M^{-2}\ sec^{-1}$ for chloride, bromide, iodide, and thiocyanate, respectively. The mechanistic implications of these results are discussed in the context of possible linear free energy relationships. It is concluded that nitrosation reactions implicated in the coordination chemistry of O-bonded nitrite involve, in addition to the previously established species N_2O_3 and NO^+, the participation of species XNO, where $X^- = Cl^-, Br^-, I^-$, and SCN^-.

Introduction

Kinetic and mechanistic studies of diazotization and deamination reactions[2] have uncovered three pathways for nitrosation, namely nitrosation *via* N_2O_3, NO^+ (or H_2ONO^+), and XNO ($X^- = Cl^-, Br^-, I^-, SCN^-$). In the coordination chemistry of nitrite ion, the N_2O_3 path has been detected in the formation reactions of nitritopentaammine complexes of cobalt(III),[3] chromium(III), rhodium(III), iridium(III), and platinum(IV)[4] from the corresponding aquo complexes. These types of reactions have been shown to proceed without metal–oxygen bond breaking[5] according to the rate law $k[HNO_2]^2[M(NH_3)_5OH^{2+}]$.[3,4] The kinetic and tracer results have been interpreted on the basis of O-nitrosation by N_2O_3 as depicted in eq 1. More



(1)

recently, the NO^+ path has been uncovered in the acid-catalyzed aquations of nitrito complexes of chromium(III),[6-8] cobalt(III), rhodium(III), and iridium(III).[9]

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[1] (a) This work was supported by Grant GP-9669 from the National Science Foundation. (b) Abstracted in part from the B.S. thesis of D. E. Klimek, State University of New York at Stony Brook, May 1970.

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