

in redox reactivity observed during steps III and IV of the Fe(III)-S(IV) system. The main redox process occurs during steps III and IIIa, and the main overall oxidation product is SO_4^{2-} with a minor production of $\text{S}_2\text{O}_6^{2-}$, especially in the presence of O_2 . In some of the Pt(IV) and Co(III) systems the redox process exhibits a characteristic pH dependence, which can be interpreted in terms of a more reactive protonated sulfito complex.^{9,11,13} A similar effect presumably accounts for the pH dependence of step III as found in this study (see eq 9).

We are not aware of studies on the redox kinetics of bridged metal sulfito complexes that could serve as an appropriate comparison with the reactions suggested to account for step IV of the decomposition process. The oxidation products found in this study, viz. SO_4^{2-} and $\text{S}_2\text{O}_6^{2-}$, do not exclude the partial formation of $\text{S}_2\text{O}_7^{2-}$ either as an intermediate or stable product species, as reported in the literature.^{25,26} The mechanism for the metal-catalyzed autoxidation in (11), or the mechanism suggested by Conklin and Hoffmann,²¹ incorporates the formation of SO_3 , which along with SO_4^{2-} could be present in solution as $\text{S}_2\text{O}_7^{2-}$. In this

respect it is important to note that the authors^{25,26} conclude from their experiments that $\text{S}_2\text{O}_7^{2-}$ is formed from one oxygen and two bisulfite molecules and that its formation shows a complicated dependence on trace amounts of metal ions such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Mn^{2+} . In aqueous solution $\text{S}_2\text{O}_7^{2-}$ can dissociate according to (12), which is similar to the mechanism for the formation of



HSO_3^- from $\text{S}_2\text{O}_5^{2-}$. It follows that the mechanistic results of this study may be relevant for the understanding of the formation of $\text{S}_2\text{O}_7^{2-}$ during the autoxidation of S(IV) oxides.

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Synthesis and Reactivity of Pyridine *N*-Oxide Complexes of Cobalt(III)

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The syntheses of four new pentaamminecobalt(III) complexes with pyridine *N*-oxide, 4-methylpyridine *N*-oxide, 2-cyanopyridine *N*-oxide, and 4-cyanopyridine *N*-oxide are described. The first two ligands bond through the oxygen, while the latter two ligands are bonded via the nitrile group nitrogen. Reaction kinetics have been used to investigate the reactivity of these complexes. The rate constant for aquation of the pyridine *N*-oxide complex at 25 °C is $2.51 \times 10^{-6} \text{ s}^{-1}$. Chromium(II) reduction of the pyridine *N*-oxide complex is an inner-sphere process with a rate constant at 25 °C of $0.371 \text{ M}^{-1} \text{ s}^{-1}$, an activation enthalpy of $3.75 \pm 1.2 \text{ kcal mol}^{-1}$, and an activation entropy of $-48 \pm 4 \text{ cal K}^{-1} \text{ mol}^{-1}$. The 4-cyanopyridine *N*-oxide complex undergoes facile base hydrolysis of the nitrile function to a bound amide. The rate constant for this process at 25 °C is $4030 \pm 125 \text{ M}^{-1} \text{ s}^{-1}$. The 2-cyanopyridine *N*-oxide complex exhibits this same nitrile group conversion even in acidic solution, where water is shown to function as a competitive attacking nucleophile.

Introduction

Few cobalt(III) amine *N*-oxide complexes have been reported, in sharp contrast to the large number of complexes known with other transition metals.¹⁻⁵ Nathan et al. described the synthesis of three Co(III) complexes with bidentate ligands containing at least one amine *N*-oxide function in 1979⁶ and offered several reasons for the dearth of other examples. Among these were the weak donor properties of the *N*-oxide function and the difficulty of nonaqueous oxidation of Co(II) precursors. Hence, most examples of *N*-oxide complexes utilize chelating ligands.⁶⁻⁹ Indeed, the only example of a monodentate amine *N*-oxide complex appears to be the *trans*-bis(diethylglyoximate)cobalt(III) pyridine

N-oxide complexes reported by Ablov et al.¹⁰ This article reports the facile, high-yield synthesis of both pentaammine(pyridine *N*-oxide)cobalt(III) and complexes with substituted pyridine *N*-oxides. The reactivity of these complexes is also reported via kinetic studies of aquation, electron transfer by chromium(II) reduction, and ligand reactivity.

Experimental Section

Materials. Pyridine *N*-oxide from Aldrich Chemical Co., Inc., and 4-methylpyridine *N*-oxide from Eastman Organic Chemicals were recrystallized from toluene before use. 2- and 4-cyanopyridine *N*-oxides were prepared from their cyanopyridines (Aldrich) by the method of Ochiai.¹¹ Literature methods were employed to prepare $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$ ¹² and $[\text{Co}(\text{NH}_3)_3\text{OSO}_2\text{CF}_3](\text{CF}_3\text{SO}_3)_2$ ("cobalt triflate").¹³ Solvents for synthetic procedures were dried over 4-Å molecular sieves before use.

House-supplied distilled water was deionized through an Illinois Water Treatment Universal Model 2 resin cartridge for kinetic studies. Sodium perchlorate (G. F. Smith Chemical Co.) stock solutions for ionic strength

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control were prepared and standardized as reported previously.¹⁴ Sodium hydroxide solutions were prepared by serial dilution of Dilut-It concentrates (J. T. Baker Chemical Co.). Chromium(II) perchlorate solutions were prepared by zinc amalgam reduction of chromium(III) perchlorate (G. F. Smith) solutions and standardized as described previously.¹⁵ Perchloric acid (G. F. Smith) solutions were standardized by titration against NaOH.

Synthesis of Complexes. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA. Visible spectra were obtained on a Cary 17 ultraviolet-visible-near-IR spectrophotometer in 0.01 M HClO₄ solutions. Infrared spectra were obtained on a Perkin-Elmer Model 599 spectrophotometer as KI pellets. **Warning!** Perchlorate salts are potentially explosive and should be handled with caution and in small amounts.

Pentaammine(pyridine *N*-oxide)cobalt(III) Perchlorate, [(NH₃)₅CoO-NC₅H₃](ClO₄)₃. To 30 mL of dry acetone were added 3 g of cobalt triflate complex and 5 g of pyridine *N*-oxide. The solution was stoppered, warmed to 45 °C, and stirred for 75 min. A 10-mL quantity of 5 M perchloric acid was added, producing a purple precipitate, which was filtered out, redissolved in a minimum of water (ca. 5 mL), and recrystallized by slow dropwise addition of 70% HClO₄. The product was washed with methanol and then diethyl ether and dried in vacuo. Yields of 40–65% of glistening purple flakes are normally obtained.

Anal. Calcd for [(NH₃)₅CoO-NC₅H₃](ClO₄)₃: C, 11.17; H, 3.75; N, 15.63. Found: C, 11.22; H, 3.79; N, 15.62. Visible spectrum: λ_{max} 521 nm (ε 101 M⁻¹ cm⁻¹).

Pentaammine(4-methylpyridine *N*-oxide)cobalt(III) Perchlorate-1.5-Water, [(NH₃)₅CoONC₅H₄CH₃](ClO₄)₃·1.5H₂O. An identical procedure is used for the synthesis and purification of this complex except ice-cold methanol is used for the wash, as the complex exhibits moderate solubility in this solvent. Yields of 40–50% are normally obtained.

Anal. Calcd for [(NH₃)₅CoONC₅H₄CH₃](ClO₄)₃·1.5H₂O: C, 12.46; H, 4.35; N, 14.52. Found: C, 12.49; H, 4.29; N, 14.52. Visible spectrum: λ_{max} 522 nm (ε 113 M⁻¹ cm⁻¹).

Pentaammine(4-cyanopyridine *N*-oxide)cobalt(III) Perchlorate-Water, [(NH₃)₅CoNCC₅H₄NO](ClO₄)₃·H₂O. The procedure given by Balahura¹² for the preparation and isolation of nitrile complexes in triethyl phosphate solutions using azidopentaamminecobalt(III) perchlorate, NOBF₄, and excess ligand was followed. The orange-yellow product obtained after 2 h of heating on a steam bath and precipitation was recrystallized by dissolution in a minimum of water (ca. 5 mL) followed by addition of 70% HClO₄. The resultant yellow precipitate was washed with methanol and diethyl ether and dried in vacuo. Yields of 35–45% are normally obtained.

Anal. Calcd for [(NH₃)₅CoNCC₅H₄NO](ClO₄)₃·H₂O: C, 12.42; H, 3.65; N, 16.89. Found: C, 12.41; H, 3.67; N, 16.87. Visible spectrum: λ_{max} 469 nm (ε 84.8 M⁻¹ cm⁻¹). Infrared spectrum: 2295 cm⁻¹ (nitrile stretch).

Pentaammine(2-cyanopyridine *N*-oxide)cobalt(III) Perchlorate, [(NH₃)₅CoNCC₅H₄NO](ClO₄)₃. This preparation is very sensitive to traces of water, as will be discussed later. Therefore, unless the cobalt triflate used in the synthesis is freshly prepared, it should be dried in vacuo at 110 °C for 2 h before use. To 1.3 g of cobalt triflate in 15 mL of dry acetone is added 1 g of 2-cyanopyridine *N*-oxide. The solution is stirred for 2 h at 35 °C, at which time a precipitate of the orange triflate salt of the complex will have formed (ca. 0.3 g). The precipitate is filtered out, dissolved rapidly in 3 mL of water, and rapidly precipitated with 2 mL of 70% HClO₄. This precipitate is filtered out, washed with methanol and diethyl ether, and dried in vacuo.

Anal. Calcd for [(NH₃)₅CoNCC₅H₄NO](ClO₄)₃: C, 12.81; H, 3.40; N, 17.43. Found: C, 12.62; H, 3.44; N, 17.30. Visible spectrum: λ_{max} 471 nm (ε 69.6 M⁻¹ cm⁻¹). Infrared spectrum: 2300 cm⁻¹ (nitrile stretch).

Kinetic Studies. The slower aquation, electron-transfer, and acid hydrolysis reactions were followed on the Cary 17 instrument, while the faster base hydrolysis reaction was monitored on a Hi-Tech Scientific Model SF-51 stopped-flow spectrophotometer. Both instruments were equipped with a Forma Scientific Model 2095 refrigerated-heating water bath for temperature control. The aquation reaction was monitored at 520 nm, the electron-transfer (ET) reaction was monitored at 350 nm, and the nitrile hydrolysis reactions were monitored at 305 nm (base) and 335 nm (acid). Pseudo-first-order conditions were maintained for the ET and base hydrolysis reactions by using at least 10-fold molar excesses of chromium(II) and hydroxide, respectively. In all cases, ionic strength was maintained at 1.0 M with NaClO₄/HClO₄ or NaClO₄/NaOH. Rate constants were extracted from slopes of log (absorbance change)

Table I. Experimental Rate Constants for Aquation of Pentaammine(pyridine *N*-oxide)cobalt(III)^a

<i>T</i> , °C	<i>k</i> , s ⁻¹	[HClO ₄], M
25.0	(2.51 ± 0.06) × 10 ⁻⁶	0.20
42.0	(2.42 ± 0.04) × 10 ⁻⁵	0.20
42.0	(2.22 ± 0.08) × 10 ⁻⁵	0.020
42.0	(2.52 ± 0.12) × 10 ⁻⁵	0.005
56.4	(1.40 ± 0.06) × 10 ⁻⁴	0.20

^a*I* = 1.0 M (NaClO₄/HClO₄).

Table II. Kinetic Data for Aquation Reactions of Pentaamminecobalt(III) Complexes with Neutral O-Donors as the Leaving Group L

L ^a	10 ⁶ <i>k</i> , s ⁻¹ (25 °C)	Δ <i>H</i> [‡] , kcal mol ⁻¹	Δ <i>S</i> [‡] , cal K ⁻¹ mol ⁻¹	ref
EtOH	65	25.0	6.2	<i>b</i>
MeOH	55	24.3	3.5	<i>b</i>
DMSO	20	24.7 ± 0.3	4.5 ± 0.4	<i>c</i>
H ₂ O	5.9	26.6 ± 0.3	6.7 ± 1	<i>d</i>
py- <i>N</i> -O	2.5	24.3 ± 0.5	-2.6 ± 1.5	<i>e</i>
DMF	1.8 ^f	27.2 ± 1.0	5.1 ± 2.2	<i>g</i>

^aLigand abbreviations: EtOH, ethanol; MeOH, methanol; DMSO, dimethyl sulfoxide; py-*N*-O, pyridine *N*-oxide; DMF, dimethylformamide. ^bBorghini, E.; Monacelli, F. *Inorg. Chim. Acta* 1977, 23, 53. ^cRodriguez, N. f. Kremer, E.; Piriz Mac-Coll, C. R.; Beyer, L. Z. *Anorg. Allg. Chem.* 1975, 412, 59. ^dHunt, H. R.; Taube, H. *J. Am. Chem. Soc.* 1958, 80, 2642. ^eThis work. ^f28.9 °C. ^gReynolds, W. L.; Knoll, M. A. *Int. J. Chem. Kinet.* 1976, 8, 389.

versus time plots, which were linear from 4 to 6 half-lives. Activation parameters were obtained from Eyring plots utilizing at least three temperatures spanning 20 deg or more.

Results and Discussion

Characterization of Complexes. The bonding mode of the pyridine *N*-oxide moiety in both the pyridine *N*-oxide and 4-methylpyridine *N*-oxide complexes must be via the oxygen atom. The occurrence of peak maxima in the visible region at 521 and 522 nm, respectively, is consistent with this assignment, being typical of CoN₅O chromophores.

Bonding in both the 2- and 4-cyanopyridine *N*-oxide complexes is via the nitrile group nitrogen. This is supported by the positions and molar absorptivities of the visible peak maxima and the presence of nitrile stretches at ca. 2300 cm⁻¹.¹² The product obtained from the synthesis of the 4-cyanopyridine *N*-oxide complex was submitted to cation exchange on SP-Sephadex resin in hopes of detecting an O-bound linkage isomer. However, no purple product was detected, even in trace amounts. Furthermore, the synthesis was repeated with the cobalt triflate precursor in acetone, but again, cation exchange indicated that only nitrile-bound product was formed. Further evidence for nitrile group bonding in these latter two complexes is provided by the well-characterized and facile nitrile-to-amide conversion in dilute base.^{12,14,16}

Numerous attempts were made to synthesize the complex of 3-cyanopyridine *N*-oxide. However, the synthesis was successful in only one case, producing an O-bonded complex in very low yield. The complex gave an excellent elemental analysis but was observed to decompose very rapidly in neutral or basic solution and slowly in acidic solution, liberating ammonia in all cases. We continue to seek a reliable synthetic route to this complex and are unable to speculate at this time as to why this O-bound complex is unstable, especially in light of the robust nature of the two other complexes reported in this study.

Aquation Kinetics. The results of individual kinetic runs of the aquation reaction of the pentaammine(pyridine *N*-oxide)cobalt(III) complex are presented in Table I. As expected for a simple aquation reaction of cobalt(III), the reaction is independent of acid concentration in the range 0.005–0.20 M HClO₄.

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Table III. Rate Constants for Cr(II) Reduction of Pentaammine(pyridine *N*-oxide)cobalt(III)

<i>T</i> , °C	<i>k</i> , M ⁻¹ s ⁻¹	[H ⁺] range, M	[Cr ²⁺] range, M
15.8	0.329 ± 0.011	0.40 only	0.010–0.10
25.0	0.371 ± 0.013	0.0575–0.80	0.010–0.10
35.3	0.530 ± 0.015	0.40 only	0.0050–0.050

Activation parameters are presented in Table II along with published results for aquation reactions of some other pentaamminecobalt(III) complexes with neutral O-donor ligands. These other results have been obtained at ionic strengths near the 1.0 M value employed in this study. The entropy of activation of our reaction is near zero, which is normal for Co(III) aquations with neutral leaving groups.¹⁷ Somewhat surprising is the rate constant for this aquation reaction. Pyridine *N*-oxide exhibits one of the smaller rate constants of aquation for O-donors, this for a ligand reported to be a weak donor.⁶

Electron Transfer. Rate constants for the reduction of pentaammine(pyridine *N*-oxide)cobalt(III) by hexaaquachromium(II) are presented in Table III. Each reported rate constant represents the slope of a *k*(obsd) versus [Cr(II)] plot with from five to eight data points. Least-squares intercepts of each plot were zero within ±σ. The 25 °C results clearly indicate the lack of an acid-dependent term in the rate law, which is simply first order in oxidant and reductant. The majority of the kinetic runs were performed at a wavelength of 350 nm, while a few were run at 521 nm with no change in *k*(obsd). Activation parameters obtained from an Eyring plot of the temperature dependency yielded an enthalpy of activation of 3.75 ± 1.2 kcal mol⁻¹ and an entropy of activation of -48 ± 4 cal K⁻¹ mol⁻¹.

The question of whether an electron-transfer reaction proceeds by an inner- or outer-sphere mechanism is central to all such studies. The oxygen of the ligated *N*-oxide has a lone pair of electrons available for binding to Cr(II), and hence, an inner-sphere pathway is possible. Certainly Cr(II) reacts predominantly by inner-sphere pathways when possible, and the activation enthalpy for this reaction is atypical of outer-sphere Cr(II) reductions. The rate constants reported in Table III are also larger than those found in most outer-sphere Cr(II)/Co(III) redox reactions. Additionally, the pyridine *N*-oxide ligand is reducible, which would favor inner-sphere electron transfer by the chemical mechanism. Pyridine *N*-oxides have well-defined one- and two-electron-reduction potentials.¹⁸ Also, free *N*-oxides can be reduced directly with Cr(II), and the kinetics of this process have been studied.¹⁹

While the above observations suggest an inner-sphere mechanism for this reaction, direct evidence would be provided by the isolation of a chromium(III)–pyridine *N*-oxide product from the reaction. Although this has not been realized, the existence of such a product has been deduced from cation-exchange chromatography. Product mixtures from 1:1 stoichiometric reactions between the Co(III) complex and Cr(II) were charged onto columns of Dowex 50W-X8-200 resin in the Na⁺ form. Elution with sodium perchlorate/perchloric acid mixtures first moved the pink hexaaquacobalt(II) band. Further elution moved the Cr(III) product band, but when removed from the column and analyzed spectrally, it was found to be hexaaquachromium(III).

Since absorbance values of the product mixtures were too high to accommodate hexaaquachromium(III) as the Cr(III) product of this reaction, a closer monitoring of the ion-exchange experiment was undertaken in which the elution of pyridine *N*-oxide from the column was followed by using its distinctive ultraviolet spectrum. Pyridine *N*-oxide was not found to move through the column with the solvent front as would be expected for a neutral molecule. Rather it was slowly released over a period of tens of minutes. Solutions of free pyridine *N*-oxide were passed through columns

Table IV. Rate Constants for Base Hydrolysis of the 4-Cyanopyridine *N*-Oxide Complex of Pentaamminecobalt(III)

<i>T</i> , °C	<i>k</i> , M ⁻¹ s ⁻¹	[OH ⁻] range, M
16.5	1900 ± 23	0.0010–0.010
25.1	4030 ± 125	0.0030–0.030
36.0	7850 ± 140	0.0010–0.010

Table V. Rate Constants for Nitrile-to-Amide Hydrolysis of the 2-Cyanopyridine *N*-Oxide Complex in Acidic Solution at 25 °C

[HClO ₄], M	ionic strength, M	10 ⁴ <i>k</i> _{obs} , s ⁻¹
0.0113	0.0113	(1.31 ± 0.02)
0.0113	0.023	(1.26 ± 0.05)
0.0113	0.057	(1.16 ± 0.02)
0.0113	0.10	(1.11 ± 0.03)
0.020	0.020	(1.19 ± 0.03)

both in the presence of and without hexaaquachromium(III) and eluted with the solvent front in each case. It was also observed that washing the Dowex resin with copious amounts of water before use retarded the release of pyridine *N*-oxide from reaction mixtures, but never enough to isolate a bound complex. However, the slow release from product mixtures can most readily be explained by slow decomposition of a chromium(III) product that is induced by the Dowex resin or a resin impurity. Therefore, we feel justified in assigning an inner-sphere mechanism to this electron transfer.

Nitrile Base Hydrolysis. Rate constants for the nitrile-to-amide base hydrolysis reaction of the 4-cyanopyridine complex are presented in Table IV. Each reported rate constant is the least-squares slope of a *k*(obsd) versus [OH⁻] plot consisting of from 10 to 16 data points. The least-squares intercept of each plot was 0 to ±1σ. The rate law for the reaction then is simple first order in Co(III) complex and first order in hydroxide concentrations. The Eyring plot of the data in Table IV yielded an enthalpy of activation of 12.4 ± 1.1 kcal mol⁻¹ and an entropy of activation of -0.8 ± 3.7 cal K⁻¹ mol⁻¹.

The rate law of the reaction is identical with that seen in earlier studies with other nitrile ligands.^{12,14,16} The activation parameters are also typical of this reaction.¹⁴ However, the rate constant is larger than any reported to date for a pentaamminecobalt(III) complex with the exception of those hydrolyses where neighboring group participation is a factor.²⁰ With use of the Hammett correlation reported for this reaction,¹⁶ the rate constant at 25 °C has been utilized to calculate a σ value of 1.19 for the γ-pyridine *N*-oxide moiety. Values of σ (and σ⁻ as well as σ⁰) reported in the literature vary widely for the *N*-oxide function owing to its ability to function as both an electron-donating and an electron-accepting group.²¹ However, our value does agree reasonably with the 1.14 value reported by Dimitrijevic et al.²² This may be rather fortuitous, since their study was performed in a different solvent (absolute ethanol). Nevertheless, it is obvious that the *N*-oxide group is acting as a strong electron-withdrawing group in the nitrile hydrolysis reaction.

Bound Nitrile Hydrolysis in Acidic Solution. Acid hydrolysis of a bound nitrile to a bound amide has been observed for ruthenium(III) complexes by Lavalley²³ but had never been observed with Co(III) complexes. Therefore, when the typical yellow-to-orange color change associated with this reaction was observed during our initial recrystallization of this complex from 1 M HClO₄, we were quite surprised. The infrared spectrum of this orange product indicated the absence of the nitrile function and was identical with the orange product obtained by treatment of the nitrile complex with base. Lavalley found that water was the active nucleophile with his Ru(III) nitrile complexes, and given the sensitivity of our synthesis to traces of water, we assumed a

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similar situation might apply. Table V presents kinetic data at differing ionic strengths in acidic solution. The observed rate constants do show a clear trend toward smaller values at higher ionic strengths. However, when we apply the revised Davies equation for ionic strength dependence²⁴ to the rate data, the charge on the attacking nucleophile (assuming the cation to be +3) is calculated to be -0.41. Therefore, the data would indicate

(24) Davies, C. W. *Ion Association*; Butterworths: London, 1962; p 41.

that even in 0.11 M perchloric acid, a hydroxide attack pathway is still operative. However, in order to account for the calculated charge, water must also contribute to the hydrolysis reaction. Since a similar reactivity is not present with the 4-cyanopyridine *N*-oxide complex, neighboring group participation by the *N*-oxide function adjacent to the nitrile group is indicated. To answer whether only water is being activated by the *N*-oxide group or both water and hydroxide requires further kinetic studies, which are under way at this time.

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Substitution Kinetics of *trans*-[O₂(Py)₄Tc]⁺ in Methanol, DMF, and MeOH/DMF Mixtures (Py = Pyridine, Picoline, and Lutidine)

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The substitution kinetics of [O₂(Py)₄Tc]⁺, where Py = pyridine, 4-methylpyridine, and 3,5-dimethylpyridine, have been studied with 4-aminopyridine, 4-(dimethylamino)pyridine, imidazole, ethylenediamine, cyanide, and cyclam as incoming ligands in alcohol and the first four also in DMF. In alcohols, the reaction proceeds by a solvent-mediated mechanism and is independent of both the incoming and leaving ligands. For the substitution of 4-(dimethylamino)pyridine onto [O₂(py)₄Tc]⁺ in methanol, $k = (2.41 \pm 0.02) \times 10^2 \text{ s}^{-1}$, $\Delta H^\ddagger = 97.6 \pm 3 \text{ kJ/mol}$, and $\Delta S^\ddagger = 63.5 \pm 2.5 \text{ J/(mol K)}$. In DMF the reactions proceed by a dissociative mechanism according to the rate law $d[\text{O}_2\text{A}_4\text{Tc}]/dt = k_1 k_2 [\text{O}_2(\text{Py})_4\text{Tc}][\text{A}] / (k_{-1}[\text{Py}] + k_2[\text{A}])$, where A is the incoming ligand. For the substitution of 4-(dimethylamino)pyridine onto [O₂(py)₄Tc]⁺ in DMF, $k_1 k_2 / k_{-1} = 0.18 \pm 0.03 \text{ s}^{-1}$ and $k_1 = 0.60 \pm 0.04 \text{ s}^{-1}$. Up to $X_{\text{MeOH}} = 0.1$, adding alcohol to DMF increases substitution rates; however, higher concentrations result in a decrease.

As a result of its central location in the periodic table, relatively small differences in solution environment or ligands often result in fairly large changes in the chemistry of the synthetic element technetium.^{1,2} It follows that technetium complexes may provide an excellent basis for systematically investigating the consequences of subtle effects on reactivity, geometry, and oxidation state of transition-metal ions. Compounds containing the oxo-technetium(V) cores [O=Tc]³⁺ and [O=Tc=O]⁺ are among the most common starting materials for the synthesis of new technetium compounds.³⁻⁸ These moieties also occur in radiodiagnostic imaging agents^{9,10} and are involved as intermediates in the formation of many lower valent complexes from [TcO₄]⁻. Despite their importance in synthesis, there have been few investigations of the reaction mechanisms of these ions.¹¹ Quantitative studies of the substitution kinetics of *trans*-dioxo-technetium(V) ions should provide insight into the reactivity of oxo complexes in general, facilitate the development of new technetium syntheses, and aid in deciphering the metabolic fates

of important technetium radiopharmaceuticals as well as in understanding their interactions with biological molecules.

An example of the effects generated by minor ligand modifications is seen in the net formation constants of mixed-valent μ -oxo technetium species, which vary by almost an order of magnitude for each methyl group added in the series py = pyridine, picoline, and lutidine, even though these groups present no appreciable steric hindrance.¹² The variation in isomerization constants ($K_{\text{iso}} = [\text{dissym}]/[\text{asym}]$) between the dissymmetric [Cl(Py)₄TcOTc(Py)Cl₄] and asymmetric [Cl(Py)₃ClTcOTc(Py)Cl₃(Py)] complexes in this series is less dramatic, increasing only by a factor of 3 in proceeding from pyridine to lutidine.¹² Complexes of the type *trans*-[O₂(Py)₄Tc]⁺ have recently been shown to be versatile synthetic starting materials, since the pyridine ligands are fairly easily substituted.^{6,13} As expected,⁶⁻⁸ substitution of the pyridine ligands occurs in a stepwise fashion, which Pearlstein and Davison have used to advantage in developing a synthetic route to a variety of mixed-ligand complexes with a combination of halides, alkoxides, and aromatic amines.¹³ In this study, the substitution kinetics of *trans*-[O₂(Py)₄Tc]⁺ are investigated in alcohol and DMF solvents in order to assess the effects of minor variations in ligand and variations in mechanism as a function of the solvent.

Abbreviations: Py, generic pyridine ligand; py, pyridine; pic, 4-picoline; lut, 3,5-lutidine; Apy, 4-aminopyridine; DMApy, 4-(dimethylamino)pyridine; Im, imidazole, en, ethylenediamine; cyclam, 1,4,8,11-tetraazacyclotetradecane.

Experimental Section

Synthesis. The starting material, [(*n*-Bu)₄N][TcOCl₄], was prepared from (NH₄)TcO₄ (Oak Ridge) by the method of Cotton (X = Cl).¹⁴

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