

Electron Transfer. 66. Mediation by Ligands Bearing a Remote Isonicotinoyl Group<sup>1</sup>

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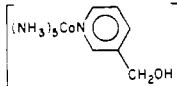
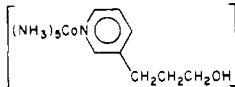
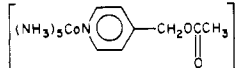
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Five aminohydrin complexes of  $(\text{NH}_3)_5\text{Co}^{\text{III}}$  have been prepared in which the coordinating nitrogen is separated from a remote OH by a variety of insulating fragments. These have been converted by acylation to isonicotinate, 4-pyC(=O)-, and nicotinate, 3-pyC(=O)-, ester derivatives. Specific rates for reductions of these complexes, using  $\text{Eu}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{U}^{3+}$ , and  $\text{Cr}^{2+}$ , are compared. All unacylated and nicotinoyl complexes are reduced at the low specific rates characteristic of straightforward outer-sphere reactions. Europium(II) reductions of the isonicotinoyl derivatives are markedly accelerated ( $10^3$ -fold) and are strongly autocatalytic; moreover, specific rates for the primary reductions in this group ( $k_{\text{Eu}}$  values) fall within an unusually narrow range and lie remarkably close to those for  $\text{Eu}^{2+}$  reductions of the liberated ligands (the initial step in the autocatalytic sequence). The primary reactions in this group constitute a clear-cut example of an electron-transfer reaction that proceeds by preliminary reduction of a ligand, i.e., the radical-ion or chemical mechanism. For reductions by  $\text{V}^{2+}$ , this mechanism does not compete effectively with the usual outer-sphere path. With  $\text{U}^{3+}$ -isonicotinoyl systems, striking rate enhancements pointing to operation of the chemical mechanism are again observed, but autocatalysis does not occur, due possibly to overreduction of the radical intermediate by excess  $\text{U}^{3+}$ . For Cr(II) reductions of the isonicotinoyl complexes, weak autocatalysis and modest enhancement attributable to a modification of the chemical mechanism (eq 6-9) are observed; attenuation of these effects probably occurs because departure of Cr(III) from the Cr(III)-bound radical is slow in comparison to homolysis of such a radical, re-forming Cr(II). Values of  $k_{\text{Cr}}$  fall far below (2-5 powers of 10) those for a number of isonicotinoyl-derived  $-\text{COOC}^{\text{III}}$  complexes featuring interrupted conjugation, confirming the earlier suggestion that a doubly bridged intermediate of type XVIII intervenes in the very rapid reactions by  $\text{Cr}^{2+}$  (but not necessarily in those by  $\text{Eu}^{2+}$ ). Discrepancies in behavior are noted between Co(III)-bound radicals generated by  $\text{Eu}^{2+}$  and the same radicals generated by action of  $\text{CO}_2^-$  or  $\cdot\text{C}(\text{CH}_3)_2\text{OH}$ ; such differences probably mirror specific ionic medium effects in systems featuring closely balanced competing reactions.

Several earlier papers<sup>2</sup> described systems in which an ordinarily sluggish reduction of a cobalt(III) complex by  $\text{Cr}^{2+}$ ,  $\text{Eu}^{2+}$ ,  $\text{V}^{2+}$ , or  $\text{U}^{3+}$  was markedly catalyzed by a noncoordinated pyridine derivative. Catalysts of this type have been shown to operate by undergoing preliminary one-electron reduction to aromatic radicals, which, in turn, are known<sup>3</sup> to react very rapidly with Co(III) centers.

A report appearing in 1979 dealt with attempts to prepare an intramolecular analogue of such catalytic systems in which the oxidizing and catalytic functions were incorporated into a single complex.<sup>4</sup> It was anticipated that initial reductive attack on such a difunctional species would occur at the catalytic center and that this would be followed by rapid electron transfer to Co(III), resulting in an overall rate of reduction that would be determined mainly by the rate of initiation. Such a reaction sequence would constitute a particularly well-defined example of reduction by the radical-ion or chemical mechanism.<sup>5-7</sup> The oxidants used were designed to preclude conjugative interaction (of the usual type) between

Table I. Pentaamminecobalt(III) Perchlorates Prepared by Direct Ligation

complex	heating time, min	temp, °C
$(\text{NH}_3)_5\text{CoNH}_2\text{CH}_2\text{CH}_2\text{OH}(\text{ClO}_4)_3$ (I) <sup>a</sup>	40	70
$(\text{NH}_3)_5\text{CoNH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}(\text{ClO}_4)_3$ (II) <sup>a</sup>	30	70
$(\text{NH}_3)_5\text{CoNH}_2\text{CH}_2\text{CH}_2\text{NHC}_2\text{H}_5(\text{ClO}_4)_3$ (III) <sup>a</sup>	25	30
 $(\text{ClO}_4)_3$ (IV) <sup>b</sup>	45	80
 $(\text{ClO}_4)_3$ (V) <sup>b</sup>	40	80
 $(\text{ClO}_4)_3$ (VII) <sup>b</sup>	40	90-95

<sup>a</sup> Prepared in dimethyl sulfoxide.<sup>16</sup> <sup>b</sup> Prepared in *N,N*-diethylacetamide.<sup>17</sup>

- (1) Joint sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant No. 8022881) is gratefully acknowledged.
- (2) (a) Norris, C.; Nordmeyer, F. *J. Am. Chem. Soc.* **1971**, *93*, 4044. (b) Fanchiang, Y.-T.; Carlson, R. R.; Thamburaj, P. K.; Gould, E. S. *Ibid.* **1977**, *99*, 1073. (c) Fanchiang, Y.-T.; Thomas, J. C.; Neff, V. D.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1942. (d) Fanchiang, Y.-T.; Gould, E. S. *Ibid.* **1977**, *16*, 2516; **1978**, *17*, 1138. (e) Loar, M. K.; Fanchiang, Y.-T.; Gould, E. S. *Ibid.* **1978**, *17*, 3689.
- (3) See, for example: Cohen, H.; Meyerstein, D. *Isr. J. Chem.* **1974**, *12*, 1049.
- (4) Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1979**, *18*, 1289.
- (5) The chemical mechanism for electron transfer between ligated metal centers has often been proposed<sup>6</sup> but much less frequently demonstrated.<sup>7</sup>
- (6) See, for example: (a) Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 3138. (b) Gould, E. S. *J. Am. Chem. Soc.* **1965**, *87*, 4730. (c) Nordmeyer, F.; Taube, H. *Ibid.* **1968**, *90*, 1162. (d) Diaz, H.; Taube, H. *Inorg. Chem.* **1970**, *9*, 1304. (e) Itzkowitz, M. M.; Nordmeyer, F. *Ibid.* **1975**, *14*, 2124.
- (7) (a) Hoffman, M. Z.; Simic, M. *J. Am. Chem. Soc.* **1972**, *94*, 1757. (b) Gould, E. S. *Ibid.* **1972**, *94*, 4360. (c) Srinivasan, V. S.; Rajasekar, N.; Singh, A. N.; Radlowski, C. A.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 2824.

the two centers by connecting them with a saturated insulating fragment, but since they were cobalt(III)-bound carboxyl derivatives, mechanistic ambiguities associated with possible initial attack at the carbonyl oxygen were encountered.

The oxidants chosen for the present extension feature  $\text{Co}^{\text{III}}-\text{N}$  linkages. The absence of carboxyl groups, both free and coordinated, leads to a more straightforward interpretation of redox behavior. Inclusion of the reductant U(III) adds further detail to the picture.

## Experimental Section

**Materials.** Solutions of  $\text{Eu}(\text{ClO}_4)_2$ ,<sup>8</sup>  $\text{V}(\text{ClO}_4)_2$ ,<sup>9</sup>  $\text{U}(\text{ClO}_4)_3$ ,<sup>10</sup>  $\text{V}(\text{ClO}_4)_3$ ,<sup>11</sup> and  $\text{Cr}(\text{ClO}_4)_2$ <sup>12</sup> were prepared as described. Organic

- (8) (a) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673. (b) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.
- (9) (a) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769. (b) Linck, R. G. *Inorg. Chem.* **1970**, *9*, 2529.
- (10) Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 330.

ligands (Aldrich products) were used as received. Predried dimethylformamide, employed in acylations, was stored over molecular sieves (Linde 4-Å) for several days before use. Triethylamine was refluxed with phthalic anhydride and then distilled from this reagent in order to remove traces of primary amines, secondary amines, and water. 4-Pyridylmethyl acetate, 4-pyCH<sub>2</sub>OAc, was prepared by acetylation of the corresponding alcohol as described.<sup>13</sup> Isonicotinic and nicotinic anhydrides were prepared, under rigorously dry conditions, by modifications of the procedures of Rinderknecht<sup>14</sup> and stored in a vacuum desiccator. Aquopentaamminecobalt(III) bromide,<sup>15</sup> (carbonato)pentaamminecobalt(III) nitrate,<sup>12</sup> and aquopentaamminecobalt(III) perchlorate<sup>12</sup> were prepared as described. For experiments with Co<sup>III</sup>-U<sup>III</sup> systems, it was essential that the oxidants be nitrate free;<sup>10</sup> in such instances, cobalt complexes were prepared from nitrate-free aquo perchlorate, which was, in turn, obtained from the aquo bromide by recrystallizing twice from dilute HClO<sub>4</sub>.

**Preparations of Cobalt(III) Complexes.** N-bound (NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup> complexes of ethanolamine, 3-amino-1-propanol, and *N*-ethylethanediamine (C<sub>2</sub>H<sub>5</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) were prepared by the method of Sargeson and co-workers,<sup>16</sup> in which 7 g of aquopentaamminecobalt(III) perchlorate was first converted to the corresponding dimethyl sulfoxide derivative by treatment with 20 mL of the sulfoxide. The N-donor ligand (5–10 mL) was then added to the resulting solution while heating and stirring were maintained. Heating times and temperatures are listed in Table I. The reaction mixture was then cooled and washed with ether, and the washings were discarded. To the oily residue was then added 20 mL of ethanol with stirring, after which the product was reprecipitated with 150 mL of ether. After further successive washings with ether, benzene, and again with ether, the product was dissolved in 30 mL of water and then precipitated as a solid by dropwise addition of concentrated HClO<sub>4</sub>. The crude complex was filtered off and dissolved in a minimum volume of cold water; the resultant mixture was then loaded on a column of Bio-Gel P-2. Elution with water yielded a violet forerun and then the desired orange product. The latter fraction was then concentrated by rotary evaporation at 45 °C, yielding a yellow solid that was recrystallized from 2 M HClO<sub>4</sub>. In the case of the very soluble complex of *N*-ethylethanediamine acidification was omitted, and separation on Bio-Gel was followed by rotary evaporation, precipitation by addition of ethanol, and then recrystallization from aqueous NaClO<sub>4</sub>; the resulting product was the nonprotonated tris(perchlorate).

Attempted analogous preparations of the complexes of *N*-methyl- and *N*-phenylethanediamine and that of piperazine were unsuccessful despite several procedural modifications.

Pyridine-derived complexes were prepared in *N,N*-diethylacetamide by the method of Johnson.<sup>17</sup> Separations on Bio-Gel were used for this group of complexes as well.<sup>18</sup> The ester function on the 4-CH<sub>2</sub>OAc complex (VI) was hydrolyzed by heating in 0.5 M HClO<sub>4</sub> at 90–95 °C for 7 h, after which the resulting 4-CH<sub>2</sub>OH derivative was isolated by evaporation, chromatography on Bio-Gel, and precipitation with HClO<sub>4</sub> in the usual manner.

Acylated complexes (nicotinoyl and isonicotinoyl derivatives) were prepared by dissolving 0.5–0.8 g of the parent complex in a minimum volume of dry dimethylformamide. Ten drops of dry triethylamine and 2.0 g of the appropriate anhydride were added. The preparation was protected from atmospheric moisture while stirring was maintained for 1 h. The reaction mixture was then washed, first with ether, then with benzene containing 3 mL of triethylamine, then with benzene alone, and, finally, with ether alone. All washings were discarded. The resulting oil was dissolved in an equal volume of water and filtered. Dropwise addition of concentrated HClO<sub>4</sub> to the filtrate precipitated

the acylated complex as its protonated tetrakis(perchlorate), which was recrystallized from dilute HClO<sub>4</sub>.

Analyses and spectral characteristics of cobalt(III) complexes prepared here for the first time are given in Table II.

**Rate Measurements.** Rates were estimated from measurements of absorbance decreases on the Cary 14 or Beckman Model 5260 recording spectrophotometer or the Durrum-Gibson stopped-flow spectrophotometer as described.<sup>6b,12,19</sup> Measurements were made at 475 nm. Except for special cases described below, reactions were first order each in Co(III) and reductant but were generally carried out under pseudo-first-order conditions with at least a 10-fold excess of reductant. Reductions with U<sup>3+</sup> were run in 0.20 M HClO<sub>4</sub>, and those with the other reductants were carried out in 1.0 M HClO<sub>4</sub>. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run agreed to within 6%, and average values did not differ significantly from those obtained from logarithmic plots of absorbance differences against reaction times. Specific rates obtained from replicate runs on the Cary or Beckman spectrophotometer checked to better than 10%, whereas reactions on the Durrum (with the same pair of master solutions) were repeated until decay curves for three consecutive runs were superimposable. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

The more rapid europium(II) reductions, each involving an isonicotinoyl derivative, yielded, instead of logarithmic curves, decay traces that were very nearly linear, indicating strong autocatalysis of the type previously noted.<sup>4,8</sup> Reactions showing such behavior were followed essentially to completion. When the fastest reactions in this group were carried out in the presence of a large excess of Eu<sup>3+</sup>, autocatalysis were severely inhibited<sup>11</sup> and nearly normal first-order curves were obtained. Some reductions with vanadium(II) and chromium(II) also exhibited evidence for autocatalysis, but this was much less pronounced. No autocatalysis was observed in the (much faster) reductions by U<sup>3+</sup>.

**Stoichiometric Studies.** Stoichiometry experiments, in which Co(III) and a ligand bound to it were allowed to compete for a deficient quantity of U<sup>3+</sup> or Eu<sup>2+</sup>, were carried out as described.<sup>4,12,17</sup> Results are presented in Table III. The procedure was standardized by using the formate derivative of (NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>, which is known to react rapidly with both reductants, giving Co<sup>2+</sup> quantitatively.<sup>8b,10</sup> The more sluggishly reacting systems, including all those involving V<sup>2+</sup> and Cr<sup>2+</sup>, were not examined in this manner, since in such cases the reductant is partially consumed by oxygen that slowly diffuses into the vessel, thus complicating interpretation of the results.<sup>4</sup>

## Results and Discussion

The nearly quantitative yields of Co(II) resulting from U<sup>3+</sup> reduction of the three unacylated aliphatic complexes (Table III, X = H) are expected, for these ligands are devoid of reducible functions. Reductions of the unacylated pyridine complexes IV–VI likewise proceed without complication, for the pyridine rings have no electron-withdrawing groups that would facilitate reduction of the ring system. Departures from 1:1 stoichiometry among the nicotinoyl-substituted complexes (X = Nic) are measureable but slight, for although U<sup>3+</sup> has been shown to reduce nicotinate-related species,<sup>2c</sup> these reductions are generally slow, due, in large part, to a relatively unfavorable difference in formal potentials. Reduction of the unacylated and nicotinoyl ligands by the less powerful reductants, Eu<sup>2+</sup>, V<sup>2+</sup>, and Cr<sup>2+</sup>, may likewise be assumed to compete negligibly with reduction of Co(III). For each of the isonicotinoyl-substituted complexes (X = Inic), reductions by Eu<sup>2+</sup> and U<sup>3+</sup> are rapid, and yields of Co<sup>2+</sup> substantially below 100% are obtained, reflecting the ease with which 4-pyC(=O)– species undergo reduction.<sup>20,21</sup> Partial ligand reduction should not, in itself, lead to major errors in the observed

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(13) French, J. E.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 6951.

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(15) Schlessinger, G. C. "Inorganic Laboratory Preparations"; Chemical Publishing Co.: New York, 1962; p 209.

(16) Gainsford, A. R.; Pizer, R. D.; Sargeson, A. M.; Whimp, P. O. *J. Am. Chem. Soc.* **1981**, *103*, 792.

(17) Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1929. Ligand leading to the acetoxy-substituted complex, VII, was carried out under N<sub>2</sub>.

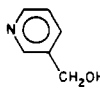
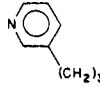
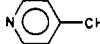
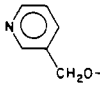
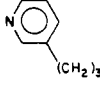
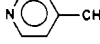
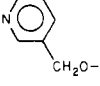
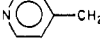
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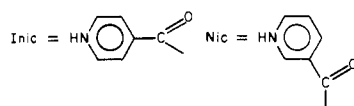
(20) The recognized<sup>2c,21</sup> stabilization of a pyridyl radical by a γ-C=O substituent (in contrast to the corresponding β-C=O substituent) is doubtless a conjugative effect. In valence-bond terminology, structures in which the unpaired electron is situated on the pyridine nitrogen atom may contribute to the γ radical, but not that of the β.

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Table II. Analyses of Pentaamminecobalt(III) Complexes of N-Donor Ligands

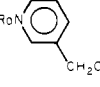
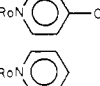
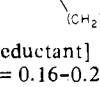
ligand R	% C		% H		% Co		$\lambda_{\max}$ , nm	$\epsilon_1^a$	$\lambda_{\max}$ , nm	$\epsilon_2^a$
	calcd	found	calcd	found	calcd	found <sup>b</sup>				
Unacylated Complexes, $R(\text{NH}_3)_5\text{Co}(\text{ClO}_4)_3$										
$\text{NH}_2(\text{CH}_2)_2\text{OH}$ (I)	4.77	4.83	4.37	4.17	11.7	11.4	478	63	341	53
$\text{NH}_2(\text{CH}_2)_3\text{OH}$ (II)	6.96	6.94	4.64	4.59	11.4	11.4	476	67	341	58
 (IV)	13.10	13.28	3.99	4.07	10.7	10.6	474	64	335	63
 (V)	16.60	16.42	4.49	4.29	10.2	10.0	474	67		
 (VII)	16.20	16.43	4.04	4.12	9.9	10.0	474	70		
Isonicotinoyl Derivatives, $R(\text{NH}_3)_5\text{Co}(\text{ClO}_4)_4^c$										
$\text{NH}_2(\text{CH}_2)_2\text{O-Inic}$ (VIII)	13.54	13.68	3.67	3.73	8.3	8.4	478	68	337	74
$\text{NH}_2(\text{CH}_2)_3\text{O-Inic}$ (IX)	14.94	15.06	3.87	3.75	8.2	8.4	477	69	340	76
 (X)	19.02	18.85	3.43	3.62	7.8	7.3	473	59	336	62
 (XI)	21.40	21.62	3.82	3.91	7.5	7.3	474	66		
 (XII)	19.02	19.25	3.43	3.60	7.8	7.6	474	67	335	73
$\text{NH}_2(\text{CH}_2)_2\text{N}(\text{C}_2\text{H}_5)\text{Inic}$ (XIII)	16.30	16.47	4.21	4.31	8.0	7.9	480	70	330	98
Nicotinoyl Derivatives, $R(\text{NH}_3)_5\text{Co}(\text{ClO}_4)_4^c$										
$\text{NH}_2(\text{CH}_2)_2\text{O-Nic}$ (XIV)	13.54	13.38	3.67	3.86	8.3	8.4	478	69	340	60
$\text{NH}_2(\text{CH}_2)_3\text{O-Nic}$ (XV)	14.94	14.75	3.87	3.83	8.2	8.1	478	68	340	58
 (XVI)	19.02	18.95	3.43	3.60	7.8	7.4	474	64	336	62
 (XVII)	19.02	19.08	3.43	3.50	7.8	7.1	475	68	330 <sup>d</sup>	74

<sup>a</sup> Extinction coefficients in  $\text{M}^{-1} \text{cm}^{-1}$ . <sup>b</sup> See ref 12. <sup>c</sup> Structures for isonicotinoyl (Inic) and nicotinoyl (Nic):



<sup>d</sup> Shoulder.

Table III. Yields of Co(II) from Reductions of Pentaamminecobalt(III) Complexes with Europium(II) and Uranium(III)<sup>a</sup>

complex <sup>b</sup>	% yield of $\text{Co}^{2+}$			
	X = H $\text{U}^{3+}$	X = Inic		X = Nic $\text{U}^{3+}$
$\text{RoNH}_2(\text{CH}_2)_2\text{O-X}$	97	93	91	98
$\text{RoNH}_2(\text{CH}_2)_3\text{O-X}$	99	92	89	96
$\text{RoNH}_2(\text{CH}_2)_2\text{NH}(\text{C}_2\text{H}_5)\text{X}$	96	90	74	
	98	86	88	92
	98	93	64	96
	98	90	91	

<sup>a</sup> [reductant] = 0.003–0.004 M; [oxidant] = 0.009–0.012 M;  $[\text{H}^+] = 0.16\text{--}0.20$  M. Reductant was added to  $\text{Co(III)}$ . <sup>b</sup> Ro = "roseo" =  $(\text{NH}_3)_5\text{Co}^{\text{III}}$ ; see Table II for structures of Inic and Nic.

specific rates, which are measured with the reductant in large excess, but its occurrence carries with it strong mechanistic implications.

Of the kinetic data assembled in Table IV, the rate constants pertaining to reductions by  $\text{Eu}^{2+}$  ( $k_{\text{Eu}}$  values) are the most informative. Specific rates for the unacylated pyridyl-carbinol derivatives, IV, V, and VI, lie very close to that for  $(\text{NH}_3)_5\text{Co}(\text{py})^{3+}$  ( $0.083 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>8a</sup> (which may be considered to be a parent species) and are about 10 times those for the aliphatic aminoalcohol complexes, I and II. This difference, which is observed also for reductions by  $\text{V}^{2+}$  and  $\text{U}^{3+}$ ,<sup>22</sup> doubtless reflects partial electron withdrawal from  $\text{Co(III)}$ -bound nitrogen by the aromatic ring system, an effect which has been shown<sup>23</sup> to facilitate outer-sphere electron transfer. Moreover, conversion of the remote OH groups in

(22) The Marcus model for outer-sphere electron-transfer reactions stipulates that the relative rates pertaining to a series of oxidants should be independent of the reductant taken. See, for example: Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(23) (a) Bifano, C.; Linck, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 3945. (b) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

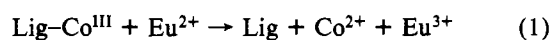
Table IV. Specific Rates of Reduction of Pentaamminecobalt(III) Complexes of N-Donor Ligands<sup>a</sup>

oxidant <sup>b</sup>	$k_{Eu}$	$k_V$	$k_U$	$k_{Cr}$
[RoNH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> OH] <sup>3+</sup> (I)	0.0093 <sup>d</sup>	0.055	5.6	
[RoNH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> OH] <sup>3+</sup> (II)	0.0085 <sup>d</sup>	0.034	3.5	
(IV)	0.079	0.34	54 <sup>c</sup>	
(V)	0.066	0.26	47 <sup>c</sup>	
(VI)	0.10	0.35	60 <sup>c</sup>	0.0044
(VII)		0.49		
[RoNH <sub>2</sub> (CH <sub>2</sub> O-Inic)] <sup>4+</sup> (VIII)	7.4 <sup>e</sup>	0.12 <sup>f</sup>	1.4 × 10 <sup>4</sup>	
[RoNH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> O-Inic] <sup>4+</sup> (IX)	3.7 <sup>e</sup>	0.051 <sup>f</sup>	1.2 × 10 <sup>4</sup>	0.0088 <sup>d,g</sup>
(X)	12.0 <sup>e</sup>	0.68 <sup>f</sup>	1.5 × 10 <sup>4</sup>	
(XI)	4.9 <sup>e</sup>	0.29	1.0 × 10 <sup>4</sup>	
(XII)	18.5 <sup>e</sup>		4.5 × 10 <sup>4</sup>	0.0088 <sup>d,g</sup>
(XIII)	0.11		43	
[RoNH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> O-Nic] <sup>4+</sup> (XIV)	0.012 <sup>d</sup>	0.079	10	
[RoNH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> O-Nic] <sup>4+</sup> (XV)	0.010	0.040	5.3	
(XVI)	0.13	0.62		
(XVII)	0.30	0.60	1.5 × 10 <sup>2c</sup>	

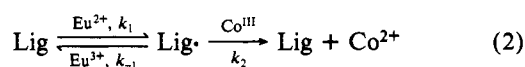
<sup>a</sup> Specific rates are in M<sup>-1</sup> s<sup>-1</sup> at 25 °C. Reductions with U(III) were carried out in 0.20 M HClO<sub>4</sub> unless otherwise noted. Reductions with Eu(II), V(II), and Cr(II) were run in 1.0 M HClO<sub>4</sub>. <sup>b</sup> Ro = "roseo" = (NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>; see Table II for structures of Inic and Nic. <sup>c</sup> Reactions in 0.50 M HClO<sub>4</sub>. <sup>d</sup> Values obtained from initial rates. <sup>e</sup> Strong autocatalysis observed (see text). <sup>f</sup> Moderate autocatalysis observed; this could be suppressed by addition of V(ClO<sub>4</sub>)<sub>3</sub> (V(III)/Co(III) = 30).<sup>11</sup> <sup>g</sup> Moderate autocatalysis observed.

these oxidants to nicotinate (3-pyridinecarboxylate) esters (complexes XIV–XVII) leads to only marginal accelerations.

Incorporation of a remote isonicotinate (4-pyridinecarboxylate) function, however, results not only in 10<sup>3</sup>-fold rate enhancements but also in a fundamental alteration of the kinetic picture, for reductions of the ester derivatives VIII–XII with excess Eu<sup>2+</sup> yield traces that are nearly linear rather than logarithmic, pointing to strong autocatalysis by the ester ligand liberated in the initial reduction<sup>2a,4,8</sup>



Superposition of the catalytic process, which has been demonstrated<sup>2</sup> to operate via sequence 2 onto the primary reaction,



$$\text{rate} = [\text{Eu}^{2+}][k_1x + k_{Eu}(a - x)] \quad (3)$$

leads,<sup>4</sup> when Eu<sup>2+</sup> is taken in excess, to rate law 3, where *a* represents the initial concentration of Co(III), *x* the extent

of reaction, and  $k_{Eu}$  the specific rate of the uncatalyzed reaction. With Eu<sup>2+</sup> in large excess, its concentration remains nearly constant and  $k_{Eu}$  and  $k_1$  may be estimated from the slope of the kinetic curve at the beginning and near the end of the reaction. Such specific rates, pertaining to the isonicotinate-substituted oxidants, are compared in Table V. Note that when  $k_{Eu}$  and  $k_1$  are nearly equal, a linear kinetic profile results.

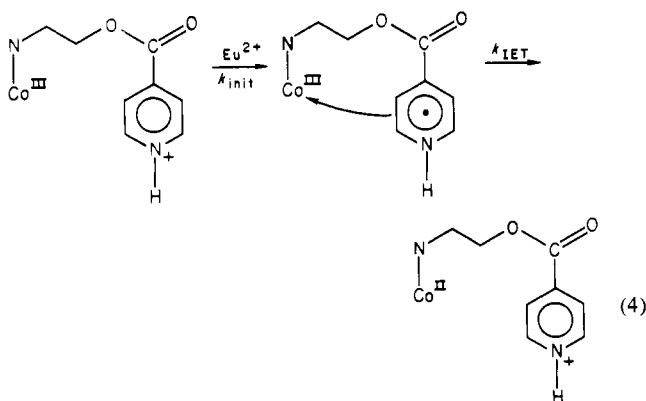
Despite the wide structural variation among isonicotinate complexes VII–XII, values of  $k_{Eu}$  are seen to fall within a remarkably narrow range. Even more striking is the similarity between  $k_{Eu}$  (pertaining to the primary reaction) and  $k_1$  (pertaining to reduction of the free ligand) for each complex. It is thus difficult to avoid the conclusion that all specific rates listed in Table V are determined, to a major extent, by a common process, the transfer of an electron from Eu<sup>2+</sup> to the isonicotinate function, and that the rate of this transfer is but slightly altered by modification of the remainder of the ligand and virtually unaffected by ligation of the remote donor nitrogen to Co<sup>III</sup>. The primary reactions then constitute an unusually clear-cut example of an electron transfer between

Table V. Specific Rates for the Uncatalyzed and Ligand-Catalyzed Reductions, with Europium(II), of Cobalt(III) Complexes Having a Remote Isonicotinate Ester Function<sup>a</sup>

complex <sup>b</sup>	$k_{Eu}^c$	$k_1^d$
$[RoNH_2(CH_2)_2O-Inic]^{4+}$ (VIII)	7.4	9.5
$[RoNH_2(CH_2)_3O-Inic]^{4+}$ (IX)	3.7	4.4
$[Ro-N(CH_2)_2O-Inic]^{4+}$ (X)	12.0	16
$[RoN(CH_2)_3O-Inic]^{4+}$ (XI)	4.9	4.9
$[RoN(CH_2)_2O-Inic]^{4+}$ (XII)	18.5	19

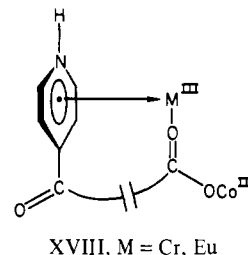
<sup>a</sup> Specific rates are in  $M^{-1} s^{-1}$  at 25 °C; reaction medium 1.0 M  $HClO_4$ . <sup>b</sup> Ro = "roseo" =  $(NH_3)_5Co^{III}$ ; for structure of Inic, see Table II. <sup>c</sup> Specific rates for the uncatalyzed reductions, evaluated from initial slopes of nearly linear kinetic curves (see text). <sup>d</sup> Specific rates for the initial step ( $Eu^{2+} + Lig \rightarrow Eu^{3+} + Lig$ ) of the ligand-catalyzed reaction, evaluated from the slopes of kinetic curves during the last 5–10% reaction (see text).

metal clusters that proceeds by preliminary reduction of a ligand, i.e., by the radical-cation or chemical mechanism<sup>5–7</sup>



Structural variation within this series would be expected to affect the specific rate of internal electron transfer,  $k_{IET}$ , but this step may be presumed to be much more rapid than the initiation step.<sup>24–26</sup>

The isonicotinoyl-substituted complexes VIII–XII differ from the oxidants considered in earlier related studies,<sup>4,27</sup> in which  $Co(III)$  was bound to the remainder of the mediating ligand through a carboxyl function. Observed rate enhancements in reductions of the latter derivatives were attributed, with some reservation, to the intermediacy of chelated structures of type XVIII, in which  $Cr^{III}$  or  $Eu^{III}$  was presumed



to be attached both to the carboxyl group and, by  $\pi$  bonding, to the pyridine ring. However, the persistence of enhanced  $k_{Eu}$  values in the systems at hand, which are devoid of the  $-COOC^{III}$  unit, demonstrates that intervention of such doubly bridged intermediate is not essential to the more rapid reactions by this lanthanide center.<sup>28</sup> Initial attack by  $Eu^{2+}$ , predominantly an inner-sphere process,<sup>2c</sup> then occurs mainly at the carbonyl function of the isonicotinoyl group.

Note that the accelerating action of isonicotinate becomes markedly diminished when it is incorporated as a substituent on the *N*-ethylated diamine ligand (complex XIII). This attenuation probably mirrors a combination of two factors. Isonicotinamide itself is known to react with  $Eu^{2+}$  only about one sixth as rapidly as do isonicotinic esters.<sup>29</sup> Moreover, attachment of both an ethyl and an ethylene group to the atom (nitrogen) adjacent to the carbonyl undergoing attack would be expected to be reflected in a further decrease. Consideration of related carboxylato systems<sup>30</sup> suggests at least a second 6-fold drop in rate, and this steric effect may be bolstered by the recognized inflexibility<sup>31</sup> of the peptide system.

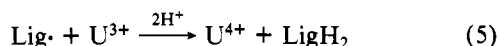
In contrast to  $Eu^{2+}$  reactions, the reductions by  $V^{2+}$  in the present series give no hint of rate increases stemming from incorporation of the isonicotinoyl group. The difference is not unexpected, for  $V^{2+}$  is known<sup>2c</sup> to reduce related heterocyclic systems only  $10^{-3}$  to  $10^{-2}$  times as rapidly as does  $Eu^{2+}$ ,<sup>32–34</sup> whereas outer-sphere reductions of  $Co(III)$  are almost invariably about 3 times as rapid for  $V^{2+}$  as for  $Eu^{2+}$ .<sup>23b</sup> Hence, in this case, reduction via the chemical mechanism can no longer compete effectively with the usual outer-sphere path, which involves only interaction between the metal centers. Slight, but perceptible, autocatalysis is observed for three of the V(II)-isonicotinoyl systems near the conclusions of the reactions, at which point ( $Co^{III}$ ) has become small and the concentration of the ligand relatively large. Thus, we see, as in earlier instances,<sup>2c,d,34b</sup> that under properly adjusted conditions  $V^{2+}$  reduction of pyridine ring systems may assume a mechanistic role.

- (24) No instance appears to have been reported in which an internally mediated reduction of bound  $Co(III)$  by  $Eu^{2+}$  (as distinguished from reduction catalyzed by an external species) is retarded by addition of excess  $Eu^{3+}$ . The implication is that internal electron transfer is rapid enough to preclude chemical diversion of the radical-cation intermediate. It may also be inferred that the departure from 1:1 stoichiometry observed in this series (Table III) reflect reduction of the ligand after its release in the primary reaction rather than irreversible reduction before reduction of  $Co(III)$  (as has been observed for nitro-substituted complexes).<sup>25</sup> Neither bimolecular radical-radical reactions (dimerization or disproportionation) nor "overreduction" of the radical by a second  $Eu^{2+}$  ion<sup>28</sup> would be expected to compete significantly with the indicated rapid internal electron transfer.
- (25) (a) Gould, E. S. *J. Am. Chem. Soc.* **1966**, *88*, 2983. (b) Reid, R.; Fan, F.-R. F.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 2766.
- (26) See, for example: Singh, A. N.; Radlowski, C. A.; Reed, J. W.; Krishnamurthy, V. V.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 211.
- (27) Srinivasan, V. S.; Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 2094.

- (28) We cannot exclude the possibility that  $Eu^{2+}$  reductions of the earlier  $-COOC^{III}$  complexes<sup>4,27</sup> proceed in part through intermediates analogous to XVIII, especially since a number of reported specific rates exceed the  $k_{Eu}$  values for VIII–XII. For evidence against similarly bridged intermediates in  $Eu(II)$  reductions of  $Co(III)$ , as catalyzed by isonicotinoyl systems featuring interrupted conjugation, see: Ram, M. S.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 2454.
- (29) Radlowski, C. A.; Chum, P.-W.; Hua, L.; Heh, J.; Gould, E. S. *Inorg. Chem.* **1980**, *19*, 401.
- (30) Reduction, by  $Eu^{2+}$ , of the diethylacetato derivative of  $(NH_3)_5Co^{III}$  has been reported by Fan<sup>8b</sup> to proceed one-sixth as rapidly as that of the corresponding acetato complex under similar conditions. The comparative steric situations about the carbonyl groups in these complexes are analogous to those in isonicotinamide itself and the *N,N*-disubstituted isonicotinamido complex XIII.
- (31) See for example: Robin, M. B.; Bovey, F. A.; Basch, B. In "The Chemistry of the Amides"; Zabicky, J. Ed.; Wiley-Interscience: New York, 1970; p 34.
- (32) The relatively slow reduction of isonicotinoyl systems by  $V^{2+}$  may be reasonably attributed to the insufficiently negative potential ( $E^\circ = -0.242$  V) associated with this center, rather than to the limit on inner-sphere rates imposed by sluggish substitution on V(II).<sup>9,33</sup> A number of inner-sphere reductions by  $V^{2+}$  have been found to proceed at specific rates several times the  $k_V$  values in Table IV.<sup>34</sup>
- (33) Sutin, N. *Acc. Chem. Res.* **1968**, *1*, 225.
- (34) (a) Price, H. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1. (b) Chen, J. C.; Gould, E. S. *J. Am. Chem. Soc.* **1973**, *95*, 5539.

Reductions by  $U^{3+}$ , like those by  $Eu^{2+}$ , are strikingly accelerated by attachment of the isonicotinate ester function. Here, again, we are doubtless seeing reduction by the chemical mechanism, for the  $k_U$  values pertaining to the isonicotinate complexes VIII–XII not only fall very close to each other but also lie near the reported<sup>2e</sup> specific rate for the 1e reduction, by  $U^{3+}$ , of isonicotinic acid ( $2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  at  $\mu = 0.50$ ). But there is a serious complication here—under our conditions,  $U^{3+}$  reactions exhibit no autocatalytic component.

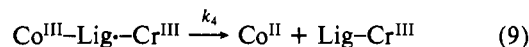
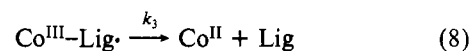
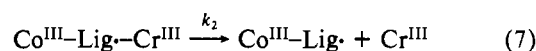
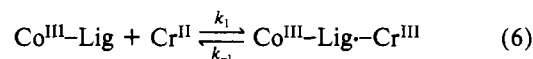
This absence of autocatalysis cannot reasonably be ascribed to a "blocking off" of the catalytic site by coordination to U(IV) (as appears to be the case in some Cr(II)–Cr(III) systems),<sup>35</sup> for ligand substitution about U(IV) centers has been found to be rapid.<sup>2e</sup> However, the substantial departures from 1:1 stoichiometry ( $Co^{2+}$  released/ $U^{3+}$  taken) observed for  $U^{3+}$ –isonicotinate reactions (Table III) provide a clue as to what may be happening. The low yields of  $Co^{2+}$  indicate not only that  $U^{3+}$  reduces the free ligand in such systems but also that the radical produced is diverted irreversibly to one or more species that do not readily reduce Co(III). Because of the strongly negative potential associated with  $U^{3+}$  ( $E^\circ = -0.63 \text{ V}$ ),<sup>36</sup> the degree of conversion to the isonicotinoyl radical, under steady-state conditions, should be much greater than is the case with  $Eu^{2+}$  or  $V^{2+}$ . Hence, the irreversible bimolecular reactions (dimerization and disproportionation), which consume the radicals, would be expected to become more prominent. More important, overreduction of the radical to an unreactive dihydro species (reaction 5), a process that has



been found to intrude in certain catalyzed reductions by Eu(II),<sup>26</sup> may become the principal fate of the aromatic radicals generated by  $U^{3+}$  in our kinetic experiments. This could be the case if the specific rates for overreduction of the radical by  $U^{3+}$  were comparable to, or greater than, those for its reaction with Co(III) ( $10^4$ – $10^6 \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>2b,d</sup> for the ratio ( $U^{3+}$ )/(Co(III)) is near 10 at the beginning of these reactions and becomes much greater as the reactions proceed.<sup>37</sup>

The  $Cr^{2+}$  reductions of isonicotinate derivatives IX and XII, although slow, proceed at twice the specific rate exhibited by the unacylated oxidant VI and also by several related pyridine complexes.<sup>8a,38</sup> Such enhancements are so small that we would hesitate to rationalize them on a structural basis were it not for the attendant occurrence of autocatalysis, indicating that in these systems, as is the case with reductions by  $Eu^{2+}$ , electron transfer to the isonicotinoyl function is playing an auxiliary role, which, in this instance, is perceptible only because the usual outer-sphere reactions by  $Cr^{2+}$  are unusually sluggish.<sup>23b</sup> The effects due to radical-cation intervention are about  $10^{-3}$  times the magnitude of those here observed for  $Eu^{2+}$ , an attenuation that is much too marked to be attributed merely to the lower rate of initiation by  $Cr^{2+}$ .<sup>39</sup> An essential difference between the two reductants is that Eu(III), formed in the initial act of electron transfer from  $Eu^{2+}$ , becomes separated almost immediately from the aromatic radical intermediate whereas Cr(III), a substitution-inert center, lingers.

With this aspect in mind, we may represent a Co(III)–Cr(II) reaction proceeding by the chemical mechanism as the sequence (6)–(9). Application of the steady-state approxi-

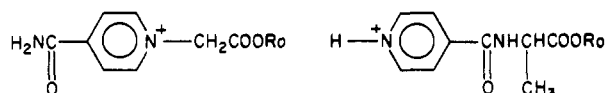
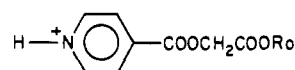
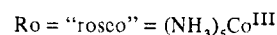


mation to the two radical intermediates leads to rate law 10.

$$\text{rate} = d[\text{Co}^{\text{II}}]/dt = [\text{Co}^{\text{III}}\text{-Lig}][\text{Cr}^{\text{II}}] \frac{k_1(k_2 + k_4)}{k_{-1} + k_2 + k_4} \quad (10)$$

If  $k_2$  (pertaining to the heterolysis of  $\text{Co}^{\text{III}}\text{-Lig-Cr}^{\text{III}}$ ) or  $k_4$  (pertaining to its collapse into products), or both of these, greatly exceeds  $k_1$  (pertaining to reversal of the initial transfer), the overall reaction rate would be determined by  $k_1$ , as is the case for  $Eu^{2+}$  and  $U^{3+}$ . When, however,  $k_{-1}$  is much greater than either  $k_2$  or  $k_4$ , the loss of  $Cr^{\text{III}}$  from  $\text{Co}^{\text{III}}\text{-Lig-Cr}^{\text{III}}$  constitutes a kinetic bottleneck, the net rate becomes a more complex function of the four individual  $k$  values, and the apparent specific rate falls to a small fraction of  $k_1$ . A closely analogous treatment, leading again to two limiting kinetic situations, applies to catalysis by the liberated ligand.<sup>40</sup>

The  $k_{Cr}$  values recorded here fall far below the specific rates, reported previously,<sup>4,27</sup> for (carboxylato)cobalt(III) complexes XIX–XXI, in which conjugation between the pyridine ring

XIX,  $k_{Cr} = 660$ XX,  $k_{Cr} = 13.1$ XXI,  $k_{Cr} = 4.2$ 

and  $-\text{COOCo}^{\text{III}}$  is interrupted by a saturated fragment. With oxidants of the latter type, as in the present series, rate enhancements disappear if isonicotinoyl is replaced by the more difficultly reducible<sup>20</sup> nicotinoyl group. Our results then confirm the earlier conclusion<sup>4</sup> that both the ligated carboxyl and the isonicotinoyl functions contribute, in a major fashion, to the more striking accelerations observed with  $Cr^{2+}$ .<sup>41</sup> A doubly bridged intermediate of type XVIII thus remains a reasonable possibility for reductions by  $Cr^{2+}$ ,<sup>42</sup> although, as we have seen, there is serious doubt as to its intervention in  $Eu^{2+}$  systems.

Finally, this work bears upon the question as to whether a radical formed by inner-sphere  $Eu^{2+}$  reduction (which therefore occupies, shortly after its generation, a position in the secondary coordination sphere of  $Eu^{3+}$ ) behaves in the same

(35) Fanchiang, Y.-T.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 1142.

(36) Ahrland, S.; Liljenzin, J. O.; Rydberg, J. "Comprehensive Inorganic Chemistry"; Pergamon Press: Oxford, 1973; Vol. 45, p 519.

(37) Note, however, that catalysis of U(III)–Co(III) reactions by uncoordinated isonicotinoyl derivatives has been observed<sup>2e</sup> in systems where the ratio U(III)/Co(III) is near  $10^{-2}$ . In such instances, serious deterioration of the catalyst occurs.

(38) (a) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792. (b) Wang, Y.; Gould, E. S. *Ibid.* **1969**, *91*, 4998.

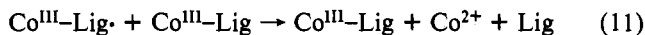
(39) Measurements by Fanchiang<sup>35</sup> indicate that 1e reductions of pyridine-carboxylic esters by  $Cr^{2+}$  are about one-tenth as rapid as the corresponding reductions by  $Eu^{2+}$ .

(40) A corollary to this argument is that Cr(III)-bound radicals reduce Co(III) centers much more slowly than do the corresponding nonligated radicals. While a significant difference in this direction is to be expected on the electrostatic basis alone, direct confirmation of this conclusion is desirable.

(41) In terms of the sequence (6)–(9), interposition of a carboxyl group between Co(III) and the isonicotinoyl function suffering primary attack would be expected to decrease  $k_{-1}$  and increase  $k_4$ , leading to a rate determined, as in the case of Eu(II) reactions, largely by  $k_1$ .

(42) Recall also that Cr(III) is found to be bound to the carboxyl group in the primary product formed from  $Cr^{2+}$  reduction of complex XIX, thus pointing to chromium-carboxyl bonding in the transition state.<sup>4</sup>

manner as a "freer" radical resulting from outer-sphere reduction by a very reactive neutral or negative species. Recent pulse radiolytic experiments by Cohen and co-workers<sup>43</sup> point to substantial differences. Reaction of complexes XIX and XXI with either  $\text{CO}_2^{\cdot-}$  or  $\cdot\text{C}(\text{CH}_3)_2\text{OH}$  yielded the corresponding cobalt(III)-bound isonicotinoyl radicals, the decay of which (to  $\text{Co}^{2+}$ ) may be monitored. The radical from XXI, as expected, decays unimolecularly by internal electron transfer, but those from several other isonicotinoyl complexes, including that from XIX, react predominantly with the parent Co(III) complex in a bimolecular path, (11). No evidence for the latter path is evident in reduction of complex XIX by  $\text{Eu}(\text{II})$ .<sup>44</sup>



Although the exact structural features governing the partition between decay paths for radical-cations in Cohen's systems have not been pinpointed, it seems reasonable that a

bimolecular reaction between a tripositive ion and a dipositive radical would be less favored in the vicinity of a tripositive  $\text{Eu}^{3+}$  ion than with the latter species absent. In any event, these differences serve to remind us that electron-transfer reactions, like proton transfers,<sup>45</sup> may be subject to significant kinetic medium effects that can be quite specific both to the nature of the supporting electrolyte<sup>46</sup> and to the particular reaction at hand.<sup>47</sup> In systems featuring a single reaction, these effects are reflected merely in changes in kinetic parameters. Where there are closely balanced competing reactions, however, differential ionic medium effects may operate so that the predominant reaction in one medium may become a minor contributor in another.

**Registry No.** I, 88129-97-9; II, 88129-99-1; III, 88130-01-2; IV, 28237-77-6; V, 88130-03-4; VI, 28589-22-2; VII, 88130-05-6; VIII, 88130-08-9; IX, 88130-11-4; X, 88130-14-7; XI, 88130-17-0; XII, 88130-20-5; XIII, 88130-23-8; XIV, 88130-26-1; XV, 88130-29-4; XVI, 88130-32-9; XVII, 88130-35-2;  $\text{Eu}(\text{ClO}_4)_2$ , 16645-73-1;  $\text{V}(\text{ClO}_4)_2$ , 27819-85-8;  $\text{U}(\text{ClO}_4)_3$ , 88130-36-3;  $\text{Cr}(\text{ClO}_4)_2$ , 13931-95-8.

(43) Cohen, H.; Gould, E. S.; Meyerstein, D.; Nutkovich, M.; Radlowski, C. A. *Inorg. Chem.* **1983**, *22*, 1374.

(44) If reaction 11 were important in systems involving  $\text{Eu}^{2+}$  and complex XIX, the net reaction would be second rather than first order in Co(III) in the presence of excess  $\text{Eu}^{3+}$ . Kinetic profiles for the disappearance of Co(III) (0.001 M) in the presence of 0.08 M  $\text{Eu}^{3+}$  exhibit no distortion indicative of a second-order component.<sup>4</sup>

(45) See, for example: (a) More O'Ferrall, R. A.; Ridd, J. H. *J. Chem. Soc.* **1963**, 5035. (b) Guthrie, R. D.; Pendergraft, G. W.; Young, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 5877.

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## New Oxotechnetium(V) Complexes of *N,N'*-Ethylenebis(acetylacetonate imine), *N,N'*-Ethylenebis(salicylideneamine), and *o*-Phenylenebis(salicylideneamine). X-ray Structures of the Complexes of *N,N'*-Ethylenebis(acetylacetonate imine) and *N,N'*-Ethylenebis(salicylideneamine)

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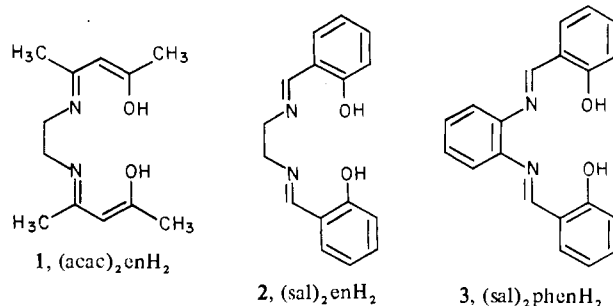
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New technetium(V) oxo complexes of tetradentate Schiff base ligands have been synthesized and characterized. X-ray structure determination shows that the *N,N'*-ethylenebis(acetylacetonate iminato) complex  $[\text{TcO}(\text{H}_2\text{O})(\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2)]^+$  has a distorted octahedral coordination geometry, containing a *trans*-oxoquaatechnetium(V) core. Such a *trans*- $\text{TcO}(\text{OH})_2^{3+}$  core is intermediate between the previously well-characterized monooxo,  $\text{TcO}^{3+}$ , and *trans*-dioxo,  $\text{TcO}_2^+$ , cores. The complex was isolated as a mixed chloride/bromide salt  $[\text{TcO}(\text{H}_2\text{O})(\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2)]\text{Br}_{0.25}\text{Cl}_{0.75}$ , which crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 10.935$  (4) Å,  $b = 9.877$  (4) Å,  $c = 7.324$  (3) Å,  $\alpha = 87.266$  (9)°,  $\beta = 102.498$  (12)°,  $\gamma = 97.845$  (9)°, and  $R = 0.0215$  for 2370 diffractometer data with  $I \geq 3\sigma(I)$ . The *N,N'*-ethylenebis(salicylideneaminato) complex  $[\text{TcOCl}(\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2)]$  also has a pseudooctahedral coordination geometry but contains a *trans*-oxochlorotechnetium(V) core and crystallizes in space group  $P2_12_1$  with  $a = 26.653$  (11) Å,  $b = 11.697$  (5) Å,  $c = 10.529$  (3) Å, and  $R = 0.0642$  for 2105 diffractometer data with  $I \geq 3\sigma(I)$ .

### Introduction

Although technetium has been studied since 1937,<sup>2</sup> much of the development of its coordination chemistry has occurred in the past decade.<sup>3</sup> A large part of this activity has arisen as a consequence of the utility of  $^{99\text{m}}\text{Tc}$  in nuclear medicine;  $^{99\text{m}}\text{Tc}$  has virtually ideal nuclear properties for use in radiopharmaceuticals.<sup>4</sup> However, the half-life of  $^{99\text{m}}\text{Tc}$  is only 6 h and its long-lived daughter,  $^{99}\text{Tc}$  ( $t_{1/2} = 2.12 \times 10^5$  years), is normally used for preparative and other studies.  $^{99}\text{Tc}$

complexes of a range of organic ligands have been reported, and in several cases their biological activity (organ specificity) has been investigated.<sup>3</sup> Although transition-metal complexes of the "classical" tetradentate Schiff base ligands 1-3 have



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