Conclusions

Both the chemical and electrochemical reduction of S_4N_4 and the deprotonation of $S_4N_4H_4$ lead to the formation of $S_3N_3^-$. This ion is also formed from S_4N_4 and sodium amide in liquid ammonia. The reactions of S_4N_4 with liquid ammonia, secondary amines, or cyanide all produce the $S_4N_5^-$ ion. Thus, the $S_3N_3^-$ and $S_4N_5^-$ ions play a central role in the chemical reactions of S_4N_4 under reducing conditions or with nucleophiles. These two species are the only well-characterized binary S–N anions. Previous claims of the isolation of other S–N anions in the reactions of S_4N_4 with nucleophiles or on reduction should be discounted, since all these reactions have now been shown to lead to the formation of $S_3N_3^-$ and/or $S_4N_5^-$.

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Registry No. $S_4N_4H_4$, 293-40-3; KH, 7693-26-7; S_4N_4, 28950-34-7; K, 7440-09-7; NH_3, 7664-41-7; $NaNH_2$, 7782-92-5; piperidine, 110-89-4; piperidyllithium, 4442-11-9; KCN, 151-50-8; $K^+S_3N_3^-$, 68051-22-9; $K^+S_4N_5^-$, 65101-94-2; $Me_4N^+S_3N_3^-$, 65207-98-9; $NH_4^+S_4N_5^-$, 58904-51-1; $[C_5H_{10}NH_2]^+S_4N_5^-$, 68001-78-5; $Li^+S_4N_5^-$, 65101-93-1; $Bu_4N^+S_4N_5^-$, 58894-68-1.

References and Notes

(1) D. Chapman and A. G. Massey, *Trans. Faraday Soc.*, **58**, 1291 (1962).
(2) R. A. Meinzer, D. W. Pratt, and R. J. Myers, *J. Am. Chem. Soc.*, **91**, 6623 (1969).
(3) J. D. Williford, R. E. VanReet, M. P. Eastman, and K. B. Prater, *J. Electrochem. Soc.*, **120**, 1498 (1973).
(4) M. Becke-Goehring and R. Schwarz, *Z. Anorg. Allg. Chem.*, **296**, 3 (1958).
(5) A. J. Banister and D. Younger, *J. Inorg. Nucl. Chem.*, **32**, 3766 (1970).
(6) (a) O. J. Scherer and G. Wolmershäuser, *Angew. Chem., Int. Ed. Engl.*, **14**, 485 (1975); (b) W. Flues, O. J. Scherer, J. Weiss, and G. Wolmershäuser, *ibid.*, **15**, 379 (1976); (c) J. Bojes, P. M. Boorman, and T. Chivers, *Inorg. Nucl. Chem. Lett.*, **12**, 551 (1976).
(7) (a) J. Bojes and T. Chivers, *J. Chem. Soc., Chem. Commun.*, 453 (1977); (b) J. Bojes and T. Chivers, *Inorg. Chem.*, **17**, 318 (1978); (c) J. Bojes and T. Chivers, *J. Chem. Soc., Chem. Commun.*, 391 (1978).
(8) T. Chivers, and I. Drummond, *Inorg. Chem.*, **13**, 1222 (1974).
(9) O. J. Scherer and G. Wolmershäuser, *Chem. Ber.*, **110**, 3241 (1977).
(10) M. Villena-Blanco and W. L. Jolly, *Inorg. Synth.*, **9**, 98 (1967).
(11) G. Brauer, "Handbook of Preparative Inorganic Chemistry", Vol. 1, Academic Press, New York, N.Y., 1963, p 411.
(12) C. A. Brown, *J. Org. Chem.*, **39**, 3913 (1974).
(13) R. Steudel, F. Rose, R. Reinhardt, and H. Bradaczek, *Z. Naturforsch., B*, **32**, 488 (1977).
(14) A. I. Vogel, "Macro and Semimicro Qualitative Inorganic Analysis", 4th ed, Longmans, London, 1965, p 219.
(15) O. R. Brown, *J. Electroanal. Chem.*, **34**, 419 (1972).
(16) R. Gleiter, *J. Chem. Soc., A*, 3174 (1970).
(17) C. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, **10**, 2781 (1971).
(18) A. J. Banister, *Nature (London), Phys. Sci.*, **237**, 92 (1972).
(19) A. P. Zipp and E. C. Evers, *Inorg. Chem.*, **8**, 1746 (1969).
(20) J. T. Nelson and J. J. Lagowski, *Inorg. Chem.*, **6**, 1292 (1967).
(21) R. D. Smith, J. R. Wyatt, J. J. DeCorpo, F. E. Saalfeld, M. J. Moran, and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **99**, 1726 (1977).
(22) R. Schenk, *Justus Liebigs Ann. Chem.*, **290**, 171 (1896).
(23) T. Chivers and I. Drummond, *Inorg. Chem.*, **11**, 2525 (1972).
(24) T. Chivers and I. Drummond, *J. Chem. Soc., Dalton Trans.*, 631 (1974).
(25) E. Fluck, M. Becke-Geohring, and G. Dehoust, *Z. Anorg. Allg. Chem.*, **312**, 60 (1961).

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Reduction of (Ethylenediaminetetraacetato)cobaltate(III) and Related Complexes by Titanium(III)

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The kinetics of the reduction of three (ethylenediaminetetraacetato)cobaltate(III) complexes by titanium(III) in aqueous chloride medium have been investigated at 25 °C and ionic strength 1.0 M (HCl + NaCl). The $Co(EDTA)^-$ complex is reduced according to the rate law $-d \ln [Co(EDTA)^-]/dt = a[H^+]^{-1}[Ti(III)]/(1 + K_h[H^+]^{-1}) + c[H^+]^{-1}[Ti(III)]^2$, while the rate law for the reduction of $Co(HEDTA)OH_2$ and $Co(HEDTA)Cl^-$ is of the form $-d \ln [Co(HEDTA)L]/dt = a[H^+]^{-1}[Ti(III)]/(1 + K_h[H^+]^{-1})$. The computed K_h values are similar for all the three oxidizing agents and correspond to the $Ti^{3+}(aq)$ acid dissociation constant. The composite constant a has the values 0.29, 3.0, and 9.0 s^{-1} for the reduction of $Co(EDTA)^-$, $Co(HEDTA)OH_2$, and $Co(HEDTA)Cl^-$. A comparison with other reducing agents is made and the mechanistic implications are discussed.

Introduction

In several kinetic studies (ethylenediaminetetraacetato)cobaltate(III) and related complexes have been used to characterize mechanistic behavior of some transition-metal reducing agents. On the basis of indirect arguments it was shown that Fe^{2+} reduces $Co(HEDTA)Cl^-$ and $Co(HETA)OH^-$ complexes (HEDTA = monoprotonated EDTA, HETA = *N*-hydroxyethylenediamine-*N*,*N'*,*N'*-triacetate) by an inner-sphere mechanism with chloro and hydroxo ligands acting as bridges.[1,2] More speculative arguments were used to suggest that Fe^{2+} reduces $Co(HEDTA)OH_2$, $Co(HETA)OH_2$, and hexadentate $Co(EDTA)^-$ by an inner-sphere mechanism, with the carboxylato group of the coordinated acetate acting as a bridge.[2] Inner-sphere reduction of the same series of complexes by Cr^{2+} was proved by analyses of the Cr(III) products, which contained transferred polycarboxylato and (for the $Co(HEDTA)Cl^-$ reaction) chloro ligands.[3] It was recently elegantly shown, by a comparison of the substitution rates on the Co(III) centers and the redox rates, that the $Fe(CN)_6^{4-}$ reduction of $Co(EDTA)^-$, $Co(EDTA)OH_2^-$, and $Co(EDTA)Cl^{2-}$ proceeds through an outer-sphere mechanism.[4]

In view of the preceding literature data it was of interest to study the reactivity of titanium(III) toward EDTA complexes of cobalt(III). Titanium(III) was shown not to exhibit preference toward chloride as a bridge[5,6] and to exhibit preference toward carboxylato groups, including acetato ligand.[7] Here we report a kinetic study on the titanium(III) reduction of $Co(EDTA)^-$, $Co(HEDTA)OH_2$, and $Co(HEDTA)Cl^-$ at 25 °C in an aqueous chloride medium of 1.0 M ionic strength (HCl + NaCl).

Experimental Section

Materials. The complexes $KCo(EDTA)\cdot 2H_2O$ and $KCo(HEDTA)Cl$ were prepared according to the method of Dwyer et al.[8,9] The dihydrate $KCo(EDTA)\cdot 2H_2O$ was dehydrated by heating at 105 °C to constant weight. The identity of the complexes was established from their UV–visible spectra with visible absorption maxima (molar

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absorptivity) at 535 nm (311 mol^{-1} L cm^{-1}) for $Co(EDTA)^-$ and at 583 nm (232 mol^{-1} L cm^{-1}) for $Co(HEDTA)Cl^-$, in agreement with the literature data.[4] The complex $Co(HEDTA)OH_2$ was prepared in solution by equilibrating 0.2 M $Co(EDTA)^-$ in 4 M HCl at 25 °C.[10] After equilibrium was attained, the solution still contained about 15% $Co(EDTA)^-$. Prolonged storage of this solution led to a change in its visible absorption spectrum presumably due to the opening of another chelate ring. The solutions were therefore always freshly made by overnight equilibration.

Titanium(III) solutions in aqueous chloride media were prepared, analyzed, and used as previously described.[11] The solutions were handled in a glass syringe with a platinum needle. All the solutions were purged with purified nitrogen gas prior to addition of Ti(III). Other materials were of the same brand and purity as used in the previous study.

Kinetic Measurements. The kinetics of the reactions were followed spectrophotometrically. Decreases of absorption were measured at 535 nm for $Co(EDTA)^-$ and 583 nm for $Co(HEDTA)Cl^-$, the wavelengths of the absorption maxima of these two Co(III) complexes, and at 590 nm for $Co(HEDTA)OH_2$, the isosbestic wavelength of $Co(HEDTA)OH_2$ and $Co(EDTA)^-$. Most of the kinetic runs were monitored in a Durrum D-130 stopped-flow apparatus combined with a Zeiss Jena SPM2 monochromator. Some of the slower kinetic runs involving the $Co(EDTA)^-$ complex were monitored in a Cary 17 spectrophotometer equipped with a thermostated cell compartment and cell holder. The results of those runs investigated by both techniques agreed very well.

Conditions for pseudo-first-order kinetics were established by the use of at least 17-fold excess of titanium(III) over cobalt(III). Specific rates for the reduction of $Co(EDTA)^-$ and $Co(HEDTA)Cl^-$ were calculated from the slopes of standard plots. Preliminary experiments indicated that these plots deviate from linearity in a manner that suggests autocatalysis when conditions of relatively high Co(III) concentrations were used. Blank experiments involving additions of the individual products to the reacting solution revealed that the EDTA ligand, freed by the redox process and by the lability of the Co(II) product, was the only product responsible for autocatalysis, presumably due to complexing of labile titanium (III). This effect was eliminated by the use of low Co(III) and the relatively high Ti(III) concentrations used in subsequent runs, for which linearity of the log $(A_t - A_\infty)$ vs. time plots was preserved for at least 3 half-lives.

The kinetics of the reduction of $Co(HEDTA)OH_2$ were not pseudo first order because of the presence of about 15% $Co(EDTA)^-$ in the Co(III) solution, the former EDTA complex oxidizing Ti(III) about 1 order of magnitude faster than the latter one. Since the two Co(III) complexes give the same reduction products, for kinetics being monitored at the isosbestic point of the two Co(III) complexes eq 1

$$A_t - A_\infty = (A_0 - A_\infty)\left(\frac{P_0}{100e^{-k_1t}} - \frac{P_0}{100e^{-k_2t}} + e^{-k_2t}\right) \qquad (1)$$

can be applied, where k_1 is the pseudo-first-order rate constant for the $Co(HEDTA)OH_2$ + Ti(III) reaction, k_2 is the constant for the $Co(EDTA)^-$ + Ti(III) reaction, P_0 is the percentage of the $Co(HEDTA)OH_2$ in the mixture of Co(III) reactants at zero reaction time, and A's are reaction solution absorptions at the corresponding times t. The k_2 values were determined separately in the runs with pure $Co(EDTA)^-$ reactant, but since actual P_0 was not known, k_1 and P_0 were computed by an iterative method using a nonlinear least-squares computer program. The trial k_1 and P_0 values were obtained by an approximate graphical analysis of the log $(A_t - A_\infty)$ vs. t plots.

To avoid participation of the possible substitution reactions 2 and 3 in the overall redox process, the Co(III) solutions were freshly made prior to each run. The redox reactions were much faster than those for substitution (eq 2 and 3).[10,12]

$$Co(EDTA)^- + H^+ + H_2O \rightleftharpoons Co(HEDTA)H_2O \qquad (2)$$

$$Co(HEDTA)Cl^- \rightleftharpoons Co(EDTA)^- + H^+ + Cl^- \qquad (3)$$

All the runs were performed at 25 °C in chloride ionic medium and μ = 1.0 M adjusted by HCl and NaCl.

Stoichiometry. The stoichiometry of the reduction of $Co(EDTA)^-$ was measured by analyzing unreacted Ti(III) and Co(II) produced after the reaction was 99% or more completed. The range of (1.05–4.0) × 10^{-3} M in $Co(EDTA)^-$ initial concentration and of (1.15–3.14) × 10^{-3} M in Ti(III) concentration was employed. Analytical methods used were the same as previously described.[11]

Table I. Rate Constants for the Oxidation of Titanium(III) by $Co(EDTA)^-$ Ion at 25 °C and μ = 1.0 M (HCl + NaCl)[a]

$[H^+]$/mM	[Ti(III)]/mM	$10^3k_{obsd}/s^{-1}$
700	49.0	37.4
700	22.9	13.1
700	10.0	4.7
700	9.8	4.6
700	5.9	2.56
700	2.94	1.29
100	49.8	490
100	25.0	141
100[b]	25.0	149
100[c]	25.0	157
100	10.2	37.5
100	10.0	42
100	5.00	16.1
25.0	26.9	950
25.0	10.0	208
25.0	7.5	139
25.0	5.00	78
25.0	2.50	33.8
10.0	10.8	550
10.0	10.7	515
10.0	6.0	243
10.0	3.00	88
10.0	1.00	23.4
5.00	5.38	310
5.00	5.00	290
5.00	4.00	193
5.00	3.00	133
5.00	2.00	77
5.00	1.00	27.0

[a] $[Co(EDTA)^-]$ = 5.0 × 10^{-5} M, λ 535 nm. [b] $[Co(EDTA)^-]$ = 1.00 × 10^{-4} M. [c] $[Co(EDTA)^-]$ = 2.0 × 10^{-4} M.

Results

Reaction between (Ethylenediaminetetraacetato)cobalt(III) Ion and Titanium(III). Although a 1:1 stoichiometry for this reaction, eq 4, can be straightforwardly assumed, it has been

$$Co(EDTA)^- + Ti(III) \xrightarrow{k_{obsd}} Co(II) + Ti(IV) \qquad (4)$$

experimentally verified that Co(II) was produced in quantity equivalent to 99–103% of the oxidant or reductant taken, whichever was in deficiency, within the (H^+) range 0.008–1.0 M. The UV–visible spectra of the reaction mixture taken after the completion of the reaction have shown that the possible primary Co(II) redox products, $Co^{II}(EDTA)$ or $Co^{II}(EDTA)Ti^{IV}$, undergo labile substitution to reach an equilibrium, the nature and position of which are acidity dependent.

Blank runs involving $Co^{II}(EDTA)$, Ti(III), and Ti(IV), under the conditions of actual kinetic runs, were performed to establish whether the product substitution reaction interfered with the monitoring of the redox reaction. No change in absorption was observed on the time scale and at the wavelength examined ($t \geq 50$ ms, 535 nm), and the redox reaction could be followed unobstructed. The pseudo-first-order rate constants, k_{obsd}, observed at different acidities are presented in Table I. From the last column in Table I it is evident that the reaction is more than first order with respect to Ti(III) concentration. The plots of k_{obsd}/[Ti(III)] vs. Ti(III) concentration for different acidities are shown in Figure 1. Linearity of the plots at each experimental acidity is consistent with expression 5. A least-squares treatment of the straight

$$-d[Co(EDTA)^-]/dt = k_{obsd}[Co(EDTA)^-] = k_{II}[Co(EDTA)^-][Ti(III)] + k_{III}[Co(EDTA)^-][Ti(III)]^2 \qquad (5)$$

lines obtained by plotting k_{obsd}/[Ti(III)] vs. [Ti(III)] was used to calculate k_{II} and k_{III} constants. The values for the different acidities used are given in Table II. Both k_{II} and k_{III} increase

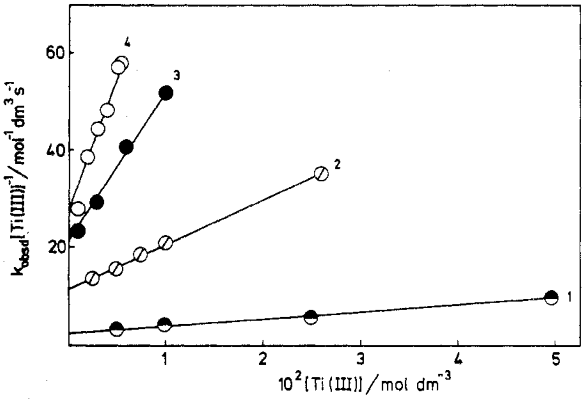


Figure 1. Dependence of $k_{obsd}[Ti(III)]^{-1}$ upon Ti(III) concentration for the Ti(III) reduction of Co(EDTA)$^-$ at 25 °C in 1.0 M ionic strength (NaCl) at the acidity of (1) 0.1 M, (2) 0.025 M, (3) 0.01 M, and (4) 0.005 M.

Table II. The Rate Constants k_{II} and k_{III} for the Reaction between Co(EDTA)$^-$ and Ti(III) at Different Acidities, t = 25 °C, μ = 1.0 M (HCl + NaCl)

	k_{II}/M^{-1} s^{-1}		
[H$^+$]/mM	*a*	*b*	k_{III}/M^{-2} s^{-1}
700	0.40	0.41	7.5
100	2.5	2.7	1.40 × 10^2
25.0	11.5	9.6	8.9 × 10^2
10.0	21	20	2.9 × 10^3
5.0	28	30	5.4 × 10^3

[a] Obtained from the expression $k_{obsd}/[Ti(III)] = k_{II} + k_{III}\cdot[Ti(III)]$. [b] Calculated by a computer fitting according to eq 6.

with decreasing acidity. The dependence of k_{II} on acidity is well described by empirical eq 6, as seen from the comparison

$$k_{II} = a/(b + [H^+]) \qquad (6)$$

of the experimental and fitted k_{II} values shown in Table II. The acidity dependence of k_{III} is not well defined and is only roughly approximated by eq 7. Constants $a = 0.29 \pm 0.11$

$$k_{III} = c/[H^+] \qquad (7)$$

s^{-1}, $b = (4.6 \pm 1.4) \times 10^{-3}$ M, and $c = 8.2$ M^{-1} s^{-1} were computed using a nonlinear least-squares computer routine. The uncertainties quoted for *a*, *b*, and *c* are standard deviation. The calculated k_{II} values agreed with the experimental ones with an average deviation of 8.1% and a maximum individual deviation of 15%.

Reduction of Aquo(ethylenediaminetetraacetato)- and Chloro(ethylenediaminetetraacetato)cobalt(III) Ions by Titanium(III). As in the reaction with CoEDTA$^-$, UV-visible spectra taken after the completion of the reaction between Co(HEDTA)OH$_2$ or Co(HEDTA)Cl$^-$ and Ti(III) have shown that the redox products attain a labile substitution equilibrium. Blank kinetic experiments have proved, however, that the substitution reactions could not be kinetically seen under the experimental conditions and that they did not interfere with the measurements of the redox reaction. The two redox reactions are first order with respect to Co(III) concentration and the pseudo-first-order rate constants, k_{obsd}, observed for the reaction of Co(HEDTA)OH$_2$ are presented in Table III, and those observed for the reaction of Co(HEDTA)Cl$^-$ in Table IV. From the data in Tables III and IV obtained for a particular acidity it is evident that the rate is of the first order with respect to titanium(III) concentration and, contrary to the reaction of the Co(EDTA)$^-$ ion, that there is no additional term involving a second-order dependence on Ti(III) concentration. The second-order rate constants, $k_{II} = k_{obsd}/[Ti(III)]$, increase with decreasing acidity. The nature of the dependence was graphically shown to comply with eq 6. The rate law is thus given by eq 8. Constants $a = 3.0 \pm 0.1$ s^{-1},

$$-d[Co(III)]/dt = a[Co(III)][Ti(III)]/(b + [H^+]) \quad (8)$$

$b = (3.3 \pm 0.4) \times 10^{-3}$ M for the reaction of Co(HEDTA)OH$_2$ and $a = 9.0 \pm 0.3$ s^{-1}, $b = (5.7 \pm 0.4) \times 10^{-3}$ M for the reaction of Co(HEDTA)Cl$^-$ were obtained by a computer treatment of the data in Tables III and IV according to $k_{obsd} = a[Ti(III)]/(b + [H^+])$ using a nonlinear least-squares method. The uncertainties quoted are standard deviation. The calculated k_{calcd} values, shown in the tables, agreed with the experimental k_{obsd} with the average deviation of 4.9 and 6.2% and a maximum individual deviation of 18.9 and 18.5% for Co(HEDTA)OH$_2$ and Co(HEDTA)Cl$^-$, respectively.

Table III. Rate Constants for the Oxidation of Titanium(III) by the Co(HEDTA)OH$_2$ Ion at 25 °C, μ = 1.0 M (HCl + NaCl)[a]

[H$^+$]/mM	[Ti(III)]/mM	k_{obsd}/s^{-1}	k_{calcd}/s^{-1} [b]
700	2.47	0.0104	0.0104
700	10.0	0.042	0.043
700	25.0	0.114	0.106
100	5.00	0.136	0.144
100	5.00	0.149	0.144
100	10.0	0.286	0.288
100	25.0	0.74	0.72
100	50.0	1.66	1.44
25.0	2.50	0.27	0.26
25.0	5.00	0.52	0.53
25.0	10.0	0.88	1.05
10.0	1.00	0.222	0.224
10.0	3.00	0.71	0.67
10.0	6.00	1.28	1.34
5.00	1.00	0.38	0.36
5.00	2.00	0.69	0.72
5.00	3.00	1.17	1.07
5.00	3.00	1.04	1.07

[a] [Co(HEDTA)H$_2$O] = (7.7-6) × 10^{-5} M, λ 590 nm. [b] Calculated from $k_{calcd} = a[Ti(III)]/(b + [H^+])$, a = 3.0 s^{-1}, b = 3.3 × 10^{-3} M.

Table IV. Rate Constants for the Oxidation of Titanium(III) by the Co(HEDTA)Cl$^-$ Ion at 25 °C, μ = 1.0 M (HC + NaCl)[a]

[H$^+$]/mM	[Ti(III)]/mM	k_{obsd}/s^{-1}	k_{calcd}/s^{-1} [b]
988	1.04	0.0103	0.0094
800	14.9	0.187	0.166
250	15.0	0.57	0.53
140	15.0	0.95	0.92
100	25.0	2.23	2.12
100	10.0	0.86	0.85
50.8	10.0	1.58	1.59
33.4	10.0	2.28	2.30
25.0	25.0	6.9	7.3
25.0	5.00	1.47	1.46
25.0	2.50	0.66	0.73
15.1	10.3	4.4	4.4
10.0	10.8	6.1	6.2
6.58	7.16	5.0	5.2
5.00	5.38	4.4	4.5
4.17	4.51	4.1	4.1
3.81	4.09	3.5	3.9
3.57	3.84	4.1	3.7
3.33	3.58	3.2	3.6
3.00	3.22	3.4	3.3
2.63	2.83	3.3	3.0
2.27	2.44	3.0	2.7
2.13	2.24	3.2	2.6
2.00	2.15	3.0	3.5

[a] [Co(HEDTA)Cl$^-$] = 7.5 × 10^{-5} M, λ 583 nm. [b] Calculated from $k_{calcd} = a[Ti(III)]/(b + [H^+])$, a = 9.0 s^{-1}, b = 5.7 × 10^{-3} M.

Discussion

The general form of the acidity dependence of the overall second-order rate constant, k_{II}, given by eq 6 for reductions

Table V. Rates of Reduction of Co(III)-EDTA Complexes at 25 °C and $\mu = 1.0$ M and Their Ratios

		reducing agent			
		Fe-$(CN)_6^{4-}$ [a] k/M^{-1} s^{-1}	Ti(III) a/s^{-1}	Fe^{2+} [b] kK/ M^{-1} s^{-1}	Cr^{2+} [c] kK/ M^{-1} s^{-1}
I	$Co(EDTA)^-$	0.21	0.29	6.0×10^{-4}	1.6×10^5
II	$Co(HEDTA)OH_2$ or $Co(EDTA)OH_2^-$	3.4	3.0	8.5×10^{-3}	1.3×10^5
III	$Co(HEDTA)Cl^-$ or $Co(EDTA)Cl^{2-}$	7.0	9.0	1.36	2.5×10^6

	ratio of constants			
	$Fe(CN)_6^{4-}$	Ti(III)	Fe^{2+}	Cr^{2+}
II/I	16	11	14	0.8
III/I	33	31	2×10^3	16

[a] Reference 4, $\mu = 0.59$ M, pH 4.6. [b] Reference 2. [c] Reference 3, 20 °C.

by titanium(III), has been observed for a number of oxidizing agents,[5-7,11,13] which themselves are not involved in significant protolytic equilibria under the conditions employed. It reflects a high redox reactivity of monohydroxytitanium(III) species relative to that of aquotitanium(III) species. The computer fitting of the constants a and b according to eq 6 for the Ti(III) reduction of $Co(EDTA)^-$, $Co(HEDTA)OH_2$, and $Co(HEDTA)Cl^-$ has produced $b = 4.6 \times 10^{-3}$, 3.3×10^{-3}, and 5.7×10^{-3} M, respectively. These are similar values and are close to the value $K_h = 3.5 \times 10^{-3}$ M for the titanium(III) hydrolysis constant, expression 9, at 25 °C and $\mu = 1.0$ M

$$Ti^{3+} \rightleftharpoons TiOH^{2+} + H^+ \qquad (9)$$

(NaCl), obtained from an extensive kinetic study of two typical outer-sphere reactions, the reduction of $Co(phen)_3^{3+}$ and $Co(terpy)_2^{3+}$.[13] The agreement of the computed constants b with K_h is very good, taking into consideration that b's were computed from runs at a small number of different acid concentrations and that the protolytic equilibrium 10 could

$$Co(HEDTA)L^{n-} \overset{K_1}{\rightleftharpoons} Co(EDTA)L^{(n+1)-} + H^+ \qquad (10)$$

possibly also interfere with the kinetics. The pK_1 is about 3 for L = OH_2 or Cl.[10,14] In the acidity range used in this work the predominant species were $Co(HEDTA)OH_2$ and $Co(HEDTA)Cl^-$, respectively, and at the lowest [H^+] used the concentration of $Co(EDTA)OH_2^-$ did not exceed 17% and that of $Co(EDTA)Cl^{2-}$ did not exceed 33% of the total Co(III). The b values computed also indicate that the protonated and deprotonated Co(III) species do not react with significantly different rates.

It appears that the constant b in eq 6 is K_h as defined by eq 9 and that eq 6 can be interpreted through eq 11, where

$$k_{II} = a[H^+]^{-1}/(1 + K_h[H^+]^{-1}) \qquad (11)$$

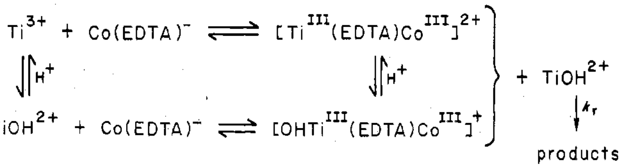
the assigment of the parameter a depends on the mechanism. If an outer-sphere mechanism operates, then $TiOH^{2+}$ is the reactive species and $a = kK_h$, where k is the redox rate constant. If an inner-sphere mechanism is operative, then the Co(III)–$TiOH^{n+}$ binuclear precursor complex carries the redox rate with a specific rate k' and $a = k'K'K_h$ or $a = k'K$, where K' and K are as defined by eq 12 and 13. The nature of the

$$Co(III) + TiOH^{2+} \overset{K'}{\rightleftharpoons} Co^{III}\text{–}TiOH^{n+} \qquad (12)$$

$$Co(III) + Ti^{3+} \overset{K}{\rightleftharpoons} Co^{III}\text{–}TiOH^{n+} + H^+ \qquad (13)$$

dependence of k_{obsd} upon [Ti(III)] shows that the fast equilibria governed by K or by K', if existing, are shifted toward free Ti(III) and Co(III) species.

Scheme I



The rate parameters for reduction of EDTA complexes of cobalt(III) by four different reducing agents are listed in Table V. Ratios of the rate constants are also included in the table. Haim et al. have shown that the reduction of the listed Co(III) complexes by $Fe(CN)_6^{4-}$ occurs through an outer-sphere mechanism.[4] From Table V it is seen that ratios of the rates for the reduction of $Co(HEDTA)OH_2$ or $Co(EDTA)OH_2^-$ and $Co(EDTA)^-$ (II/I) are similar for the reduction by $Fe(CN)_6^{4-}$, Ti(III), and Fe^{2+}. Ratios of the rates for the reduction of $Co(HEDTA)Cl^-$ or $Co(EDTA)Cl^{2-}$ and $Co(EDTA)^-$ (III/I) by $Fe(CN)_6^{4-}$ and Ti(III) are also very similar. The indication appears to be that all the quoted reactions proceed by an outer-sphere mechanism. Ratio III/I for reduction by Fe^{2+} is very much larger due to the opening of a new route, the chloride bridged inner-sphere path for reduction of $Co(HEDTA)Cl^-$,[2] while the rate ratios II/I and III/I for reduction by Cr^{2+} also do not follow the former trend, in accordance with the inner-sphere mechanism which was demonstrated by product analysis.[3]

The implication that Ti(III) reduces $Co(EDTA)^-$, $Co(HEDTA)OH_2$, and $Co(HEDTA)Cl^-$ by the outer-sphere mechanism drawn from this consideration of the rate ratios differs from our expectation. Titanium(III) shows a high affinity toward uncoordinated EDTA ligand[15] even in the pH 0.5–2 region.[16] Also, a likelihood of coordination of $Co(EDTA)L^{n-}$ complexes to another metal center through the free acetato arm of the bound EDTA has been demonstrated by the preparation of $Co(NH_3)_5(EDTA)CoOH_2^{2+}$ and other analogous binuclear complexes.[17] On the other hand, an indication was offered for the inner-sphere titanium(III) reduction of $Co(NH_3)_5OOCCH_3^{2+}$ through the acetato bridge.[7] An inner-sphere titanium(III) reduction of $Co(EDTA)^-$, $Co(HEDTA)OH_2$, and $Co(HEDTA)Cl^-$ is, thus, also likely.

There is an additional consideration of the results obtained in this work indicating that Ti(III) reduction of the Co(III)–EDTA complexes or of some of them may proceed by an inner-sphere mechanism. Reduction of $Co(EDTA)^-$ obeys a two-term rate law, eq 5, the second term involving the square of the Ti(III) concentration. In an outer-sphere mechanism the square term might be due to reduction by a Ti(III) dimer; however, there do not appear to be obvious reasons why this behavior would only be specific for $Co(EDTA)^-$. Also, there is no independent evidence for a Ti(III) dimer in the higher acidities used. The $[Ti(III)]^2$ term in the rate law for reduction of $Co(EDTA)^-$ can be explained by Scheme I, where the redox process involving the second Ti(III) ion, k_r, may be outer or inner sphere. In the $Co(HEDTA)OH_2$ and $Co(HEDTA)Cl^-$ ions, EDTA ligand is bound in a pentadentate mode, having an unbound acetato arm. Binuclear precursor complexes of these ions with Ti(III) may be of a different structural nature from that formed by $Co(EDTA)^-$, allowing an efficient inner-sphere electron transfer within the binuclear complex. Competing chances of a second Ti(III) ion toward the binuclear precursor are diminished in this way and hence there appear no $[Ti(III)]^2$ terms in the rate law for Ti(III) reduction of $Co(HEDTA)OH_2$ and $Co(HEDTA)Cl^-$.

The question of outer-sphere vs. inner-sphere mechanisms for the Ti(III) reduction of these Co(III)–EDTA complexes is not settled by the experimental evidence offered by this work. A comparison with kinetic data for reduction by $Ru(NH_3)_6^{2+}$ might be useful since a linear rate correlation on the log–log scale for the outer-sphere reduction of Co(III) centers by Ti(III) and $Ru(NH_3)_6^{2+}$ has been recently shown.[6]

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Registry No. $Co(EDTA)^-$, 15136-66-0; $Co(HEDTA)OH_2$, 54713-24-5; $Co(HEDTA)Cl^-$, 54735-69-2; Ti^{3+}, 22541-75-9.

References and Notes

(1) A. Pidcock and W. C. E. Higginson, *J. Chem. Soc.*, 2798 (1963).
(2) P. B. Wood and W. C. E. Higginson, *J. Chem. Soc.*, 2116 (1965).
(3) P. B. Wood and W. C. E. Higginson, *J. Chem. Soc. A*, 1645 (1966).
(4) L. Rosenhein, D. Speiser, and A. Haim, *Inorg. Chem.*, **13**, 1571 (1974).
(5) M. Orhanović and J. E. Earley, *Inorg. Chem.*, **14**, 1478 (1975).
(6) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976).
(7) A. H. Martin and E. S. Gould, *Inorg. Chem.*, **14**, 873 (1975).
(8) F. P. Dwyer, E. C. Gyarfas, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).
(9) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1958).
(10) I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958).
(11) A. Bakač and M. Orhanović, *Inorg. Chim. Acta*, **21**, 173 (1976).
(12) R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1998 (1960).
(13) A. Bakač, R. Marčec, and M. Orhanović, *Inorg. Chem.*, **16**, 3133 (1977).
(14) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).
(15) J. Podlahova and J. Podlaha, *J. Inorg. Nucl. Chem.*, **28**, 2267 (1966).
(16) E. G. Jakovleva, N. I. Pechurova, L. I. Martinenko, and V. I. Spicin, *Zh. Neorg. Khim.*, **18** (6), 1519 (1973).
(17) H. Ogino, K. Tsukahara, and N. Tanaka, *Inorg. Chem.*, **16**, 1215 (1977).

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A Kinetic Study of Anation of Thiocyanate and Azide to Aquaoxo((2-pyridylmethyl)iminodiacetato)vanadium(IV) and the Aquation of the Product in Aqueous Solution. A Direct Basal Site Substitution

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Substitution reactions between water in aquaoxo((2-pyridylmethyl)iminodiacetato)vanadium(IV), $VO(pmida)H_2O$ [(4–8) $\times 10^{-4}$ M, M = mol dm^{-3}], and NCS^- (0.02–0.31 M) and N_3^- (0.02–0.4 M) have been kinetically studied by the stopped-flow method in aqueous solutions of pH 3.2–4.7 and 3.6–4.9 at ionic strength 1.0, respectively. The pseudo-first-order rate constant k_0 is expressed by $k_0 = k_b + k_f[X^-]$ ($X^- = NCS^-$ or N_3^-), where k_b and k_f stand for the first- and second-order rate constants of the aquation of $VO(pmida)X^-$ and the anation of X^- to $VO(pmida)H_2O$, respectively. The rate constants and activation parameters are as follows: k_b and k_f are 0.061 and 0.13 s^{-1} and 0.26 and 3.7 $M^{-1}\ s^{-1}$ at 25 °C for NCS^- and N_3^-, respectively; the corresponding $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are 61.4, 63.5, 48.9, and 47.2 kJ mol^{-1} and −61, −47, −90, and −75 J $mol^{-1}\ K^{-1}$. These reactions must reflect a direct basal site substitution of the oxovanadium(IV) complex and seem to proceed via an associative mechanism.

Introduction

The substitution reaction of oxovanadium(IV) complexes includes various rapid processes at varying coordination sites and has been investigated mainly by NMR, ESR, and stopped-flow spectrometry.[1-11] The mechanisms of these reactions are different from one another and cannot be directly compared. The exchange of solvent molecules between the coordination site and the bulk solvent is claimed to have a first-order rate constant $>10^7\ s^{-1}$,[1-3] whereas that at the basal site is $\approx 10^3\ s^{-1}$ at room temperature.[1,2,5,6] On the other hand, chelation of a bidentate ligand is much slower ($\approx 10^1\ s^{-1}$ at 25 °C[11,12]).

The substitution at the basal site can proceed either by a direct substitution or by an intramolecular process from the apical site. For discriminating these two processes we have synthesized the new compound aquaoxo((2-pyridylmethyl)iminodiacetato)vanadium(IV), $VO(pmida)H_2O$, in the crystalline state and elucidated the structure by X-ray crystallography,[13] to find that the trans site to the oxo ligand is occupied by the tertiary amine (Figure 1). So far as this structure is maintained in solution, the replacement of the aqua ligand by a unidentate ligand can proceed only by a direct substitution. We have found that addition of thiocyanate or azide ions into the aqueous solution results in the replacement of coordinated water, and the rate can be measured by a stopped-flow technique at room temperature ($X^- = NCS^-$ or N_3^-).

$$VO(pmida)H_2O + X^- \rightleftharpoons VO(pmida)X^- + H_2O \quad (1)$$

This paper deals with the result of kinetic studies and the discussion of the reaction mechanism.

Experimental Section

Materials. The complex $[VO(pmida)H_2O]\cdot 2H_2O$ was synthesized by a given method,[13] and the purity was checked by IR and UV spectra, elemental analysis of carbon, hydrogen, and nitrogen, and the pK_a measurement (6.4 at 25 °C and I = 1.0). Ammonium oxo((2-pyridylmethyl)iminodiacetato)thiocyanatovanadium(IV), $NH_4[VO(pmida)(NCS)]$, was prepared by mixing the aqua complex with a large excess of ammonium thiocyanate in aqueous solution and setting aside for 24 h. The violet crystals were washed with a mixture of ethanol and water and then ethanol and air-dried. Anal. Calcd for $C_{11}H_{14}N_4O_5V$: C, 36.17; H, 4.03; N, 15.68. Found: C, 36.17; H, 3.84; N, 15.34. Infrared absorption [$\tilde{\nu}$(C–S) 772, $\tilde{\nu}$(C–N) 2098 cm^{-1}] supported the coordination of NCS^- by the nitrogen atom. Attempts to prepare a crystalline azido complex have turned out unsuccessful.

The ionic strength was adjusted with commercial Special Grade sodium perchlorate and lithium perchlorate. The latter was prepared from the carbonate and perchloric acid and doubly recrystallized. Sodium thiocyanate was recrystallized from aqueous ethanol, and the concentration of the aqueous solution was determined by titration with mercury(II) nitrate with iron(III) ions as indicator.[14] Sodium azide was recrystallized from aqueous ethanol. Lithium azide was prepared by adding a calculated amount of barium azide solution to a lithium sulfate solution. The suspension was centrifuged, filtered, and treated with ethanol to obtain colorless crystals, which were recrystallized

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