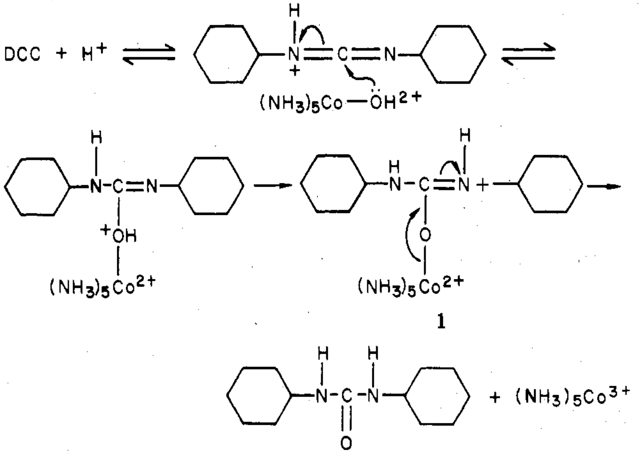
Scheme I



At this stage several mechanisms for the DCC/acetic acid promoted solvolysis of the aqua complex in DMF can be considered. It is possible that, under these conditions, there could be a kinetically significant concentration of the hydroxo complex along with acetate ion and the conjugate acid of DCC. If this is so, the mechanism set out in Scheme I is feasible. Certainly, a similar mechanism must be postulated for the process in which Ag^+ serves as an electrophilic catalyst. There is also precedent for a reaction of this type in that *N,N'*-dicyclohexyl-*O*-methylisourea is formed quantitatively from DCC and methanol in the presence of a hydrogen phosphate ester as an acid catalyst.[6] This mechanism requires that the oxygen atom of the aqua complex be transferred to the dicyclohexyl area. A reaction (run 25) was performed with ^{18}O-labeled aqua complex and a deficiency of acetic acid so as to avoid dilution of the urea by material produced in formation of acetic anhydride. Although 52% of the aqua complex was converted to DMF complex, only 7% (±12%) of the oxygen label was found in the urea produced. We therefore conclude that the mechanism in Scheme I is not involved.

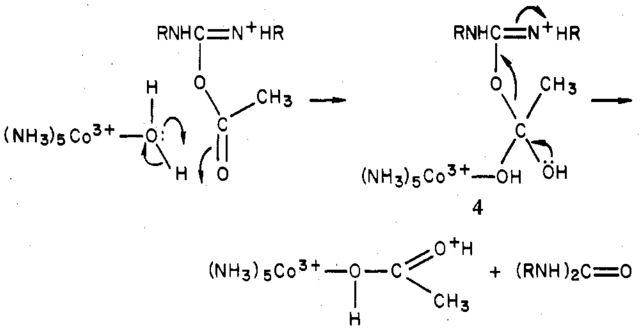
A more attractive mechanism involves attack by the aqua complex on the *O*-acetyl isomer (**2**) or its conjugate acid (**3**)

$$\underset{\mathbf{2}}{RNHC(OAc){=}NR} \qquad \underset{\mathbf{3}}{RNHC(OAc){=}N^+HR}$$

which are known[4,8] to be involved in the formation of acetic anhydride from acetic acid and DCC. The species of the types **2** and **3** are considerably more reactive than DCC or its conjugate acid, so much so that they can be attacked by quite weak nucleophiles. For example, in the case of the reaction of 2,6-dichloro-4-nitrophenol with DCC, the intermediate *O*-aryl ether analogous to **2** has been shown to be an active esterifying agent.[9] Furthermore, it has been shown that even as weak a nucleophile as *p*-nitrophenol is capable of reacting with **2** to give *p*-nitrophenyl acetate.[8]

The DMF complex could be formed through two possible routes. If attack by the aqua complex on **3** occurs (with concomitant proton transfer), the intermediate dication **4** (Scheme II) so formed would presumably dissociate extremely rapidly. Alternatively, **3** may be sufficiently electrophilic to react directly with DMF to yield the urea and the species $CH_3CO—OCN{=}N^+(CH_3)_2$ (**5**) which has been shown to rapidly effect solvolysis of the aqua complex.[3] A decision between the intermediates **4** and **5** has been reached through a study of the ^{18}O-labeled aqua complex. It has been shown[3] that the attack of **5**, generated by the reaction of Ag^+ with acetyl chloride in DMF, involves its imino carbon and results in essentially total retention (92 ± 3%) of the label in the DMF complex. In the present reaction, the DMF complex isolated also retained all the ^{18}O label (107 ± 2%) present in the aqua compound. We therefore conclude that the intermediate **5** rather than **4** is involved in the solvolysis reaction.

Scheme II



Registry No. Aquopentaamminecobalt(III) perchlorate, 13820-81-0; Ro-OAc, 16632-78-3; Ro-DMF, 31125-61-8; Ro-OSb, 69926-71-2; DCC, 538-75-0.

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Redox (and Substitution) Properties of the Titanium(III) Ethylenediaminetetraacetate Complex

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A number of studies on the reduction of cobalt(III) complexes by the titanium(III)–aquo ion, which generally reacts as $Ti(H_2O)_5OH^{2+}$, have been reported recently.[1-6] We now consider mechanistic features of the reduction of three key Co(III) complexes $Co(NH_3)_6^{3+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(NH_3)_5H_2O^{3+}$ with the Ti(III)–edta complex (edta ≡ ethylenediaminetetraacetate). At pH ca. 2 and less, the latter is believed to have the structure $Ti(edtaH)H_2O$, where on titration with base, acid dissociation pK_a values of 2.02 (carboxylate proton) and 8.64 (H_2O proton) are observed.[7] The edta is in other words quinquedentate with the free carboxylate arm protonated and H_2O occupying the sixth coordination position. It is here concluded that a log–log correlation of rate constants for the reduction of Co(III) complexes by Ti(III)–edta and $Ru(NH_3)_6^{2+}$ gives an anomalously low slope as observed previously for the Ti(III)–aquo ion.[4,6] With $Co(NH_3)_5H_2O^{3+}$ as oxidant, the Ti(III)–edta reaction, unlike that with the Ti(III)–aquo ion, utilizes an inner-sphere pathway, the implications of which are that the H_2O of $Ti(edtaH)H_2O$ is exceptionally labile.

Experimental Section

Solutions of hexaaquotitanium(III) chloride in dilute HCl and LiCl were as described previously.[4] Solutions of edta were made up by weight from the disodium salt (Fisions, AR). All experiments involving

Table I. Second-Order Rate Constants, k, for the Oxidation of Ti(III)-edta with Co(III) Complexes at 25 °C and $I = 0.10$ M (LiCl)

$[H^+]$, M	$10^3 \times$ [Ti(III)], M	$10^4 \times$ [Co(III)], M	k, $M^{-1}\ s^{-1}$
	Oxidant $Co(NH_3)_6^{3+}$		
0.087	5.0	5.0	0.164
0.082	7.7	7.7	0.164
0.082	7.7	7.7	0.166
0.041	5.0	5.0	0.170
0.018	1.7	1.7	0.159
0.010	5.0	5.0	0.166
	Oxidant $Co(NH_3)_5Cl^{2+}$		
0.087	5.0	5.0	10.0
0.082	7.7	7.7	9.1
0.082	7.7	1.3	9.7
0.026	5.0	5.0	10.0
0.018	1.7	1.3	9.4
0.010	5.0	5.0	9.6
	Oxidant $Co(NH_3)_5H_2O^{3+}$		
0.085	5.0	5.0	104
0.065	5.0	5.0	102
0.030	7.7	1.3	200
0.030	5.0	5.0	198
0.020	5.0	5.0	276
0.017	5.0	5.0	308
0.010	5.0	5.0	570

Ti(III) were carried out under air-free (N_2) conditions by using nylon syringes and plastic (Teflon) needles. Solutions containing 1:1 and 2:1 ratios of Ti(III) (3×10^{-3} M) to edta at pH 1.5 gave identical spectra (λ_{max} 546 nm, ϵ 11.6 $M^{-1}\ cm^{-1}$). At ionic strength $I = 0.10$ M (LiCl) and $[H^+] = 0.03$–0.09 M, the absorbances of solutions of varying Ti(III):edta ratios were investigated and confirmed that a 1:1 complex was formed. Chloride salts of the Co(III) complexes were prepared as described previously.[4]

Kinetic studies (25 °C) were with the Ti(III)-edta complex in large (≥10-fold) excess; $I = 0.10$ M (LiCl). Reactions were monitored by following the decay of the Co(III) absorption maxima at 473 nm (ϵ 58 $M^{-1}\ cm^{-1}$) for $Co(NH_3)_6^{3+}$, 530 nm (ϵ 50.1 $M^{-1}\ cm^{-1}$) for $Co(NH_3)_5Cl^{2+}$, and 492 nm (ϵ 47 $M^{-1}\ cm^{-1}$) for $Co(NH_3)_5H_2O^{3+}$. The reaction with $Co(NH_3)_6^{3+}$ was monitored by conventional means on a Unicam SP500 spectrophotometer, and the two other reactions on a Durrum stopped-flow apparatus. All observations were consistent with a 1:1 reaction, Ti(III) + Co(III) → Ti(IV) + Co(II). First-order rate constants obtained from the slopes (×2.303) of plots of absorbance changes log $(A_t - A_\infty)$ against time gave a first-order dependence on reductant, and hence second-order rate constants k.

Results

Rate constants, $[H^+] = 0.010$–0.090 M, are listed in Table I. With $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ as oxidants, reactions conform to the rate law (1). At 25 °C, $I = 0.10$ M (LiCl)

$$-d[Co(III)]/dt = k[Ti(III)][Co(III)] \qquad (1)$$

and $k = 0.165 \pm 0.005\ M^{-1}\ s^{-1}$ for $Co(NH_3)_6^{3+}$, and $k = 9.6 \pm 0.4\ M^{-1}\ s^{-1}$ for $Co(NH_3)_5Cl^{2+}$. A feature of the $Co(NH_3)_5H_2O^{3+}$ reaction is the $[H^+]^{-1}$ dependence of k (Figure 1)

$$k = a + b[H^+]^{-1} \qquad (2)$$

where a is small and poorly defined ($22 \pm 12\ M^{-1}\ s^{-1}$) and $b = 5.3 \pm 0.3\ s^{-1}$.

Discussion

As noted previously[4,8] early first-row transition-metal ions, e.g., Ti(III) and V(II), exhibit a reluctance to use halide ions Cl^-, Br^-, and I^- (but not F^-) as bridging ligands for inner-sphere electron transfer. Thus reductions of both $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ by the Ti(III)-aquo ion are outer-sphere.[4] We have no evidence to suggest that this pattern of behavior is any different with Ti(III)-edta as reductant. A plot of rate constants log k_{Ti} against log k_{Ru} (or alternatively log k_V, where V^{2+} is the reductant) gives a slope of ca. 0.50 or less as in the previous studies with the Ti(III)-aquo ion,[4,6] Figure 2, and not ca. 1.0 as observed with other reductants.[9-12] Should an allowance have to be made for inner-sphere contributions in the case of the Ti(III)-edta reduction of $Co(NH_3)_5Cl^{2+}$, then the slope will be even less. The reasons for this anomalous behavior with the Ti(III) reductants is not clear. Davies and Earley[14] have observed that, for a series of Ti(III)-aquo ion reductions of Ru(III) complexes, a plot of $\Delta G°$ against $\Delta G^‡$ is close to 0.50 and have concluded that the Ru(III) reactions unlike the Co(III) reactions do not display anomalous behavior. It is apparent that the tendency of Ti(III) to be only half as selective as other reductants is a joint property of the Ti(III) and Co(III) reactants.

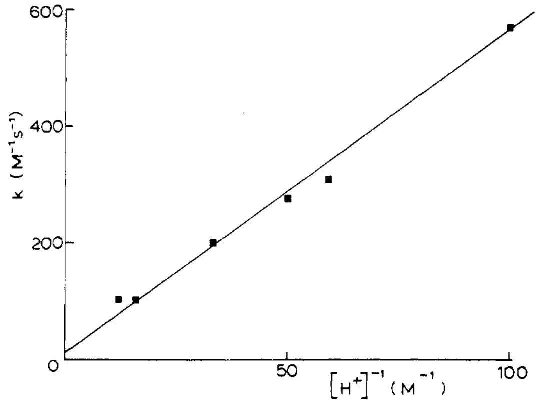

Figure 1. Dependence of k (25 °C) on $[H^+]^{-1}$ for the Ti(III)-edta reduction of $Co(NH_3)_5H_2O^{3+}$; $I = 0.10$ M (LiCl).

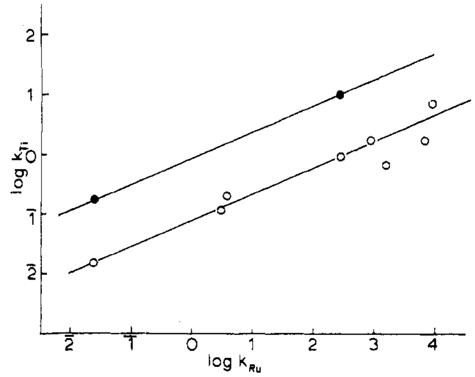

Figure 2. A comparison of rate constants (25 °C) for the Ti(III)-edta and $Ru(NH_3)_6^{2+}$ reductions of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ (●) with the previously established correlation[4] for the $Ti(H_2O)_5OH^{2+}$ and $Ru(NH_3)_6^{2+}$ reductions of a series of Co(III) complexes (○). The acid dissociation constant for $Ti(H_2O)_6^{3+}$ has been assumed to be 2×10^{-3} M. Rate constants for the $Ru(NH_3)_6^{2+}$ reductions are listed in ref 4.

The $[H^+]^{-1}$ dependence observed in the Ti(III)-edta reductions of $Co(NH_3)_5H_2O^{3+}$ is unlikely to originate from the reductant, since no similar dependence is observed in the reactions with $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$. It must originate therefore from the acid dissociation of $Co(NH_3)_5H_2O^{3+}$ ($K_a \approx 6 \times 10^{-7}$ M)[15] (eq 3). The ratio of rate

$$Co(NH_3)_5H_2O^{3+} \overset{K_a}{\rightleftharpoons} Co(NH_3)_5OH^{2+} + H^+ \qquad (3)$$

constants for the reduction of $Co(NH_3)_5OH^{2+}$ ($b/K_a \approx 10^7\ M^{-1}\ s^{-1}$) and $Co(NH_3)_5H_2O^{3+}$ (ca. 22 $M^{-1}\ s^{-1}$) is indicative of an inner-sphere pathway.[16] Formation of a bridged complex as in (4) is followed by electron transfer (eq 5). It is not

$$Ti(edtaH)H_2O + Co(NH_3)_5OH^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (edtaH)TiOHCo(NH_3)_5^{2+} + H_2O \qquad (4)$$

$$(\text{edtaH})\text{TiOHCo(NH}_3)_5^{2+} \xrightarrow{k_2} \text{products} \qquad (5)$$

known whether k_1 or k_2 is rate determining. However clearly k_1 must be equal to or greater than the rate constant (ca. 10^7 M^{-1} s^{-1}). Since K for outer-sphere association of the reactants in k_1 is unlikely to be >1 M^{-1}, the water-exchange rate constant is >ca. 10^7 s^{-1}. The rate constant for water exchange on $Ti(H_2O)_6^{3+}$ is ca. 10^5 s^{-1} [17] so that the edta appears to have a strong labilizing effect. This could well result from the presence of the uncoordinated carboxylate arm of the edta which is capable of forming a transient seven-coordinate Ti(III) species, with resultant labilization of the H_2O. An analogous mechanism has been suggested to explain the rapid complexation (replacement of H_2O) of the Cr(III)–edta complex $Cr(edta)H_2O^-$ by acetate, azide, chromate(VI), molybdate(VI), and tungstate(VI).[18,19] A similar, quite remarkable labilization has been observed also for the Ru(III)–edta complex $Ru(edta)H_2O$.[20] Whether this is a feature to be expected of all such complexes having fewer than six d electrons requires further substantiating.

Other features to note in these reactions are that the Ti(III)–edta complex is a more effective reductant than the aquo ion. Thus rate constants for the reaction of $Ti(H_2O)_5OH^{2+}$ with $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ are 0.015 and 0.95 M^{-1} s^{-1}, respectively,[21] whereas corresponding values for $Ti(edtaH)H_2O$ are 0.165 and 9.6 M^{-1} s^{-1}, i.e., a factor of ca. 10 greater. We also note that rate constants for the $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ oxidations of the Ti(III)–edta complex remain unaffected by $[H^+]$ down to 0.010 M. This suggests, since the first pK_a value is 2.02, that the reactions are insensitive as to whether the free carboxylate of the edta is protonated or not. Finally, with the presumed linear relationship in Figure 2 and a value for $k_{Ru} = 3$ M^{-1} s^{-1} for the $Ru(NH_3)_6^{2+}$ reduction of $Co(NH_3)_5H_2O^{3+}$,[22] an outer-sphere contribution to the Ti(III)–edta reduction of $Co(NH_3)_5H_2O^{3+}$ of 1–2 M^{-1} s^{-1} is obtained. It is possible that such a pathway is a dominant, or the only, contributor to the rate constant a in eq 2.

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Registry No. Ti(III)-edta, 69897-19-4; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5H_2O^{3+}$, 14403-82-8.

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(12) Alternatively, using the point for $Co(bpy)_3^{3+}$ (a revised rate constant of 1.1×10^4 M^{-1} s^{-1} has been obtained for the $Ru(NH_3)_6^{2+} + Co(bpy)_3^{3+}$ reaction[13]) and reassigning the μ-superoxo point as outer-sphere, we observe that this plot may curve upward at log $k_{Ru} > 4.0$ and assume a slope approaching 1.0. An outer-sphere assignment for the $TiOH^{2+}$ reduction of the μ-superoxo complex is consistent with previous assignments with Fe^{2+}, Cr^{2+}, and V^{2+} as reductant.[11] The previous suggestion that the $TiOH^{2+}$ reaction was inner-sphere was based on the lack of correlation with other data at log $k_{Ru} < 4.0$. We now feel that this possibility should be further considered. The correlation in ref 11 provides another possible example of a nonlinear log–log plot of rate constants.

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Hydrolysis of the *trans*-Hydroxo(sulfato)tetraammineplatinum(IV) Cation and Synthesis of *cis*-Dihydroxotetraammineplatinum(IV) Sulfate

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Sulfato complexes of platinum(IV) are rare,[1] and data on the hydrolysis of the platinum(IV)–sulfate bond are not available. In cationic ammine complexes of platinum(IV) hydrolysis of anionic ligands is quite slow and normally requires strongly alkaline conditions.[2,3] We report here an isomerization which accompanies the hydrolysis of a platinum(IV)–sulfate bond, a type of behavior which had not been previously reported for ammine complexes of platinum(IV).

Results and Discussion

The hydrolysis of *trans*-$Pt(NH_3)_4(OH)SO_4^+$ (reaction 1)

$$trans\text{-}Pt(NH_3)_4(OH)SO_4^+ + OH^- \rightarrow Pt(NH_3)_4(OH)_2^{2+} + SO_4^{2-} \qquad (1)$$

was studied in alkaline solution. High-pressure cation-exchange chromatograms of hydrolyzed solutions had two peaks, both at retention volumes corresponding to 2+ ions. The relative sizes of the two peaks was a function of the pH at which the *trans*-$Pt(NH_3)_4(OH)SO_4^+$ was hydrolyzed. The major product when hydrolysis was carried out in an ammonia solution (pH 11.1) eluted before the second component and had the same retention volume as *trans*-$Pt(NH_3)_4(OH)_2^{2+}$ (made by the reaction of H_2O_2 with $Pt(NH_3)_4^{2+}$).[4,5] The percentage of trans compound was approximately 30 at pH 13.2, 60 at pH 12.2, and 80 at pH 11.1. The hydrolysis was run on a synthetic scale in 0.3 M NaOH. From this solution a sparingly soluble sulfate salt could be isolated which had a retention volume identical to the more strongly retained ion in the chromatogram of the hydrolysis solution. The analysis of this compound corresponds to the formula $Pt(NH_3)_4(OH)_2SO_4$. This compound and *trans*-$[Pt(NH_3)_4(OH)_2]SO_4$ have ultraviolet spectra with different shapes; however, neither has a maximum at wavelengths longer than 200 nm; both do absorb strongly below 240 nm. (At 220 nm their molar absorptivities are 1.5×10^3 and 2.0×10^3 (trans).) The infrared spectra of the two compounds have peaks in the same regions but are different in the placement and intensities of the peaks. On the basis of this data it seems that the new compound is *cis*-$[Pt(NH_3)_4(OH)_2]SO_4$. The cation is quite unreactive; for example, it reacts only very slowly with 2 M HBr at 25 °C.

The chromatogram of an aged solution of *trans*-$Pt(NH_3)_4(OH)_2^{2+}$ in 0.2 M NaOH does not exhibit a peak characteristic of the cis isomer. This suggests that the cis product is formed directly from the sulfato complex. Since there are two products of the reaction, the relative concen-

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