some interesting contrasts and similarities. With regard to the binding of dioxygen, two reports[10,11] of enhanced affinity for coordination of O_2 by polymer-bound substrates have appeared, but causes for the proposed enhanced affinities have not been established. Enhancement could be due to entropic factors, a difference in metal–oxygen bond strength in the two media, solvation differences for the adduct in the different media, or a combination of these effects. Unfortunately, the EPR spectra of the polymer-bound O_2 adducts studied in this work are broadened to such an extent that it is difficult to infer whether or not the electronic structure of bound O_2 differs slightly for the two conditions. Closer consideration of the evidence for enhanced binding of O_2 by the metal complex on the polymer reveals that this reported conclusion has not been established in a completely rigorous fashion. Qualitative comparisons have been based on the relative magnitudes of the $P_{1/2}(O_2)$ values at a given temperature. For solution and polymer supported conditions, this quantity could be dominated by factors other than the metal–dioxygen adduct stability. The $P_{1/2}(O_2)$ values in solution relate to the equilibrium constant for the process 1. However, this is a net equilibrium constant

$$\mathrm{B{\cdot}CoL(soln)} + \mathrm{O_2(g)} \rightarrow \mathrm{B{\cdot}CoL{\cdot}O_2(soln)} \qquad (1)$$

for the two independent processes 2 and 3. Thus, as long as

$$\mathrm{O_2(g)} \rightarrow \mathrm{O_2(soln\ or\ polymer)} \qquad (2)$$

$$\mathrm{B{\cdot}CoL(soln\ or\ polymer)} + \mathrm{O_2(soln\ or\ polymer)} \rightarrow \mathrm{B{\cdot}CoL{\cdot}O_2(soln\ or\ polymer)} \qquad (3)$$

the medium is held constant, $P_{1/2}(O_2)$ values can be compared to provide information on metal–dioxygen interactions. However, the comparison of $P_{1/2}(O_2)$ values for systems studied in different media will contain contributions from the equilibrium constant for eq 2. Labeling the equilibrium constants for eq 1, 2, and 3 as K_1, K_2, and K_3, respectively, we note that $K_1 = K_2K_3$ and that K_2 is independent of the complex. Unless information is available regarding the thermodynamic data for eq 2, an interpretation of $P_{1/2}(O_2)$ data (on systems investigated in different media) to yield information regarding the metal–dioxygen interaction is not possible. Even with polymer variation, the polymer-bound data must be corrected for the distribution constant involving $O_2(g) \rightarrow O_2(\mathrm{polymer})$ before trends in metal binding or metal–dioxygen solvation by the medium can be deduced.

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Registry No. VB, 100-42-5; VBC, 29731-85-9; DVB, 1321-74-0; CME, 3188-13-4; polystyrene, 9003-53-6; imidazole, 288-32-4; $Co(DPGB)_2{\cdot}2MeOH$, 70046-75-2; $Co(DPGH)_2$, 63994-24-1; $Co(DPGB)_2{\cdot}B{\cdot}MeOH$, 70006-02-9; $Co(DPGB)_2{\cdot}B_2$, 70006-03-0; $Co(DPGB)_2{\cdot}N\text{-}CH_3Imid{\cdot}O_2$, 70046-77-4.

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(14) GR stands for gel resin and MR macroreticular. The percent cross-linking follows X and the percent substitution follows S. Cross-linking and substitution are in mole percent. X15(molar) = X20(% by weight) and S6(molar) ≃ S8(% by weight).
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Notes

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Reaction of Aquapentaamminecobalt(III) Perchlorate with Dicyclohexylcarbodiimide and Acetic Acid

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In a previous paper,[1] we described the facile conversion of aquapentaamminecobalt(III) salts to carboxylato complexes by the reaction of anhydrides in the presence of 2 equiv of base. Since acid anhydrides are not a class of commonly available compounds, we investigated reactions in which they were produced in situ by the reaction of the carboxylic acids with dicyclohexylcarbodiimide (DCC).[2] The process proved to be successful, but during the study it was found that the order of addition of the reactants was critical. In particular, it appeared that if the aqua complex was exposed to a mixture of DCC and the acetic acid in *N,N*-dimethylformamide (DMF) before the addition of base, substantial solvolysis occurred, and the resulting acetato complex was heavily contaminated with (*N,N*-dimethylformamido)pentaamminecobalt(III). In this paper we describe a series of experiments designed to delineate this phenomenon and to prove the mechanism of the process involved.

Experimental Section

Materials. Aquapentaamminecobalt(III) perchlorate and its ^{18}O-labeled derivative were prepared and purified as described previously.[1] The DCC used was reagent grade. DMF was purified by distillation and dried over Linde 4A molecular sieves.

Reactions. DCC and the cobalt complex were placed in a flask. Any other solid reagents were then added followed by DMF (~2 mL; see Table I). After the solid had dissolved, the appropriate liquids (if any) were added, the acid always being last.

After the appropriate reaction period, the reaction was slowed by chilling the mixture to −15 °C, and the solvent was removed in vacuo,

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Table I. Solvolysis of Aquapentaamminecobalt(III) Perchlorate in DMF at 23 °C

	concn, M					mol %[a]		
run	$RoOH_2$[a]	DCC	AcOH	other reagents (concn, M)	time, h	Ro-OAc	Ro-DMF	$Ro-OH_2$
1	0.09	0.34	0.34	DMB[b] (0.9)	3.5	100	0	0
2	0.10	0.40	0.40		3.5	7	93	0
3	0.04	0.16		SbOH[c] (0.16), DMB (0.04)	17	88[d]	0	12
4	0.04	0.16		SbOH (0.16)	17	0	100	0
5	0.08	0.08			24		26	74
6	0.08	0.24			24		24	76
7	0.03	0.12		SbO^-Na^+ (0.04)	20	0	22	78
8		0.40	0.40	RoOAc (0.10)	24	100	0	
9		0.15	3.8	RoOAc (0.08)	24	100	0	
10	0.10			Ac_2O (0.4)	3.5	10	9	81
11	0.10			Ac_2O (0.4)	24	20	61	19
12	0.08	0.30		$HClO_4$ (72%) (0.60)	17		13	87
13	0.06	0.03		TsOH (0.02)	17		7	93
14	0.08	0.24		$pyH^+ClO_4^-$ (0.08)	24		32	68
15	0.08			$pyH^+ClO_4^-$ (0.08)	24		24	76
16	0.08	0.24		$AgNO_3$ (0.24)	24		86	14
17	0.08	0.24		$AgClO_4$ (0.30)	24		71	29
18	0.08			$AgClO_4$ (0.30)	24		20	80
19	0.08	0.24		py (0.08)	24		25	75
20	0.08	0.24		DMB (0.08)	24		25	75
21	0.08	0.24		DMB (0.08), $DMBH^+$ (0.08)	24		27	73
22	0.08	0.24		py (0.12), pyH^+ (0.08)	24		49	21
23	0.10	0.30		py (0.12), pyH^+ (0.08)	24		35	19
24	0.08			py (0.08), pyH^+ (0.08)	24		24	76
25	0.44	0.40	0.40		3.5	13	52	35

[a] Ro ≡ $(NH_3)_5Co$. [b] DMB ≡ *N,N*-dimethylbenzylamine. [c] SbOH ≡ sorbic acid. [d] Sorbato complex.

the temperature never being allowed to exceed 15 °C. The oil obtained was treated with DMF (2 mL) and the evaporation repeated to ensure complete removal of acetic anhydride. The oil was extracted with ether (3 × 5 mL) to remove any unreacted DCC. The residual oil or solid was dissolved in water (3 mL) and evaporated to dryness. The solid was triturated with ethanol (3 × 3 mL) and ether (2 × 3 mL) and dried in vacuo. Yields were almost invariably in excess of 90%, and it is believed that the losses did not discriminate between different complexes. The proportions of acetato and *N,N*-dimethyformamido complexes were measured by proton NMR. The proportion of aqua complex was obtained by comparison of the UV/visible spectrum in acid and base.

^{18}O Analysis. The ^{18}O content of the aqua perchlorate was obtained by conversion to the corresponding acetatotrifluoromethanesulfonate and analysis of the methyl acetate produced on deacetoxylation.[3] It was found to be 4.840 ± 0.022% ^{18}O.

The ^{18}O-labeled dicyclohexylurea was analyzed directly with an AEI MS902 mass spectrometer as described previously.

^{18}O content of the DMF complex was obtained by converting the complex to its bromide salt and by heating the salt to 130 °C in a sealed tube. The DMF so liberated was extracted into ether. The technique used was similar to that described for the analysis of methyl acetate, the analysis being based on the relative intensities of the P and P + 2 ions.[3] It was found to be 5.163 ± 0.099% ^{18}O.

Results and Discussion

The results of a series of experiments are presented in Table I.

Treatment of the aqua complex and excess DCC in DMF with *N,N*-dimethylbenzylamine (DMB) and acetic acid (in that order) yielded the pure acetato complex (run 1). When the base was omitted, the conversion of the DMF complex was almost complete (run 2). These results were reproducible, and the same remarkable change in products has been observed with sorbic acid (runs 3 and 4). This behavior cannot be ascribed to solvolysis of the aqua complex, unreacted in the absence of base (run 5). Similarly, the aqua complex was unaffected in the presence of DCC alone (run 6) and even with the diimide in the presence of carboxylate anion (run 7).

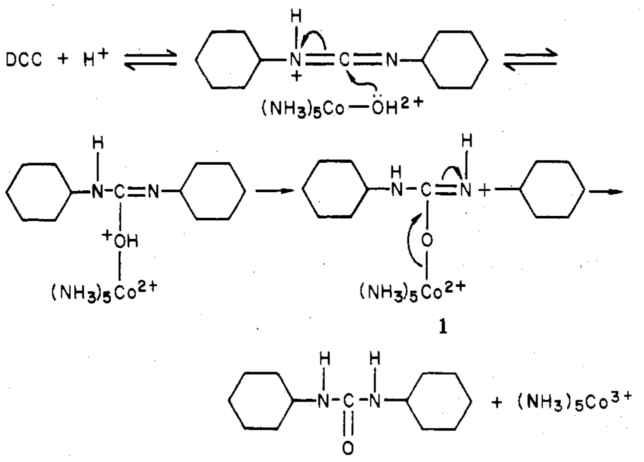
The acetato complex was found to be quite stable in solution with DCC and varied amounts of acetic acid (runs 8 and 9). Furthermore, it was not possible to ascribe the effect to acetic anhydride alone, for its production of the DMF complex was much too slow to account for the observations (runs 10 and 11).

We have already seen that the reaction occurs with sorbic acid. Other acids were tested to determine whether the reaction occurred only for carboxylic acids. Perchloric acid caused an apparent decrease in the solvolysis rate (run 12). This presumably only reflects a slightly low analysis, but there was sufficient water in the 72% acid to react with the DCC, so this result regarding the effect of acid is not conclusive. *p*-Toluenesulfonic acid (a monohydrate) was therefore used in a catalytic amount, again, with no appreciable formation of DMF complex (run 13) (this acid is known to be completely inert with DCC owing to the low nucleophilicity of its anion).[4] With pyridinium hydroperchlorate, the amount of solvent complex increased at 32% (run 14). The blank (run 15) gave 24% DMF complex. Although the difference from simple solvolysis (20–26%) is not large, conditions and measurements were such that this difference is probably significant. Yet the pK_a of pyridine hydroperchlorate (5.5) is so similar to that of acetic acid (4.75) and the difference in effects so large (especially considering the times involved) that the function of the carboxylic acid is probably not merely that of a proton donor.

The possibility of electrophilic catalysis was examined. The conversion to the DMF complex in the presence of silver ions was significant, although again the time is relatively long. Two experiments are reported (runs 16 and 17) since reproducibility was poor. No enhanced solvolysis was observed in the absence of DCC (run 18).

Both pyridine and DMB were added to test for reaction with the DCC via the hydroxo complex in the absence of acetic acid (runs 19 and 20). Again there was no enhancement in rate, nor was there with an equimolar mixture of DMB and its hydroperchlorate (run 21). Pyridine hydroperchlorate in the presence of pyridine resulted in increased formation of the DMF complex (run 22 and 23). Duplicates of both experiments agreed to within 2%, and no unusual effect was noted in the blank (run 24). The yields of the DMF and aqua complexes do not, however, provide a material balance, and the fate of the remaining cobalt was not determined.

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.

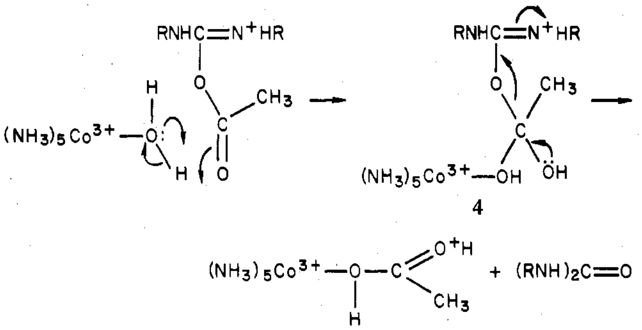
A more attractive mechanism involves attack by the aqua complex on the *O*-acetyl isomer (**2**) or its conjugate acid (**3**)

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

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