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Reaction of Polymer–Amminecobalt(III) Complexes with Chromium(II)[1]

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Received April 11, 1963

Soluble polypeptide–amminecobalt(III) complexes, obtained by reaction of aquopentaamminecobalt(III) perchlorate with polyglutamic acid, have been shown, by reaction with concentrated hydrochloric acid, to contain tetraammine- as well as pentaamminecobalt(III) ions. A rapid reaction of these complexes with aquochromium(II), reported earlier, and then ascribed to peptide mediation of electron transfer, has been shown to correlate with their tetraammine content. Comparison of the rate law for this rapid reaction with rate laws for reduction of several aquo- and acidotetraamminecobalt(III) ions suggests that the fast-reacting species in the polypeptide complexes is a carboxylatoaquotetraamminecobalt(III) ion. Polymers derived from acrylatopentaamminecobalt(III) perchlorate have been prepared, and their reactivity to aquochromium(II) ion is reported.

Unusual reactivity of polypeptide–amminecobalt(III) complexes, formed by reaction of aquopentaamminecobalt(III) perchlorate with polypeptides containing glutamic acid residues, has been reported in previous papers.[3,4] The reduction of these polymeric complexes by aquochromium(II) ion (eq. 1) was noteworthy in that there could be resolved two parallel reactions with rate constants of about 100 and 0.1 l. mole^{-1} sec.$^{-1}$ at 25°. The faster process was apparently associated with the polypeptide nature of the carboxyl ligand and was assumed to be the reduction of pentaamminecobalt(III) bound to favored sites of the polymer. The lower rate is characteristic of simple carboxylatopentaamminecobalt(III) derivatives. Because the existence of the fast reaction suggested the possibility that a peptide backbone could mediate electron-transfer reactions, more detailed examination was undertaken.

$$[(\mathrm{RCOO})\mathrm{Co}(\mathrm{NH_3})_5]^{2+} + \mathrm{Cr}^{2+} \longrightarrow [\mathrm{RCOOCr}]^{2+} + \mathrm{Co}^{2+} + 5\mathrm{NH_3} \quad (1)$$

Amminecobalt(III) complexes of poly-L- and DL-glutamic acids were prepared, as in earlier work, by treatment of partially neutralized polypeptide with excess aquopentaamminecobalt(III) perchlorate in water at 50–70°. With simpler carboxyl components, including succinic and malonic acids, these conditions yield solely carboxylatopentaammine derivatives according to eq. 2. However, reaction of carboxylatopentaamminecobalt(III) ions with concentrated hydrochloric acid yields only insoluble chloropentaamminecobalt(III) chloride, but similar treatment of the peptide complexes resulted in formation of tetrachlorocobalt(II) ion as well. A study of model substances showed that tetraamminecobalt(III) complexes are readily reduced under these conditions, presumably because their chloro substitution products are soluble and react further. The formation of tetrachlorocobalt(II) ion from the polypeptide complexes was therefore taken to mean that displacement of ammine ligands occurs during their formation and was made the basis of a measure of "disubstitution." (Disubstitution so determined, however, probably includes all cobalt(III) derivatives bearing four or fewer ammine ligands.)

$$\mathrm{RCOOH} + [(\mathrm{H_2O})\mathrm{Co}(\mathrm{NH_3})_5]^{3+} \longrightarrow [(\mathrm{RCOO})\mathrm{Co}(\mathrm{NH_3})_5]^{2+} + \mathrm{H_3O^+} \quad (2)$$

On the assumption that the rapid reaction of the polypeptide complexes with aquochromium(II) was related to the presence of polymer-bound tetraamminecobalt(III) ions, a comparison of the reduction kinetics of the peptide complexes and several model ions of established structure was undertaken.

It appeared in addition worthwhile to prepare nonpeptide polymers bearing carboxylatopentaamminecobalt(III) side chains, for study of their reaction with aquochromium(II). This preparation was readily accomplished by vinyl polymerization of acrylatopentaamminecobalt(III) perchlorate, alone and with acrylic acid or acrylamide. The reactivities of these acrylic polymers do not suggest any important influence of their polymeric nature on the electron-transfer process.

Experimental

Acrylatopentaamminecobalt(III) Perchlorate.—This salt was prepared from aquopentaamminecobalt(III) perchlorate and acrylic acid according to usual methods.[5] The inhibitor present in the acrylic acid was not removed prior to preparation of the complex. *Anal.* Calcd. for $\mathrm{Co(NH_3)_5(C_3H_3O_2)(ClO_4)_2}$: Cl, 17.1; N, 16.8. Found: Cl, 16.8; N, 16.3.

***cis*-Diaquotetraamminecobalt(III) perchlorate** was prepared by hydrolysis of the carbonatotetraammine nitrate,[6] using perchloric acid at 0°. ***trans*-Diacetatotetraamminecobalt(III) perchlorate**[7] was prepared by heating the diaquotetraammine with a tenfold excess of half-neutralized acetic acid at 70°. *Anal.* Calcd. for $\mathrm{Co(NH_3)_4(C_2H_3O_2)_2(ClO_4)}$: Cl, 10.3; N, 16.3. Found: Cl, 10.3; N, 15.7. ***cis*-Aquoacetatoetraamminecobalt(III) perchlorate**[7] resulted when the *cis*-diaquotetraammine was treated with one molar equivalent of half-neutralized acetic acid at 70°. The product ran as a single band on Dowex 50 X2 resin (sodium form) when eluted with 1 *M* sodium perchlorate.

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(1) This work was supported by a grant from the National Science Foundation, G-14324.

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(3) K. D. Kopple and G. F. Svatos, *J. Am. Chem. Soc.*, **82**, 3227 (1960).

(4) K. D. Kopple, R. R. Miller, and T. C. Muller, in "Polyamino Acids, Polypeptides and Proteins," M. A. Stahmann, Ed., University of Wisconsin Press, Madison, Wisc., 1962, p. 295.

(5) D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961).

(6) G. Schlessinger, *Inorg. Syn.*, **6**, 173 (1960).

(7) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **260**, 65 (1949).

Anal. Calcd. for $Co(NH_3)_4(H_2O)(C_2H_3O_2)(ClO_4)_2$: Cl, 17.6; N, 14.0. Found: Cl, 17.5; N, 14.1. The two acetato derivatives were previously prepared from the carbonatotetraammine.[7] In the present preparation, they crystallized on cooling the reaction mixture, which was made as concentrated as was consistent with complete solution at 70°. The absorption spectra of these substances agreed with those published by Linhard and Weigel.[8]

***cis*-N-Acetyl-β-alaninatoaquotetraamminecobalt(III) Perchlorate.**—To 1.5 g. (0.012 mole) of N-acetyl-β-alanine[9] in 3.5 ml. of water was added 1.15 ml. of 5 *N* sodium hydroxide and 4.5 g. (0.010 mole) of *cis*-diaquotetraamminecobalt(III) perchlorate. The mixture was heated 3–4 hr. at 60° and then acidified to pH 2 by means of concentrated perchloric acid. The product was precipitated by addition of ethanol and ether, redissolved in water, and chromatographed on a column of Dowex 50 X2 cation exchanger (hydrogen form) using 1 *M* sodium perchlorate as eluent. The first of three bands eluted was identified as the *trans*-diacido complex on the basis of its ready elution (low charge) and the similarity of its visible absorption spectrum to that of the known *trans*-diacetatotetraammine.[8] The second component, which was shown to be eluted at the same rate as the known acetatoaquotetraammine, was assumed to be the desired acidoaquotetraammine, and its solution in 1 *M* sodium perchlorate, as eluted, was used as a stock solution for kinetic experiments. The linearity of the integrated rate plots obtained using this solution demonstrated that it contained only one cobalt(III) species. The third band was only slowly eluted from the column and was identified as starting material.

Crystallization of the β-alaninato complex by concentration of eluted solutions was not possible because of its high water solubility. An attempt was made to obtain an analytical sample by chromatography with 0.5 *M* calcium perchlorate as eluent. The fraction bearing the desired complex was lyophilized and recrystallized four times from ethanol to effect separation of the complex from the more alcohol-soluble calcium perchlorate, but the product so isolated still contained about 12% of the calcium salt, as estimated from its analysis. In the absence of good analytical data, no clear-cut distinction between chelate acidoamidotetraammine and acidoaquotetraammine structures for this product was possible. However on the basis of the acid dependence of its reaction with chromium(II), the product was assigned the latter structure (see Discussion section).

***cis*-Malonatotetraamminecobalt(III) Perchlorate.**—To 10.4 g. (0.1 mole) of malonic acid in 10 ml. of water was added 3.0 g. (0.075 mole) of sodium hydroxide and then 4.6 g. (0.010 mole) of *cis*-diaquotetraamminecobalt(III) perchlorate. The mixture was heated to 60° for 2–3 hr., long enough to bring all reactants into solution. The work-up of the product was similar to that given above for the acetyl-β-alaninatoaquotetraammine, except that the resin was used in the sodium form. The first eluted band was identified as a *trans* isomer by its absorption spectrum.[8,10] The second band, which was eluted at a rate corresponding to the diacetatotetraammine, was considered to be the desired chelate; it possessed the absorption spectrum of a *cis* isomer[8] and, because it did not exhibit the usual hydrolytic instability of *cis*-diacidotetraammines, it could reasonably be assumed to be the chelate species. The eluted solution was used as a stock solution for kinetic studies and its homogeneity was established by the linearity of the resulting integrated rate plots.

Polypeptide–Amminecobalt(III) Complexes.—These complexes were formed by heating concentrated aqueous solutions of polyglutamic acid and aquopentaamminecobalt(III) perchlorate adjusted to pH 4–4.7 for 2–4 hr. at 50–70°. pH and temperature control were critical; insoluble brown products were formed at higher pH and also when the reaction temperature was held above 70°. As the temperature of reaction was increased, the pH at which brown precipitates formed decreased. In general no soluble complexes containing nondialyzable cobalt(III) could be formed with less than 20% "disubstitution." A typical preparative procedure follows.

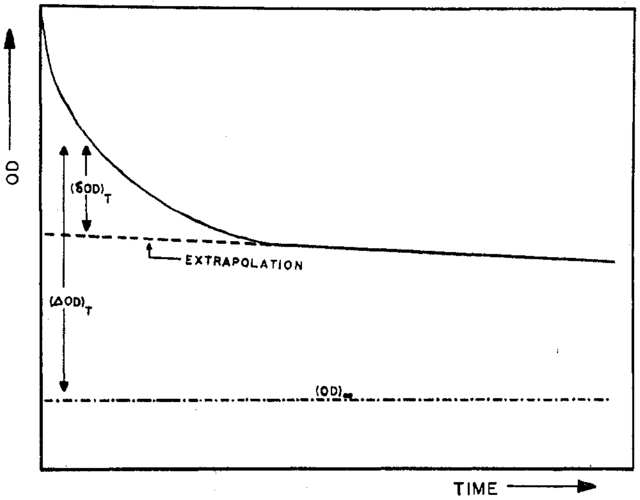

Fig. 1.—Absorption at 500 mμ maximum of cobalt(III) in polyglutamic acid complexes, during reaction with Cr^{2+}. The fast reaction is assumed to be represented by the change in δOD. Justification for the dotted extrapolation lies in the more than hundredfold difference in specific rate for the two reaction paths.

The pH of a slurry of 0.5 g. of poly-L-glutamic acid in 40 ml. of water was adjusted to 6.8. To the resulting solution was added 11 g. of aquopentaamminecobalt(III) perchlorate; the mixture was adjusted to pH 4.7 and heated to 70° for 2 hr. After reaction, the mixture was cooled to room temperature, filtered free of the considerable insoluble material that had formed, and acidified to pH 2.5 by means of dilute perchloric acid. Excess aquopentaammine was removed by overnight dialysis against 0.003 *N* perchloric acid; subsequent dialysis against pure water resulted in precipitation of the pink polymer complex. Solid complex could be obtained by lyophilization of the dialysate, but because of difficulty in redissolving the lyophilized product, solutions for kinetic studies were made by reacidifying the suspension of precipitated polymer to pH 2.5–3.0 to bring about complete solution.

The analysis of these polymers is described below. The particular preparation described had a cobalt : glutamic acid ratio of 0.5 and 71% "disubstitution." In common with the other polypeptide–amminecobalt(III) preparations, it exhibited an absorption band near 500 mμ (Table I), but the band near 350 mμ normally expected was largely masked by more intense absorption at lower wave length.

Polymers of Acrylatopentaamminecobalt(III) Perchlorate.—The homopolymer and copolymers with acrylamide and acrylic acid were prepared by polymerization in aqueous solution using a persulfate–metabisulfite initiator. They were purified by dialysis and isolated by lyophilization. A single example is given.

To 1.0 g. (0.0024 mole) of acrylatopentaamminecobalt(III) perchlorate in 50 ml. of water was added 4.0 ml. (0.056 mole) of freshly distilled acrylic acid. Oxygen was flushed from the solution by the addition of small pieces of solid carbon dioxide, and there was then added 1.5 ml. of 2% aqueous potassium persulfate, followed by 1.0 ml. of 1% sodium metabisulfite. The reacting solution was allowed to remain at room temperature overnight, then dialyzed against 0.003 *N* perchloric acid overnight. The dialyzed solution was used as a stock solution for studies of reaction with chromium(II), but samples for analysis were obtained by lyophilization. Conversion to nondialyzable polymer was quantitative.

Homopolymerization of the complex acrylate under the same conditions gave a 10% yield of nondialyzable, water-soluble polymer; conversion improved with increasing amounts of co-monomer and was virtually quantitative at a 10 : 1 ratio of components.

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[8] M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **264**, 321 (1951).

[9] J. Baddiley and E. M. Thain, *J. Chem. Soc.*, 3425 (1951).

[10] This band was assumed to be the *trans*-dimalonatotetraammine; its separation from the desired chelate is probably the result of ionization of uncoordinated carboxyl groups and consequent reduction of charge.

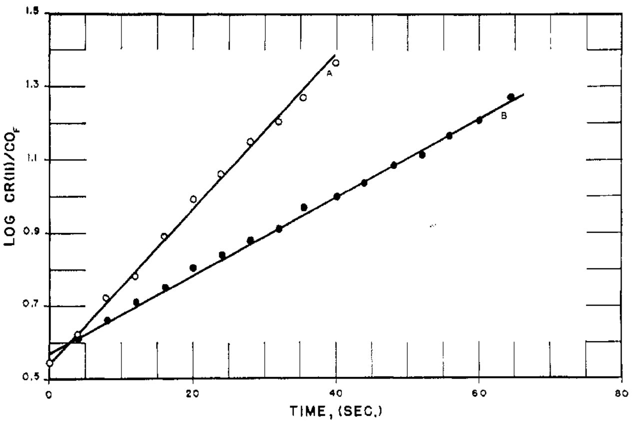

Fig. 2.—Typical second-order rate plots for fast reaction of poly-L-glutamic acid complexes, derived using analysis described in the Experimental section. [Co(III)] = 9×10^{-4} *M;* % "disubstitution" = 48; [Cr(II)] = 9×10^{-4} *M;* [H_3O^+] = 0.51 *M* (dark circles), 0.06 *M* (light circles); ionic strength 0.5; 25°.

Analysis of Cobalt(III) Complexes.—The concentration of cobalt(III) in stock solutions of the complexes was determined by a modification of the method of Nyman and Plane[11]; in this modification, the complex is hydrolyzed by concentrated alkali, and the hydrolysis products are converted to tetrachlorocobalt(II) ion by reaction with concentrated hydrochloric acid. Tetrachlorocobalt(II) is measured spectrophotometrically at 690 mμ. Standards of aquopentaamminecobalt(III) perchlorate were run with each determination. Determination of that fraction of cobalt(III) (in the unknown complexes) bearing four or fewer ammine ligands was made concurrently.

In each of three 10-ml. volumetric flasks was placed 1 ml. of a solution of unknown, of concentration such that the optical density at the 500 mμ absorption peak was about 0.6 for a 1-cm. path; in each of two other flasks was placed 1 ml. of aquopentaamminecobalt(III) perchlorate solution of similar concentration. One flask of each set was diluted to 10 ml. with water and the spectra of the diluted solutions were measured using a Cary Model 14 spectrophotometer equipped with a 0–0.2 optical density slide wire. To another flask from each set was added 1 ml. of 5 *N* sodium hydroxide; the contents of these flasks were heated 10 min. on the steam bath, cooled, mixed with 7 ml. of concentrated hydrochloric acid, cooled, and diluted to 10 ml. with water. After the precipitated sodium chloride was allowed to settle, the absorption of each solution at the 690 mμ maximum of the $CoCl_4^{2-}$ ion was determined. The concentration of cobalt in the unknown was thus established by comparison with the standard. To the third flask containing unknown was added 7 ml. of concentrated hydrochloric acid; this flask was tightly stoppered and heated in a protected area (breakage) 20 min. at about 95°, then it was cooled and its contents diluted to 10 ml. The absorption of the diluted solution at 690 mμ was determined and "disubstitution" was taken as the ratio ($CoCl_4^{2-}$ formed on acid treatment alone)/($CoCl_4^{2-}$ formed on treatment with alkali and then acid). This figure was at best reproducible only to within 10%. Values so determined from pure *cis*-diaquotetraammine were 70 and 72%, and from pure *trans*-diacetatotetraammine, 90 and 80%; therefore the estimates of "disubstitution" made by this method are probably generally low, perhaps because of incomplete reduction. A nonsystematic error lies in the variation of the 690 mμ absorption with hydrochloric acid concentration, since some loss of hydrogen chloride was apt to occur during the heating period. A more precise determination could undoubtedly be performed by carrying out the reduction in sealed ampoules and using a longer reaction time.

Chromium(II) perchlorate was prepared by electrolytic reduction of chromium(III) perchlorate solutions[12]; reduced solutions were stored under nitrogen in capped serum bottles, where they showed no appreciable decomposition in 6 months. Chromium(II) concentration was determined by the method of Tandon and Mehrotra,[13] using standard iron(III) and methylene blue as indicator. The hydrogen ion in these chromium(II) solutions was measured by titration with standard alkali, after the chromium(II) had been air-oxidized to the (III) state and then sequestered with oxalate. The acid content of the oxidized solution was taken as equal to that of the original solution less the chromium concentration.[14]

Reactions between Chromium(II) and Cobalt(III) Complexes.—Reactions were followed spectrophotometrically by the disappearance of cobalt(III) absorption in the 500 mμ region. A Cary Model 14 spectrophotometer, equipped with a recorder slide wire covering the optical density range 0.0–0.2, a thermostated cell jacket, and chart drive gears giving a chart speed of 12 sec./in., was used for most measurements. For slower reactions a chart speed of 60 sec./in. was used.

An experimental procedure similar to that of Svatos and Taube[15] was used. Chromium(II) solutions were measured and transferred from storage in serum-capped bottles by means of greased tuberculin syringes or Hamilton Teflon-sealed gas-tight syringes. Precision for both types of syringe was 1% of full volume. Air-tight joints between the needle and syringe were ensured by use of Teflon bushings. Reacting solutions were prepared by placing calculated volumes of stock solutions of all reagents except chromium(II) in a spectrophotometer cell and adding the volume of water necessary to produce the desired cobalt concentration, acidity, and ionic strength. The cell was then sealed with a serum cap and oxygen was removed by bubbling oxygen-free nitrogen through the solution *via* hypodermic needle inlet and outlet tubes. To prevent diffusion of oxygen into the cell, all serum caps were kept heavily coated with stopcock grease. Injection of the required volume of chromium(II) perchlorate solution was effected only after the contents of the cell had been allowed to reach equilibrium in the thermostated cell compartment of the spectrophotometer. With care, mixing times (the time from initial injection of reductant until significant recording could be started) could be held to 2 ± 1 sec.

The technique just described was adequate, in that data were obtained for at least 70% of reaction, for reactions complete in as short a time as 22 sec. Estimates of rate constants of the order of 300 l. mole^{-1} sec.$^{-1}$ have been made using more dilute solutions and a 10-cm. cell. Cobalt(III) concentrations were limited to those greater than about 0.001 *M* by the low extinction of the complexes (ε 50–80); a similar limitation on chromium(II) concentration was set by the limitations of serum-capped spectrophotometer cells in excluding atmospheric oxygen.

For all but the polypeptide complexes, the ratio [Cr(II)]/[Co(III)] for use in the integrated second-order rate expression was obtained from the spectrophotometer traces by use of the relationship

$$\frac{[\mathrm{Cr}]}{[\mathrm{Co}]} = 1 + \frac{[\mathrm{Cr}]_0 - [\mathrm{Co}]_0 \Delta OD_0}{[\mathrm{Co}]_0 \Delta OD}$$

where ΔOD is the difference between the instantaneous optical density and that at infinite time, measured at the absorption maximum near 500 mμ. Cr and Co refer to the ions in their initial oxidation states, (II) and (III), respectively, and subscript zero indicates initial values.

For the reactions of the polypeptide complexes it was assumed that: (a) two forms of cobalt(III) were initially present, one, Co_f, reacting rapidly, and the other, Co_s, reacting slowly with aquochromium(II); (b) the amounts of these cobalt(III) species and their specific reaction rates were in such relationship that $d[Co_s]/dt$ was effectively constant while Co_f was consumed; and (c) Co_f and Co_s had the same extinction coefficient,

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(11) C. J. Nyman and R. A. Plane, *J. Am. Chem. Soc.*, **83**, 2617 (1961).

(12) D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958); R. Flatt and F. Sommer, *Helv. Chim. Acta*, **25**, 684 (1952).

(13) J. P. Tandon and R. C. Mehrotra, *Z. anal. Chem.*, **158**, 20 (1957).

(14) D. K. Sebera, Ph.D. Dissertation, University of Chicago, 1960.

(15) G. Svatos and H. Taube, *J. Am. Chem. Soc.*, **83**, 4172 (1961).

ϵ_{Co}, at the absorption maximum near 500 mμ (note the constancy of ϵ_{Co} among the preparations of varying "disubstitution" listed in Table I) and gave rise to products equally indistinguishable at that wave length (with extinction coefficient ϵ_p). The ratio of reactants is then obtained from the expression

$$\frac{[Cr]}{[Co_f]} = \frac{([Cr]_0 - [Co]_0)(\epsilon_{Co} - \epsilon_p) + \Delta OD}{\delta OD}$$

where δOD is the absorption estimated, as shown in Fig. 1, to be that primarily of Co_f, and the other symbols are as defined above. ϵ_p was determined to be about 20; ϵ_{Co} is given in Table I. The absorption of aquochromium(II) near 500 mμ was safely neglected in deriving the relationship above. Figure 2 indicates the quality of the second-order rate plots of the fast reaction so obtained.

TABLE I

FAST REACTION OF POLYGLUTAMIC ACID–AMMINECOBALT(III) PREPARATIONS WITH Cr^{2+}

Series	% disubst.[a]	% fast[b]	k_{H_2O}[c]	k_{OH}[c]	λ_{max}, mμ	ϵ_{Co}
L	71[e]	50	25	3.7	512	81
L	48[f]	37	35	3.6	506	84
L	35[f]	32	32	3.8	506	79
DL	56	50	29	2.4	508	82
DL	32	38	27	4.2	506	77
DL	12	13	..[d]	..[d]	..	..

[a] Fraction of nondialyzable cobalt converted to $CoCl_4^{2-}$ by hydrochloric acid. [b] From kinetic runs made at 0.25 *M* acid. [c] $k_{obsd} = k_{H_2O} + k_{OH}[H_3O^+]^{-1}$, where velocity of fast reaction $= k_{obsd}[Cr(II)][Co(III)_f]$; time in sec.; 25°; ionic strength 0.4. [d] Too little fast reaction to permit determination. [e] Glutamic acid/cobalt(III) = 2. [f] Glutamic acid/cobalt(III) = 9.

Results and Discussion

Peptide Complexes.—Reactions between aquochromium(II) ion and several preparations of polyglutamic acid–amminecobalt(III) complexes were followed spectrophotometrically and separated into fast and slow processes as described in the Experimental section. Little attention was paid to the slower reaction, which proceeded at a rate comparable to that of the acrylic polymers described below. The fast reaction was analyzed as a process first order in chromium(II) and first order in a fraction of the total polymer-bound cobalt, which fraction varied from preparation to preparation. Linear second-order rate plots were obtained (Fig. 2), a result consistent with the assumption that a single species of fast-reacting cobalt(III) was present in the polymeric complexes. The data obtained in these measurements are summarized in Table I.

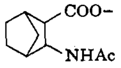
The data of Table I indicate that, for a given preparation of polypeptide complex, the fraction of peptide-bound cobalt(III) that was reduced rapidly by aquochromium(II) was, within the errors of the estimations, not larger than the fraction of peptide-bound cobalt(III) that was reduced by concentrated hydrochloric acid ("disubstitution"). Both of these quantities were increased by use of higher pH, higher temperature, or longer reaction time in preparing the complex. Because of this correlation it was assumed that the fast-reacting cobalt(III) species was a tetraammine; it was judged that the lower ammines would be so unstable hydrolytically as not to be isolated as soluble peptide complexes.

In the region over which the kinetics of the fast reaction was examined, 0.05–0.5 *M* acid, the rate expressions for all complex preparations included a term inverse in hydrogen ion concentration and did not vary significantly among the differing preparations. These rate laws were sufficiently like that found for the model tetraammine, *cis*-acetatoaquotetraamminecobalt(III) perchlorate, to support the conclusion that the fast portion of the reduction by aquochromium(II) is the result of the presence of carboxylatoaquotetraamminecobalt(III) in the polypeptide complexes. With this simpler hypothesis available, it is thus unnecessary to postulate mediation of electron transfer by the polypeptide backbone. The similarity in behavior of L- and DL-polypeptide complexes suggests that polymer backbone structure, helix or coil, is not relevant to the fast reaction; some differences would be anticipated if the peptide played an important role in the electron-transfer process. (However, both L and DL polymers may be restricted to a coil conformation by the high acidity of the medium and the presence of heavily-charged side chains, in which case no differences in behavior would be expected.)

The activity of polyglutamic acid in promoting hydrolysis of pentaamminecobalt(III) is noteworthy. For a mixture of this polymer with aquopentaammine, a few minutes at pH 5.0 and 70° suffice to bring about a rise in pH, evolution of ammonia, and the formation of brown, insoluble products. A previously formed polypeptide complex is equally susceptible to hydrolysis. Because the same hydrolytic instability is characteristic of acrylamide–acrylatopentaamminecobalt(III) copolymers, additional carboxyl or carboxylate groups in the acido ligand are not necessarily involved. (Qualitatively, copolymers of acrylatopentaammine with acrylic acid are more stable to hydrolysis than copolymers with acrylamide.) It is in fact possible to bring about loss of ligand ammonia by heating, in the dry state, carboxylatopentaammines derived from several

TABLE II

TETRAAMMINE FORMATION ON HEATING CARBOXYLATOPENTAAMMINECOBALT(III) PERCHLORATES

Carboxyl ligand	% "disubstitution"[a] Initial	Final	Hr. at 100°[e]
$AcNHCH_2COO-$	0.4	13.3	15 (130°)
$AcNHCH_2CH_2COO-$[b]	5.3	8.0	15
$AcNHCH_2CONHCH_2COO-$[b]	2.6	13.6	15
Copoly APAC/AM,[c] 1/12	1	22	15
 (*cis*, *endo*)[b]	5.0	23.2	15
		32.7	96
Poly-DL-glutamic acid	18	63	5.5
Poly-L-glutamic acid[d]	0	52	5.5

[a] Fraction of cobalt converted to $CoCl_4^{2-}$ by hydrochloric acid. [b] We are indebted to Dr. Thomas C. Muller for the preparation of these compounds. [c] APAC, acrylatopentaamminecobalt(III) perchlorate; AM, acrylamide. [d] Salt of aquopentaamminecobalt(III) and half-neutralized polyglutamic acid. [e] Heated under vacuum.

TABLE III

Cr^{2+} REDUCTION OF TETRAAMMINECOBALT(III) PERCHLORATES

Substituents	k_{obsd}[a]	λ_{max}, mμ
cis-$(H_2O)_2$	$7 + 8.4[H_3O^+]^{-1}$	503 (56), 355 (47)
cis-$(H_2O)(OAc)$	$47 + 2.8[H_3O^+]^{-1}$	510 (67), 355 (50)
cis-(H_2O)(Ac-β-ala)	$58 + 0.55[H_3O^+]^{-1}$	510 (70), 365 (58)
$(NH_3)(H_2O)$[b]	$0.5 + 1.57[H_3O^+]^{-1}$	490 (50), 344 (47)
cis-$(O_2CCH_2CO_2)$	$30 + 20[H_3O^+]$	510 (70), 360 (78)
cis-$(O_2CCH_2CH_2CO_2)$[c]	$30 + 75[H_3O^+]$	
trans-$(OAc)_2$	$15 + 50[H_3O^+]$	550 (62), 470 (25 sh), 363 (66)
$(NH_3)(OAc)$[d]	0.18	503 (71), 358 (60)

[a] l. mole^{-1} sec.$^{-1}$ at 25°, ionic strength 1.0. Velocity = k_{obsd}[Cr(II)] [Co(III)]. [b] A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959). [c] We are grateful to Dr. R. T. M. Fraser for communicating this result prior to publication. [d] Reference 5.

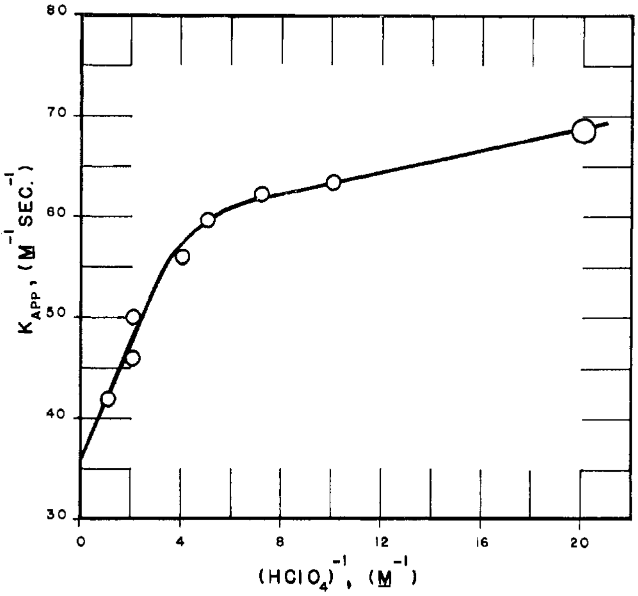


Fig. 3.—Specific rate for reaction of *cis*-acetyl-β-alaninato-aquotetraamminecobalt(III) perchlorate with Cr^{2+} at 25°; ionic strength 1.0.

nonpolymeric amido acids (Table II), and it also appears that there is some loss of ammonia in the preparation of these complexes by the usual methods. Although it thus seems that an amide function is involved in the displacement of ammonia, the kinetic data on the fast reaction of the polypeptide complexes indicate that the ultimate result of the displacement is the introduction of water as a ligand. It is open to question whether, when ammonia is displaced in the course of forming a carboxylato complex, the amide group displaces it and is itself displaced, or the amide group catalyzes direct displacement by water. More or less permanent cobalt–amide coordination seems unlikely in aqueous solution, since it did not prove possible to prepare a chelate amidocarboxylatotetraammine from acetyl-β-alanine and diaquotetraamminecobalt(III); only dicarboxylato and aquocarboxylato derivatives were obtained.

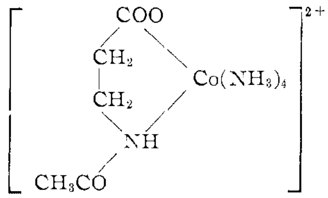
Tetraammines.—To establish the nature of the fast-reacting cobalt(III) in the polypeptide complexes, it was necessary to prepare a series of cobalt(III) tetraammines. The details of these preparations appear in the Experimental section, and the relevant kinetic data appear in Table III and Fig. 3. (The latter have, in part, been reported and discussed elsewhere,[16] but are given here for completeness.) The similarity between the rate expressions for fast-reacting cobalt(III) in the polyglutamic acid complexes and that for *cis*-aquoacetatotetraamminecobalt(III) has already been noted.

The data for *cis*-acetyl-β-alaninatoaquotetraammine, shown in Fig. 3, may be analyzed in terms of the equilibria (3) and (4), with the equilibrium constant for (3)

$$[(CH_3CONH_2CH_2CH_2COO)(H_2O)Co(NH_3)_4]^{3+} \rightleftharpoons [(CH_3CONHCH_2CH_2COO)(H_2O)Co(NH_3)_4]^{2+} + H^+ \quad (3)$$

$$[(CH_3CONHCH_2CH_2COO)(H_2O)Co(NH_3)_4]^{2+} \rightleftharpoons [(CH_3CONHCH_2CH_2COO)(OH)Co(NH_3)_4]^{+} + H^+ \quad (4)$$

estimated at about 0.23, a not unreasonable value for the acidity of a protonated amide.[17] Extrapolation of the less steep linear portion of the plot (Fig. 3), to cancel the effect of amide protonation, yields the expression given for the complex in Table III, which expression is then comparable to that for the acetatoaquo complex, where the equilibrium corresponding to (4) is responsible for the inverse acid term. The kinetic behavior indicated in Fig. 3 is consistent with the structure assigned to the β-alanine complex. It is inconsistent with the chelate structure



which does not contain a function capable of binding a proton near pH 0.

The acid-independent reactivity toward aquochromium(II) of the tetraamminecobalt(III) complexes listed in Table III is generally a hundredfold greater than that of acetatopentaamminecobalt(III) perchlorate, corresponding to about a 3 kcal. decrease in the activation barrier for electron transfer. No single reason can be given for this decrease. Since there is evidence that in at least one case, *cis*-acetatoaquotetraamminecobalt(III) perchlorate, the reacting complex is doubly bridged,[16] one might ascribe the decrease to

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[16] K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).

[17] A. R. Goldfarb, A. Mele, and N. Gutstein, *J. Am. Chem. Soc.*, **77**, 6194 (1955).

a doubly-bridged transition state,[18] were it not that such a transition state seems sterically unlikely for the *cis* complexes of the dibasic acids, succinic and malonic, and is impossible for the *trans*-diacetato complex. (The last three complexes are not much less reactive than the *cis*-acetatoaquotetraammine.) It may be that a decrease in energy level of the electron-accepting e_g orbital of cobalt(III), produced on replacement of ammonia by a weaker-field oxygen ligand, contributes to the decreased activation barrier. If this stabilization of an e_g electron is significant, however, it must be assumed that the t_{2g} and e_g orbitals are almost equally lowered in energy by replacement of ammonia by *cis* carboxylate, because the $(t_{2g})^6 \rightarrow (t_{2g})^5(e_g)$ transitions near 500 mμ are changed by no more than 300 cm.$^{-1}$ (<1 kcal.) on making this replacement (Table III).

Acrylic Polymers.—As a consequence of the method of synthesis, the complex ion in the polyacrylic acid derivatives listed in Table IV is entirely pentaammine; these polymers exhibit no fast reaction with chromium(II).

Analysis of the reaction of the acrylic polymers with chromium(II) yielded the result that, although reaction was first order in the latter, good integrated rate plots could be obtained only on the assumption of orders higher than one for cobalt(III)—as high as 2.8 for the acrylatopentaamminecobalt(III) homopolymer. Table IV gives for these polymers the orders in cobalt(III) that fit the data to 90% reaction for each case and approximate second-order rate constants (first order in cobalt(III)) obtained from the initial and final portions of reaction.

It is not likely that the abnormal kinetic order for cobalt(III) indicates that there are indeed, say, 2.8 cobalt atoms in the activated complex for reduction. More probably there is a gradual decrease in reactivity of cobalt(III) as reaction proceeds and the polymer becomes substituted with chromium(III), and so the fit to higher order is fortuitous.[19]

TABLE IV

Cr^{2+} REDUCTION OF ACRYLATOPENTAAMMINECOBALT(III) POLYMERS

Polymer		k_{initial}[a]	k_{final}[a]	Apparent order in Co
AM/APAC[b,c]	0	0.025	0.0037	2.80
	4.2	.038	.012	1.84
	13.8	.059	.014	1.62
	25.3	.069	.028	1.28
AA/APAC[b]	1.5[d]	$0.008 + 0.001[H_3O^+]^{-1}$[f]		1.34
	30[e]	$0.008 + 0.002[H_3O^+]^{-1}$		1.0

[a] Second-order rate constants estimated from initial and final portions of reaction, l. mole^{-1} sec.$^{-1}$; 25°. [b] AA, acrylic acid; AM, acrylamide; APAC, acrylatopentaamminecobalt(III) perchlorate. [c] Ionic strength 0.3. [d] Ionic strength 1.0. [e] Ionic strength 0.27. [f] Curvature of second-order rate plots neglected.

Gel formation occurred on reduction of the copolymers of high acrylamide content and on reduction of the acrylic acid copolymers when the acidity was relatively low (0.01 *M*), which indicates incorporation of amide and carboxylate side chains in the coordination sphere of chromium undergoing oxidation. This cross linking may account, in part, for the progressive inhibition of reaction.

If the second-order rate constants derived from the initial portion of reaction are examined, it is seen that there is a slight inhibition of reactivity in those polymers (acrylamide series) in which the density of charged side chains is high. There is, in the case of the copolymers with acrylic acid, some facilitation of reaction as the acidity is lowered, presumably due to adjacency of carboxylate ions to the reacting site. This last effect has been observed in the case of the malonato-[15] and *o*-phthalato-[5] pentaammines, though it is too small to be observed in the succinatopentaammine.[5]

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(18) R. Snellgrove and E. L. King, *J. Am. Chem. Soc.*, **84**, 4609 (1962), have established the doubly-bridged transition state for the exchange between *cis*-diazidochromium(III) and chromium(II); this exchange is 45 times faster than that involving monoazidochromium(III) and a singly-bridged activated complex.

(19) A somewhat analogous case, in which the reactivity of a unit changes with the fraction of polymer chain converted, is found in the mutarotation of poly-L-proline: I. Z. Steinberg, W. F. Harrington, A. Berger, M. Sela, and E. Katchalski, *ibid.*, **82**, 5263 (1960).