Specific Effects of Nucleophiles on the Mercury(II)-assisted Chloride Aquation of the Penta-amminechlorocobalt(III) Cation and of the Chloro[ethylenediaminetetra-acetato(3−)]cobaltate(III) Anion

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Simple anions (X^-) such as $CH_3CO_2^-$, Cl^-, N_3^-, Br^-, SCN^-, and CN^- influence the Hg^{2+}-assisted chloride aquation of $[CoCl(NH_3)_5]^{2+}$ and $[Co(edta)Cl]^{2-}$ (H_4edta = ethylenediamine-*NNN′N′*-tetra-acetic acid) through the formation of HgX^+. Observed rate changes reflect both the electrostatic and the inductive effects; the former predominates for $CH_3CO_2^-$, Cl^-, and N_3^-, while the latter does for CN^-. Aminopolycarboxylates, such as edta^{4-} and cdta^{4-} (H_4cdta = cyclopentane-1,2-diamine-*NNN′N′*-tetra-acetic acid) were specifically effective. A feature of the reactions with $[CoCl(NH_3)_5]^{2+}$ is the production of $[CoY(NH_3)_5]^-$ (Y = edta or cdta) alongside $[Co(NH_3)_5(OH_2)]^{3+}$.

According to the Debye–Brønsted equation, addition of an inert electrolyte increases rates of reactions between ions of the same sign, while it decreases those between ions of opposite signs. Deviations from the Debye-Brønsted equation[1–3] suggest the existence of specific interactions such as inner-sphere or outer-sphere complex formation and hydrophobic interaction.

Metal ion-assisted aquations between highly charged ions are suitable to see interactions between ions through chemical reactions.[4] We previously found that multivalent anions showed both accelerating and masking effects on the reaction between $[CoF(NH_3)_5]^{2+}$ and Al^{3+} to form $[Co(NH_3)_5(OH_2)]^{3+}$ depending on the concentration of the added anions.[5] We also found that oxalate or malonate ions produce mostly oxalato- or malonato-penta-amminecobalt(III) ions in place of penta-ammineaquacobalt(III) ions, probably because of their specific property of strongly co-ordinating to the aluminium ion with residual capacity for co-ordinating to the cobalt(III) ion.

In the present study, mercury ion-assisted aquations of the penta-amminechlorocobalt(III) cation and the chloro[ethylenediaminetetra-acetato(3−)]cobaltate(III) anion, $[CoCl(Hedta)]^-$, were allowed to proceed in the presence of various nucleophiles which strongly co-ordinate to the mercury ion. The nucleophiles used are $CH_3CO_2^-$, Cl^-, N_3^-, Br^-, SCN^-, CN^-, H_2edta^{2-}, *trans*-cyclopentane-1,2-diamine-*NNN′N′*-tetra-acetate(2−) (H_2cdta^{2-}), and dicyclohexyl-18-crown-6 (dchco) (eicosahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclo-octadecin). These anions (but not the crown ether) will electrically accelerate the reaction between Hg^{2+} and $[CoCl(NH_3)_5]^{2+}$, while their complex formation with the mercury ion will inhibit the reaction through weakening the electrophilicity of the Hg^{2+} ions. By analogy with dicarboxylate anions in the reaction of $[CoF(NH_3)_5]^{2+}$ with Al^{3+}, the aminopolycarboxylate anions can be expected to have specific effects on the reaction of $[CoCl(NH_3)_5]^{2+}$ with Hg^{2+}.

Experimental

Chemicals.—Penta-amminechlorocobalt(III) *perchlorate.* The chloride of the complex, prepared by the method of Hynes *et al.*,[6] was dissolved in hot water and was then converted to the perchlorate by treating it with concentrated perchloric acid and then cooling the solution in ice. The complex was identified spectrophotometrically.

Sodium chloro[ethylenediaminetetra-acetato(3−)*]cobaltate*(III) *dihydrate.* This was prepared by the method of Dwyer and Garvan.[7] The visible absorption spectrum of the prepared complex agreed with that reported by them.

Mercury(II) *perchlorate solution.* Mercury(II) oxide was dissolved in a 5 mol dm^{-3} perchloric acid solution, and mercury(II) perchlorate was crystallized out by cooling. The hygroscopic crystals were dissolved in a perchloric acid solution ($[HClO_4]$ = 0.05 mol dm^{-3}) and the resulting solution was used as a stock solution. The mercury(II) concentration was determined by a replacement titration with the $Na_2(H_2edta)$ solution in the presence of excess $Mg(edta)^{2-}$, using ebt ('Eriochrome Black T') as the indicator.

Sodium halides and sodium pseudo-halides. These were guaranteed reagents of Wako Pure Chemical Industries, Ltd., and were dried at 110 °C before use.

Disodium ethylenediaminetetra-acetate dihydrate. This was an analytical reagent obtained from Dojin; it was dissolved in distilled water and the pH of the solution controlled to 2—8 with crystalline sodium carbonate.

Kinetic Procedure.—The rate of the absorbance change was measured at 25 °C for the solutions containing the complex salt (5×10^{-4} mol dm^{-3}), mercury perchlorate (1.1×10^{-2} or 5.5×10^{-3} mol dm^{-3}), and other additives. The change in the absorbance was observed at 290 nm for the $[CoCl(NH_3)_5]^{2+} + Hg^{2+}$ reaction and at 510 nm for the $[CoCl(edta)]^{n-} + Hg^{2+}$ reaction, except for the following cases. (In this paper, edta and cdta are used to denote all forms of the species without specifying the degree of deprotonation, if any.) In the presence of either edta or cdta equimolar to, or in a slight excess of, the mercury ions, the absorbance changed with isosbestic points at 523, 418, and 353 nm in the former case (pH 2.8) and at 522, 413, and 355 nm in the latter case (pH 2.8). The reaction rates were followed at 495 nm in both cases. A Hitachi 200-10 spectrophotometer was used for slow reactions (with half-lives > 1 min) and a UNION RA-1300 stopped-flow spectrophotometer for fast reactions (with half-lives < 10 s). The rates were determined by plotting ln ($D_t - D_\infty$) against the time t, D_t and D_∞ being the absorbances at the time t and at the end of the reaction,

Table 1. Dependence of the rate of the $[\mathrm{CoCl(edta)}]^{n-}$ + Hg^{2+} reaction on the mercury concentration; pH 2.10 ± 0.05, $I = 0.08$ mol dm^{-3}

$[\mathrm{Hg}^{2+}]$/mol dm^{-3}	$k_{\mathrm{obs.}}$/s^{-1}
2×10^{-2}	16
1×10^{-2}	14
5.5×10^{-3}	9.8
4×10^{-3}	9.1
2×10^{-3}	5.8

Table 2. Dependence of the rate* of the $[\mathrm{CoCl(edta)}]^{n-}$ + Hg^{2+} reaction on the ionic strength; pH 1.90 ± 0.05, $[\mathrm{Hg}^{2+}] = 4 \times 10^{-3}$ mol dm^{-3}

$[\mathrm{NaClO_4}]$/ mol dm^{-3}	I/mol dm^{-3}	$k_{\mathrm{obs.}}$/s^{-1}	$k^{(12)}_{\mathrm{calc.}}$/s^{-1}	$k^{(22)}_{\mathrm{calc.}}$/s^{-1}
0	0.025	9.2		
0.02	0.045	8.5	8.9	7.8
0.05	0.075	7.7	7.8	6.5
0.10	0.13	7.2	7.1	5.3

* $k^{(12)}_{\mathrm{calc.}}$ and $k^{(22)}_{\mathrm{calc.}}$ are the rate constants calculated for the reactions $[\mathrm{CoCl(Hedta)}]^{-}$ + Hg^{2+} and $[\mathrm{CoCl(edta)}]^{2-}$ + Hg^{2+}, respectively.

respectively. The slope of this plot gives the pseudo-first-order rate constants, $k_{\mathrm{obs.}}$.

pH *Measurements*.—The pH value of the sample solution containing edta or cdta was controlled by the addition of $\mathrm{Na_2CO_3}$ crystals. The $\mathrm{pH_{obs.}}$ values of the sample solutions were determined by means of a Beckman Century SS-1 pH meter, using a Beckman 39301 glass electrode and a 39402 calomel reference electrode.

Competition in the Formation of the Cobalt(III) *Complexes for the* $[\mathrm{CoCl(NH_3)_5}]^{2+}$ + $\mathrm{HgX^+}$ (X = *Nucleophile*) *Reaction*.—As described above, the $[\mathrm{CoCl(NH_3)_5}]^{2+}$ + HgY^{2-} (Y = edta or cdta) reactions showed an absorbance change different from that for the $[\mathrm{CoCl(NH_3)_5}]^{2+}$ + Hg^{2+} reaction and the final reaction solutions contained $[\mathrm{Co^{III}(H_{\mathit{n}}Y)(NH_3)_5}]^{n-1}$. In order to determine the yields of the reaction products, the final reaction solution was added to a column of SP-Sephadex and eluted with a 0.15 mol dm^{-3} sodium sulphate solution. Two bands were observed; the first was assigned to the penta-ammine(aniono)cobalt(III) ion, $[\mathrm{Co^{III}(H_{\mathit{n}}Y)(NH_3)_5}]^{n-1}$, and the second to the penta-ammineaquacobalt(III) ion. (In the other cases only the latter complex ion could be detected.) The concentration ratio of the two complexes in the final reaction solution can be calculated from the following equation with the absorbances, D_{Y} and D_{A}, measured at the absorption maxima of the aniono (Y) and the aqua (A) complexes, respectively, and the volumes, V_{Y} and V_{A}, of the fractions of the eluate containing the complexes: equation (1). Here ε_{A} and ε_{Y} denote the molar

$$c_{\mathrm{Y}}/c_{\mathrm{A}} = \varepsilon_{\mathrm{A}} D_{\mathrm{Y}} V_{\mathrm{Y}} / \varepsilon_{\mathrm{Y}} D_{\mathrm{A}} V_{\mathrm{A}} \qquad (1)$$

absorption coefficients at the absorption maxima of respective complexes. The ε values used were 47.5 at 492 nm for the aqua complex, 75 at 505 nm for the edta complex (pH 7),[8] and 77 dm^3 mol^{-1} cm^{-1} at 505 nm for the cdta complex (pH 7).[9]*

Results and Discussion

The stoicheiometries of the reactions in the absence of the nucleophiles, reactions (2)—(5), have already been studied.[10,11]

$$\text{(A)}\ [\mathrm{CoCl(NH_3)_5}]^{2+} + \mathrm{Hg}^{2+} \xrightarrow[\mathrm{H_2O}]{k^{(A)}_{\mathrm{Hg}}} [\mathrm{Co(NH_3)_5(OH_2)}]^{3+} + \mathrm{HgCl}^{+} \qquad (2)$$

$$\text{(B)}\ [\mathrm{CoCl(edta)}]^{2-} + \mathrm{H}^{+} \xrightleftharpoons{K_a} [\mathrm{CoCl(Hedta)}]^{-} \qquad (3)$$

$$[\mathrm{CoCl(edta)}]^{2-} + \mathrm{Hg}^{2+} \xrightarrow{k^{(B1)}_{\mathrm{Hg}}} [\mathrm{Co(edta)}]^{-} + \mathrm{HgCl}^{+} \qquad (4)$$

$$[\mathrm{CoCl(Hedta)}]^{-} + \mathrm{Hg}^{2+} \xrightarrow{k^{(B2)}_{\mathrm{Hg}}} [\mathrm{Co(edta)}]^{-} + \mathrm{HgCl}^{+} \qquad (5)$$

The rate equation for reaction (A)[10] is given by equation (6). When $[\mathrm{Hg}^{2+}] \gg [\mathrm{CoCl(NH_3)_5}^{2+}]$, the observed pseudo-first-order rate constant is given by equation (7). For reaction (B),

$$\text{rate} = k^{(A)}_{\mathrm{Hg}}\, [\mathrm{CoCl(NH_3)_5}^{2+}][\mathrm{Hg}^{2+}] \qquad (6)$$

$$k_{\mathrm{obs.}} = k^{(A)}_{\mathrm{Hg}} [\mathrm{Hg}^{2+}] \qquad (7)$$

Dyke and Higginson[11] reported that when $[\mathrm{Hg}^{2+}\ ] \gg 10[\text{complex}]$, log [complex] *vs.* time t was linear but that $k_{\mathrm{obs.}}$ values derived from the log [complex] *vs.* t plots were not proportional to $[\mathrm{Hg}^{2+}]$, tending to approach limiting values with the increase in $[\mathrm{Hg}^{2+}]$. This result indicates that the reaction proceeds through an adduct such as $[\mathrm{CoCl(Y)Hg}]^{2-n}$ with a large stability constant. As the conditions of the reaction solutions in the present study for the salt effect differ from those in the literature,[11] dependencies of the rate on the mercury ion concentration and on the sodium perchlorate concentration were reinvestigated. Tables 1 and 2 give the results. For the sake of simplicity, the following reaction scheme (8) is considered, where $[\mathrm{CoCl(Y)}]^{n-}$ denotes collectively $[\mathrm{CoCl(edta)}]^{2-}$ and $[\mathrm{CoCl(Hedta)}]^{-}$, and K is constant at given pH and ionic strength. The observed rate of reaction (8) is written as equation (9).

$$[\mathrm{CoCl(Y)}]^{n-} + \mathrm{Hg}^{2+} \xrightleftharpoons{K} [\mathrm{CoCl(Y)Hg}]^{2-n} \xrightarrow{k} [\mathrm{CoY}]^{1-n} + \mathrm{HgCl}^{+} \qquad (8)$$

$$k_{\mathrm{obs.}} = kK[\mathrm{Hg}^{2+}]/(1 + K[\mathrm{Hg}^{2+}]) \qquad (9)$$

Using the results in Table 1, we obtained $K = 187 \pm 17$ dm^3 mol^{-1} and $k = 21 \pm 1$ s^{-1} as the weighted averages of the reactions of $[\mathrm{CoCl(edta)}]^{2-}$ and $[\mathrm{CoCl(Hedta)}]^{-}$ at the experimental pH. According to equation (8), the k value should be little affected by the ionic strength change, while the K value should be largely affected. The activity coefficients (y_{i}) of the species i depend on the ionic strength (I) according to the Debye–Hückel equation (10), where z_{i} is the charge number and

$$\log y_{\mathrm{i}} = -0.5115 z_{\mathrm{i}}^{2} I^{\frac{1}{2}} / (1 + 0.3291 \mathring{a} I^{\frac{1}{2}}) \qquad (10)$$

$\mathring{a}$ is the closest distance of approach of ions (in 10^{-10} m). We reported previously that the effect of $\mathrm{NaClO_4}$ on the rate of the $[\mathrm{CoCl(NH_3)_5}]^{2+}$ + Hg^{2+} reaction is explainable up to $I = 1.0$ mol dm^{-3} with equation (10) taking $\mathring{a} = 6$.[3] The effect of ionic strength on the rate constant was similarly calculated for the reactions $[\mathrm{CoCl(edta)}]^{2-}$ + Hg^{2+} and $[\mathrm{CoCl(Hedta)}]^{-}$ +

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* No solid $[\mathrm{Co(H_{\mathit{n}}cdta)(NH_3)_5}]^{n-1}$ compounds were obtained because of their high solubility in any solvent. The apparent ε value of $[\mathrm{Co(H_{\mathit{n}}cdta)(NH_3)_5}]^{n-1}$ was determined as follows. The eluate containing $[\mathrm{Co(H_{\mathit{n}}cdta)(NH_3)_5}]^{n-1}$ and $\mathrm{Na_2SO_4}$ was boiled to convert the $[\mathrm{Co(H_{\mathit{n}}cdta)(NH_3)_5}]^{n-1}$ to $[\mathrm{Co(cdta)}]^{-}$. The literature value of ε for $[\mathrm{Co(cdta)}]^{-}$ (316 at 540 nm)[9] was multiplied by the absorbance ratio of the initial to the final solution to give the ε value for $[\mathrm{Co(H_{\mathit{n}}cdta)(NH_3)_5}]^{n-1}$.

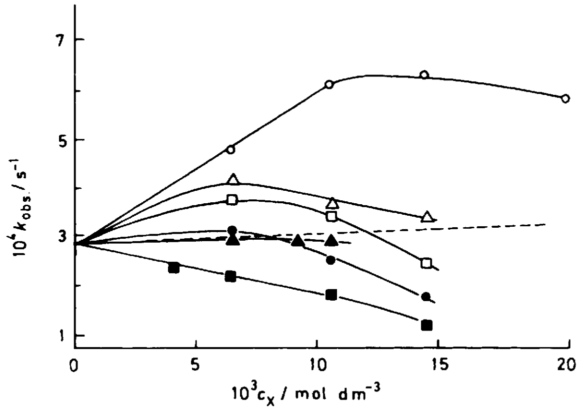

Figure 1. Effects of added nucleophiles on the reaction $[CoCl(edta)]^{n-} + Hg^{2+}$; pH 2.1 ± 0.1, $[CoCl(edta)^{n-}] = 5 \times 10^{-4}$, $[Hg^{2+}]_{total} = 5.5 \times 10^{-3}$ mol dm^{-3}. Nucleophiles (X): $CH_3CO_2^-$ (○), N_3^- (△), Cl^- (□), SCN^- (▲), Br^- (●), CN^- (■)

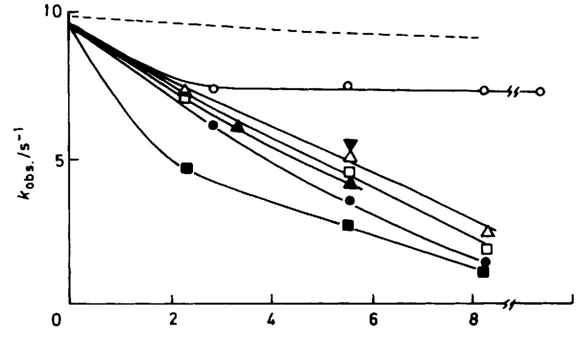

Figure 2. Effects of added nucleophiles on the reaction $[CoCl(NH_3)_5]^{2+} + Hg^{2+}$; pH 2.1 ± 0.1, $[CoCl(NH_3)_5{}^{2+}] = 5 \times 10^{-4}$, $[Hg^{2+}]_{total} = 1.1 \times 10^{-2}$ mol dm^{-3}. Nucleophiles (X): $CH_3CO_2^-$ (○), N_3^- (△), Cl^- (□), SCN^- (▲), Br^- (●), CN^- (■), dchco (▼)

Table 3. Stability constants of the mercury complexes with nucleophiles[a]

Nucleophile (X)	log K_{HgX}	log K_{HgX_2}
ClO_4^-	< 1	
$CH_3CO_2^-$	5.6[b] (4.7[c])	3.7[b] (1.0[c])
Cl^-	6.7 ± 0.1	6.5 ± 0.1
N_3^-	7.2	7.0
SCN^-	9.1[d]	7.8[d]
Br^-	9.1	8.3
CN^-	18	17
edta (Y)	22	
cdta (Y)	24	
dchco (Y)	2.7	

[a] The values are from L. G. Sillén and A. E. Martell, 'Stability Constants of Metal-Ion Complexes,' The Chemical Society, London, 1964, and Supplement, 1971, No. 1, unless indicated otherwise. [b] Ref. 13. [c] Ref. 12. [d] Ref. 14.

Hg^{2+} with å = 6. The calculated rate constants are compared with the observed ones in Table 2; the comparison shows that the reaction $[CoCl(Hedta)]^- + Hg^{2+}$ is predominant under the present condition of pH 1.9.

Effects of Univalent Anions on the Reactions of $[CoCl(edta)]^{n-}$ (*n* = 1 *or* 2) *and* $[CoCl(NH_3)_5]^{2+}$ *with* Hg^{2+}.—The experimental results are shown in Figures 1 and 2, where the broken lines indicate the effect of ionic strength ($NaClO_4$) estimated by use of equation (10). The deviations from these broken lines must be due to specific interactions between the anions and the reactants. The anions interact strongly with the mercury ion (Table 3) but only weakly with the cobalt(III) complexes {weakly attractive with $[CoCl(NH_3)_5]^{2+}$ and weakly repulsive with $[CoCl(edta)]^{n-}$}. Co-ordinating with a nucleophile, the mercury ion is expected to become less reactive to $[CoCl(edta)]^{n-}$ both from the decrease in the electric charge and from the decrease in the electrophilicity of the mercury ion. Figure 1 shows that addition of a nucleophile decreased the reaction rate, in agreement with this expectation. In the case of $[CoCl(NH_3)_5]^{2+}$, on the other hand, the co-ordination of a nucleophile to the mercury ion will electrostatically favour the reaction, but its inductive effect will act oppositely. The experimental results given in Figure 1 show that the electrostatic effect is predominant in the co-ordination of $CH_3CO_2^-$, N_3^-, and Cl^-, while the inductive effect predominates in the CN^- co-ordination. The decreases in the rate constant at higher nucleophile concentrations are probably due to the formation of 1:2 complexes. The only slight rate changes in the region of $[CH_3CO_2^-]/[Hg^{2+}] \gtrsim 1$ (Figures 1 and 2) suggest that the second formation constant is much smaller than the first for the Hg^{2+}–$CH_3CO_2^-$ system.*

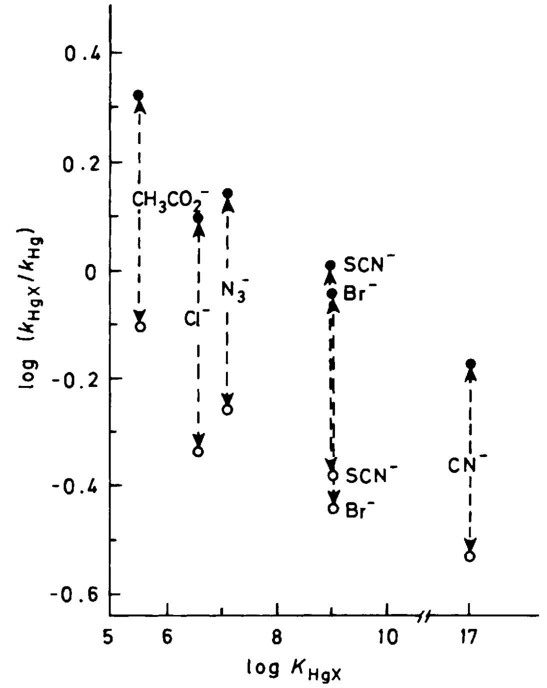

Figure 3. Relationship between the second-order rate constants for the reactions $[CoCl(edta)]^{n-} + HgX^+$ (○) and $[CoCl(NH_3)_5]^{2+} + HgX^+$ (●), and the stability constants of HgX^+

The second-order rate constant (k_{HgX}) for the reaction with HgX^+ was then obtained for each anion by use of known stability constants, K_{HgX}, K_{HgX_2}, and K_{HX}. The kinetic results were related to the stability constants by plotting log (k_{HgX}/k_{Hg}) against log K_{HgX} (Figure 3); k_{Hg} is the rate constant for the reactions with Hg^{2+}. (The rate constants were not corrected for the ionic strength change caused by the addition of anions.) Figure 3 shows that k_{HgX} tends to decrease, with the increase in K_{HgX}.

The difference in the effect of anions between the two reaction

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* The formation constants reported by Kreskov and Balyatinskaya[12] rather than those of Banerjea and Singh[13] better explain the present results.

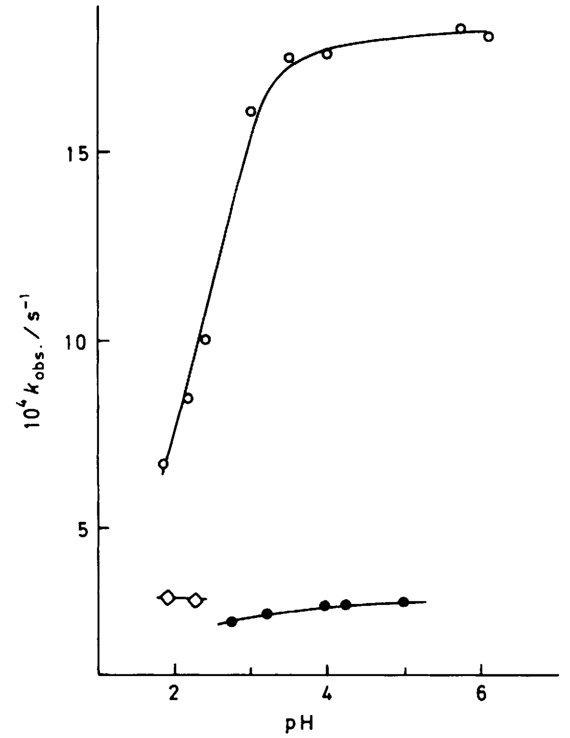

Figure 4. pH Dependency of the rate of the reaction $[CoCl(NH_3)_5]^{2+}$ + HgY^{n-}, where Y = edta (○), cdta (●), or no additives (□); $[Hg^{2+}]_{total}$ = 0.011, $[Y]_{total}$ = 0.012 mol dm^{-3}

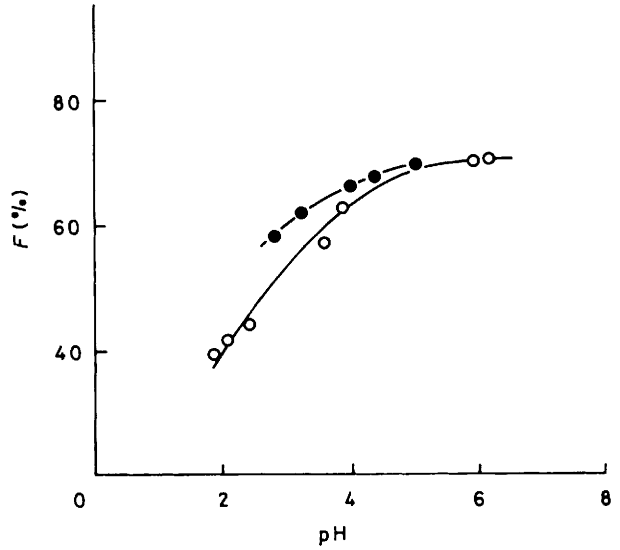

Figure 5. pH Dependency of the yields (*F*) of $[CoY(NH_3)_5]$ in the reaction $[CoCl(NH_3)_5]^{2+}$ + HgY^{n-}, where Y = edta (○) or cdta (●); $[Hg^{2+}]_{total}$ = 0.011, $[Y]_{total}$ = 0.012 mol dm^{-3} [$F = 100\ c_Y/(c_Y + c_A)$]

systems, $[CoCl(NH_3)_5]^{2+}$ + HgX^+ and $[CoCl(Hedta)]^-$ + HgX^+, reflected the difference in the charges of the reactants.

Effects of Aminopolycarboxylate Anions on the Reactions of $[CoCl(NH_3)_5]^{2+}$ *with* Hg^{2+}.—Both Hg(edta) and Hg(cdta) showed remarkable reactivities towards $[CoCl(NH_3)_5]^{2+}$. As shown in Figure 4, the reaction rate in the presence of edta and Hg^{2+} increases steeply with increasing pH values and approaches a limiting value at pH values higher than 3, while that in the presence of cdta and Hg^{2+} showed only a slight pH dependence. The much smaller reactivity of the cdta complex is a general tendency in bimolecular reactions[15] and can be ascribed to the steric hindrance which makes it impossible for two metal ions to co-ordinate each with a nitrogen atom of cdta.

Table 4. Dependence of the rate of the reaction $[CoCl(edta)]^{n-}$ + HgY on pH: $[Hg^{2+}]_{total}$ = 0.011, $[Y]_{total}$ = 0.012 mol dm^{-3}

	pH	$10^4 k_{obs.}/s^{-1}$
(*a*) Y = edta		
	2.15	15
	2.21	11
	2.34	7.3
	2.59	5.2
	3.88	0.59
	4.12	0.30
(*b*) Y = cdta		
	1.76	20
	2.48	3.6
	3.19	0.46

(*c*) Spontaneous aquation: $k_{obs.} = 0.31 \times 10^{-4}\ s^{-1}$

Table 5. Dependence of the rate of the reaction $[CoCl(edta)]^{n-}$ + $Hg(edta)^{n-}$ (*n* = 1 or 2) on the concentration ratio, $[edta]_{total}/[Hg^{2+}]_{total}$; pH 2.40 ± 0.02, $[Hg^{2+}]_{total}$ = 0.011 mol dm^{-3}

$\frac{[edta]_{total}}{[Hg^{2+}]_{total}}$	$10^4 k_{obs.}/s^{-1}$
0.95	49
1.00	7.3
1.05	6.6
1.10	6.6
1.50	6.5

As described above, the reaction product contains H_nY- and penta-ammineaquacobalt(III) complexes. Figure 5 shows the yields of the $[CoY(NH_3)_5]^-$ complexes as a function of pH. The yields approach the limiting values of *ca.* 70% for both cases. This is in marked contrast to the reaction rate, of which the limiting value showed a remarkable difference between the two cases. The formation of these $[CoY(NH_3)_5]^-$ complexes revealed the lability of the aminopolycarboxylatomercury(II) complexes in spite of their high stabilities.

In order to understand the pH dependency of the reaction, we consider the equilibria (11) and (12). The equilibrium constants,

$$Hg(edta)^{2-} + H^+ \overset{K_H^{(1)}}{\rightleftharpoons} Hg(Hedta)^- \qquad (11)$$

$$Hg(cdta)^{2-} + H^+ \overset{K_H^{(2)}}{\rightleftharpoons} Hg(Hcdta)^- \qquad (12)$$

$K_H^{(1)}$ and $K_H^{(2)}$, are known to be *ca.* 10^3.[14] This is consistent with the present results that the $k_{obs.}$ *vs.* pH plot for the $[CoCl(NH_3)_5]^{2+}$ + Hg(edta) reaction and the yields *vs.* pH plot in both the edta and cdta cases curved around pH 3.

Now let us consider the reactions involving HgY^{2-} and $Hg(HY)^-$ to analyse the results quantitatively: equations (13) and (14), where Y = edta or cdta, which are respectively

$$[CoCl(NH_3)_5]^{2+} + HgY^{2-} \xrightarrow{k_1} [Co(NH_3)_5(OH_2)]^{3+} \{\text{or } [CoY(NH_3)_5]^-\} + HgCl^+ \qquad (13)$$

$$[CoCl(NH_3)_5]^{2+} + Hg(HY)^- \xrightarrow{k_2} [Co(NH_3)_5(OH_2)]^{3+} \{\text{or } [CoY(NH_3)_5]^-\} + HgCl^+ \qquad (14)$$

$$HgY^{2-} + H^+ \overset{K_H}{\rightleftharpoons} Hg(HY)^- \qquad (15)$$

referred to by superscripts (1) and (2) below. The observed rate constant, $k_{obs.}$, can be written as in equation (16), where $[HgY]_0$ is defined in equation (17). When Y = edta, $k_1[HgY]_0$ can be

$$k_{obs.} = \frac{k_1 + k_2K_H[H^+]}{1 + K_H[H^+]}[HgY]_0 \qquad (16)$$

$$[HgY]_0 = [HgY^{2-}] + [Hg(HY)^-] \qquad (17)$$

taken to be $(1.8 \pm 0.05) \times 10^{-3}$ s^{-1} from the limiting $k_{obs.}$ value in Figure 4. Then we obtain $K_H^{(1)} = 250 \pm 30$ dm^3 mol^{-1} and $k_2^{(1)}[HgY]_0 = (4.0 \pm 0.2) \times 10^{-4}$ s^{-1} from the plot of $(k_{obs.} - k_1^{(1)}[HgY]_0)/[H^+]$ *vs.* $k_{obs.}$. When Y = cdta, we obtain similarly $k_1^{(2)}[HgY]_0 = (3.0 \pm 0.1) \times 10^{-4}$ s^{-1}, $k_2^{(2)}[HgY]_0 = (1.5 \pm 0.2) \times 10^{-4}$ s^{-1}, and $K_H^{(2)} = 200 \pm 50$ dm^3 mol^{-1}. The larger reactivity of HgY^{2-} as compared with that of $Hg(HY)^-$, or $k_1 > k_2$, is most probably due to the larger electrostatic attraction with $[CoCl(NH_3)_5]^{2+}$. This also shows that HgY^{2-} is so labile that the occupation of all the six-co-ordinate sites of the mercury ion by Y^{4-} does not seriously affect the reactivity of HgY^{2-}.

The yields of the (aminopolycarboxylato)penta-ammine-cobalt(III) complexes are estimated at 68 ± 2% for $Hg(edta)^{2-}$, 40 ± 5% for $Hg(Hedta)^-$, 68 ± 2% for $Hg(cdta)^{2-}$, and 50 ± 5% for $Hg(Hcdta)^-$ from Figure 5. The yield of the edta complex is nearly equal to that of the cdta complex, in spite of the much larger k_1 value for Y = edta than that for Y = cdta. This suggests that the competition between water molecules and aminopolycarboxylate ions to co-ordinate to the cobalt(III) ion is little affected by steric factors.

The lower yield of the edta complex than that of the cdta complex at pH $\lesssim$ 4 (Figure 5) may be related to the easier protonation of $Hg(edta)^{2-}$ [$K_H^{(1)} = 250$ dm^3 mol^{-1}] than that of $Hg(cdta)^{2-}$ [$K_H^{(2)} = 200$ dm^3 mol^{-1}].

When the pH was increased above 7, the reaction rate further increased and $Co(edta)^-$ or $Co(cdta)^-$ was found in the product; no further study has been made, however.

Reactions of $[CoCl(edta)]^{n-}$ *with the* Hg–edta *or* Hg–cdta *Complex.*—These reactions proceeded much more slowly than those involving free Hg^{2+}. The reaction rates decreased with increasing pH (Table 4), suggesting that the protonated complex mainly contributed to the reactions. Another possibility that free Hg^{2+} from the dissociation of the Hg–edta complex played an important role in the reactions was excluded by the experimental results (Table 5), which show that the concentration of excess edta did not affect the reaction rate.

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