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Synthesis and Characterization of Triaminecobalt(III) Complexes and Acid Hydrolysis Kinetics of *fac*-$[Codpt(H_2O)_nX_{3-n}]^{n+}$ (X = Cl, Br; n = 0, 1, 2)

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Abstract

The complexes $CodptX_3$ and $[Codpt(H_2O)X_2]ClO_4$ (X = Cl, Br; dpt = dipropylenetriamine = $NH(CH_2CH_2CH_2NH_2)_2$) have been prepared and characterized. Rate constants (s^{-1}) for aqueous solution at 25 °C and $\mu = 0.5$ M ($NaClO_4$), for the acid-independent sequential ractions

$$CodptX_3 \xrightarrow{k_1} fac\text{-}[Codpt(H_2O)X_2]^+ \xrightarrow{k_2}$$

$$fac\text{-}[Codpt(H_2O)_2X]^{2+} \xrightarrow{k_3} fac[Codpt(H_2O)_3]^{3+}$$

have been measured spectrophotometrically. For X = Cl: $k_1 \simeq 2 \times 10^{-2}$, $k_2 = 1.7 \times 10^{-4}$ and $k_3 = 4.8 \times 10^{-6}$, and for X = Br: $k_1 \simeq 2 \times 10^{-2}$, $k_2 = 5.25 \times 10^{-4}$ and $k_3 = 2.5 \times 10^{-5}$. The primary aquation was found to be acid independent, while the secondary and tertiary aquations were acid-inhibited reactions. For the second step, the rate of the reaction was given by the rate equation

$$\frac{-d[Codpt(H_2O)X_2^+]}{dt} = k_{obs}C_t = \frac{k_2 + k'_2K_a/[H_3O^+]}{1 + K_a/[H_3O^+]}C_t$$

where C_t is the total complex concentration in the aqua- and hydroxodihalo species, k'_2 is the rate constant for the acid-dependent pathway and K_a is the equilibrium constant between the hydroxo and aqua complex ions. The activation parameters were evaluated, for X = Cl: $\Delta H^{\ddagger}_2 = 106.3 \pm 0.4$ kJ mol^{-1} and $\Delta S^{\ddagger}_2 = 40.2 \pm 1.7$ J K^{-1} mol^{-1}, and for X = Br: $\Delta H^{\ddagger}_2 = 91.6 \pm 0.4$ kJ mol^{-1} and $\Delta S^{\ddagger}_2 = 0.4 \pm 1.7$ J K^{-1} mol^{-1}. The results are discussed and detailed comparisons of the reactivities of these complexes with other haloaminecobalt(III) species are presented.

Introduction

We recently described the role of cobalt(III)–tetraamine–aqua complexes in promoting the hydrolysis of ATP (adenosine 5′-triphosphate) [1, 2]. In support of this study, the investigation was extended to test the efficiency of cobalt(III) complexes of the linear tridentate amine dipropylenetriamine (dpt) in catalyzing the hydrolysis of ATP [3]. In relation to this work, and in order to gather further information about metal ion catalyzed reactions, detailed comparisons of the reactivities of the complexes of cobalt(III)–dpt with other tri- and tetraamines have now been made.

The kinetics of aquation in octahedral tetraamine metal complexes of the type $[MN_4XY]^{1+ \text{ or } 2+}$ (M = Co(III), Cr(III), Ir(III) or Rh(III), N_4 = non-replaceable monodentate or polydentate amines; X and Y = F, Cl, Br, I, CN, OH or H_2O) has been the subject of extensive studies [4–9]. Very few investigations have dealt with the corresponding reactions for the linear tridentate amines [10–12] in complexes of the type MN_3X_3 and $[MN_3(H_2O)X_2]^+$. The absence of kinetic studies on these systems may be due to the complications from isomerization, and the difficulties in obtaining accurate results due to the consecutive steps taking place during the aquation.

In the present study, complexes of the type $CodptX_3$ and $[Codpt(H_2O)X_2]ClO_4$ (X = Cl and Br) have been synthesized and characterized, and the kinetics of the acid hydrolysis of these complexes have been investigated under various conditions of temperature and acid concentration.

Experimental

Materials

All chemicals were of reagent grade unless otherwise noted. Dipropylenetriamine was obtained from Aldrich Chemical Co. and was used without further purification.

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General Techniques

Absorption spectra were recorded on a Cary 210 spectrophotometer. pH measurements were made using an Orion Research pH meter model 601 with a combined pH electrode. The potentiometric titration of *fac*-$[Codpt(H_2O)_3]^{3+}$ was carried out using a Radiometer pH meter PHM62 in conjuction with an autoburette (ABU12) and a titration assembly (TTA66). Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of Complexes

The complexes $CodptCl_3$ and $[Codpt(H_2O)Cl_2]$-ClO_4 were synthesized as previously described [13]. The purity was established by elemental analyses. *Anal.* Calc. for $Co(C_6H_{17}N_3)Cl_3$: C, 24.30; H, 5.78; N, 14.17. Found: C, 24.19; H, 5.81; N, 14.15%. *Anal.* Calc. for $[Co(C_6H_{17}N_3)(H_2O)Cl_2]ClO_4$: C, 19.04; H, 5.06; N, 11.10; Cl, 28.10. Found: C, 19.13; H, 5.17; N, 11.19; Cl, 28.23%.

The complex $CodptBr_3$ was prepared via $CodptCl_3$ by the method reported elsewhere [11]. *Anal.* Calc. for $Co(C_6H_{17}N_3)Br_3$: C, 16.76; H, 3.99; N, 9.78. Found: C, 17.00; H, 4.13; N, 9.76%.

The complex $[Codpt(H_2O)Br_2]ClO_4$ was synthesized by dissolving $CodptBr_3$ (1 g) in 5% aqueous HBr at 80 °C. The resulting green solution was filtered and cooled at room temperature, then $NaClO_4 \cdot H_2O$ (8 g) was added with stirring and the solution was left in the refrigerator at 4 °C. Upon continued cooling, fine green crystals separated out. These were filtered, washed with ethanol, ether and air dried (yield 0.4 g; 37%). *Anal.* Calc. for $[Co(C_6H_{17}N_3)(H_2O)Br_2]ClO_4$: C, 15.42; H, 4.10; N, 8.99; Br, 34.19; Co, 12.61. Found: C, 15.52; H, 4.15; N, 9.09; Br, 33.97; Co, 12.59%.

fac-$[Codpt(H_2O)_3]^{3+}$ was prepared by treating a solution of $CodptCl_3$ with the stoichiometric amount of $AgClO_4$ solution. The AgCl, which precipitated, was removed by centrifugation and filtration of the resulting supernatant liquid through celite, using Fisher-brand filter paper P2. The amount of AgCl produced was equivalent to the removal of the three chlorides from the complex. The purple solution containing *fac*-$[Codpt(H_2O)_3]^{3+}$ and $3ClO_4^-$ was stored in the refrigerator. No change in the spectrum was detected over a two week period. Attempts to isolate $[Codpt(H_2O)_3](ClO_4)_3$ were unsuccessful.

Kinetic Measurements

Due to the difficulty of obtaining suitable solvents for the trihalo complexes (either due to the reaction with the solvent or insolubility), the first aquation of $CodptX_3$ was studied in 1 M $HClO_4$ at 25 °C simply by observing the color change from the brown to the light green for the bromo complex and from the dark green to the greenish-blue for the chloro species as the reactions proceed. Thus it was possible to estimate the approximate half lives and hence obtain approximate values for rate constants for the first aquation steps by simple measurements with a stop-watch [14].

All rate measurements of the acid hydrolysis reactions of the aqua species were made spectrophotometrically in thermostated matched cells of 1 cm pathlength. The change in absorbance at the appropriate wavelength was monitored as a function of time. The wavelengths used for this study were ones at which substantial differences in absorbances exist between the reactants and the products. Those wavelengths were 540 and 402 nm for the hydrolysis of $[Codpt(H_2O)Cl_2]^+$, and 538 nm for $[Codpt(H_2O)Br_2]^+$. The concentration of the complexes in these runs was 4–5 mM. The acid hydrolysis for the dichloro and dibromo complexes was studied by dissolving each complex at the required temperature in aqueous solution with the appropriate concentration of $HClO_4$. The ionic strength was kept constant (0.5 M) by using $NaClO_4$. The third aquation step was studied over 0.02–0.06 M $HClO_4$ and $\mu = 0.5$ M, by dissolving the appropriate weights of $[Codpt(H_2O)X_2]ClO_4$ in thermostated aqueous $HClO_4$ solutions, and these were then first allowed to undergo the second aquation step for ~4 $t_{1/2}$. The solution was then transferred to the spectrophotometric thermostated cell and the absorbance growth was folllowed at 540 nm. The conversion of $[Codpt(H_2O)_2X]^{2+}$ into $[Codpt(H_2O)_3]^{3+}$ was found to proceed to ~92%.

Determination of the Released Halides

A solution of $[Codpt(H_2O)X_2]^+$ was allowed to hydrolyze to $[Codpt(H_2O)_2X]^{2+}$ for ~4 half lives at 25 °C. The reaction product was then charged onto a cation exchange column (10 × 1.2 cm) in the H^+ form (AG50W-X8, 100–200 mesh, A.R. from Bio-Rad), which was cooled by a jacket of circulating ice water. The products on the column were eluted with cold water until no more H^+ was liberated. The washings were collected, treated with excess standard $AgNO_3$, and the AgX which precipitated was filtered off and washed with water (acidified with HNO_3). The filtrate was then titrated with standard NH_4SCN solution using ferric alum as indicator (Volhard method) [15].

Determination of the Acid Dissociation Constants

The values for the first and second dissociation constants K_1 and K_2 for the coordinated waters in *fac*-$[Codpt(H_2O)_3]^{3+}$ were measured at 25.0 °C and $\mu = 0.1$ M ($NaClO_4$) by titrating a thermostated stirred solution of the complex with 0.10 M NaOH solution. The isomerization in the middle pH range necessitated working very quickly to obtain estimates for the dissociation constants for the pure isomers. The values for pK_1 and pK_2 were 3.98 and 7.3,

TABLE I. The electronic Spectra of some Aqua- and Haloaqua–Triaminecobalt(III) Complexes

Complex ion	Solvent	λ_{max} (ϵ)[a]	λ_{min} (ϵ)	λ_{max} (ϵ)	λ_{min} (ϵ)	Reference
fac-$[Co(NH_3)_3(H_2O)_3]^{3+}$	1 M $HClO_4$	526(60)	428(8)	361(46)	300(12)	18
fac-$[Co(2,3\text{-tri})(H_2O)_3]^{3+}$ [b]	1 M $HClO_4$	512(55.3)	433(21.1)	370(56.3)	350(51.5)	10
fac-$[Codien(H_2O)_3]^{3+}$ [c]	1 M $HClO_4$	520(99.0)	425(16.2)	365(51.7)	375(30.0)	10
fac-$[Codpt(H_2O)_3]^{3+}$	0.1 M $HClO_4$	540(53.1)	448(10.9)	375(68.0)	342(43.8)	this work
fac-$[Codpt(H_2O)_2Cl]^{2+}$	1 M $HClO_4$	540(46.6)	462(14.5)	380(65.5)	365(61.8)	this work
fac-$[Codpt(H_2O)_2Br]^{2+}$	1 M $HClO_4$	538(43.4)	448(12.6)	370(83.4)	349(74.1)	this work
fac-$[Codpt(H_2O)Cl]^{+}$	1 M $HClO_4$	550(33.2)	470(15.0)	398(78.4)	370(61.3)	this work
fac-$[Codpt(H_2O)Br_2]^{+}$	1 M $HClO_4$	538(29.7)	472(18.8)			this work

[a] λ in nm and ϵ in $M^{-1}\ cm^{-1}$. [b] 2,3-tri = *N*-(2-aminoethyl)1,3-propanediamine. [c] dien = diethylenetriamine.

respectively. The determination of pK_3 was not possible due to the formation of fine black particles at pH ≥ 9.5, which may be attributed to Co_2O_3.

Results and Discussion

Structure of [Codpt(H_2O)$_n$$X_{3-n}$]$^{n+}$ Complexes

The complexes $CodptX_3$ (X = Cl or Br) are insoluble in conc. HX, and they are unstable in dilute aqueous $HClO_4$, being hydrolyzed almost as fast as they dissolve. The same behavior was observed in the case of $CodienCl_3$ and $CrdienCl_3$ [12]. In this work, no attempts were made to assign the configuration of $CodptX_3$. However, it has been reported that the reflectance spectrum of $CodptCl_3$ is quite similar to that of $Co(TACN)Cl_3$ (TACN = 1,4,7-triazacyclononane), where the tricyclic amine TACN can only coordinate to three *cis* positions [16]. Therefore, the complex $CodptCl_3$ most likely has the facial configuration.

On the other hand, the visible spectrum of the complex cation $[Codpt(H_2O)_3]^{3+}$, generated by the method described before (see 'Experimental'), showed only two absorption bands as is typical for *cis* and *fac* isomers [17]. Further, the spectra did not show any significant signs of isomerization over a period of more than two weeks. Although two isomers were observed for the complex $[Codien(H_2O)_3]^{3+}$ ion [12], here we have evidence for only one isomer which can be assigned as having facial geometry. The spectral data for *fac*-$[Codpt(H_2O)_3]^{3+}$, and for other related systems are collected in Table I.

The initial spectral trace for the green complexes $[Codpt(H_2O)X_2]ClO_4$ (X = Cl and Br) in 1 M $HClO_4$ have the same features as *fac*-$[Codpt(H_2O)_3]^{3+}$. Therefore, the geometry of these dihalo species is assigned as facial. In dilute acid, the complex ion $[Codpt(H_2O)X_2]^{+}$ hydrolyzes to the corresponding pink halodiaqua species. The final spectrum, for the hydrolysis product, is independent of the acid concentration. The spectral parameters for such species, $[Codpt(H_2O)_2X]^{2+}$, are similar to those having the facial geometry. The visible spectra for the aqua and haloaqua complexes are depicted in Fig. 1. We conclude that the products of acid hydrolysis are not complicated by isomerization and that only one isomer of facial geometry exists in all cases.

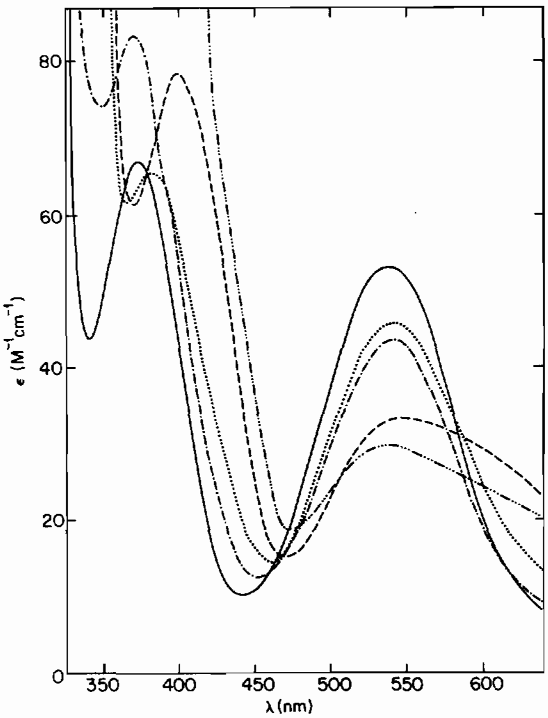

Fig. 1. Visible spectra for *fac*-$[Codpt(H_2O)_nX_{3-n}]^{n+}$ (X = Cl, Br; n = 1, 2, 3) complexes: (——) *fac*-$[Codpt(H_2O)_3]^{3+}$, (·······) *fac*-$[Codpt(H_2O)_2Cl]^{2+}$, (- - - -) *fac*-$[Codpt(H_2O)Cl_2]^{+}$, (– · –) *fac*-$[Codpt(H_2O)_2Br]^{2+}$ and (– ··· –) *fac*-$[Codpt(H_2O)Br_2]^{+}$ in 1 M $HClO_4$.

Acid Hydrolysis Kinetics for fac-[Codpt(H_2O)$_n$-X_{3-n}]$^{n+}$

The first aquation step

In dilute $HClO_4$, the complexes $CodptX_3$ undergo the first aquation to produce *fac*-$[Codpt(H_2O)X_2]^{+}$.

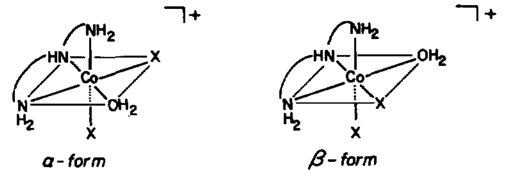

Fig. 2. Possible geometric isomers for *fac*-$[Codpt(H_2O)X_2]^+$ ion.

This aquation is too rapid to be measured by conventional spectrophotometry. Also, the possibility of using stopped flow was ruled out because of insolubility in CH_3CN and CH_2Cl_2, and because of reactions with the solvents DMSO, DMF and THF. However, an approximate rate constant for the primary aquation was obtained in 1 M $HClO_4$ and 25 °C. The rate constant (k_1) for the conversion of $CodptX_3$ into *fac*-$[Codpt(H_2O)X_2]^+$ is approximately 2×10^{-2} s^{-1} for both X = Cl and X = Br. The reaction is represented by eqn. (1)

$$CodptX_3 + H_2O \xrightarrow{k_1} fac\text{-}[Codpt(H_2O)X_2]^+ + X^- \quad (1)$$

The rates were found to be independent of $[H_3O^+]$ over the concentration range 0.7–1.2 M $HClO_4$.

There are potentially two isomeric forms for the complex cation *fac*-$[Codpt(H_2O)X_2]^+$; depending on whether the coordinated secondary amine NH group is *trans* (α-form) or *cis* (β-form) to the coordinated aqua ligand. These are represented in Fig. 2. However, based on X-ray studies, it has been pointed out that the reaction of HCl with $Codien(NO_2)_3$ forms *trans*-dinitrito *mer*-$Codien(NO_2)_2Cl$, indicating that the nitro group *trans* to the NH group in the initial complex is the most labile [19]. Thus, of the two possible isomers of the complex ion *fac*-$[Codpt(H_2O)X_2]^+$ that can be formed from $CodptX_3$ during the first aquation, the one with water *trans* to the secondary amine group of the dpt ligand is the most likely.

The second aquation step

The kinetics of the second aquation step for $CodptX_3$ (*i.e.* the loss of the first halide in $[Codpt(H_2O)X_2]^+$) was studied over the pH range 1–2 in $HClO_4$ medium with 0.5 M $NaClO_4$. The reaction proceeds according to the stoichiometric eqn. (2).

$$fac\text{-}[Codpt(H_2O)X_2]^+ + H_2O \longrightarrow fac\text{-}[Codpt(H_2O)_2X]^{2+} + X^- \quad (2)$$

The second aquation rate constant (k_2) for $CodptCl_3$ was determined in 1 M $HClO_4$ at 25 °C. The value of k_2 obtained was 1.87×10^{-4} s^{-1}, which is in good agreement with that obtained for the direct aquation of $[Codpt(H_2O)Cl_2]ClO_4$, (1.79×10^{-4} s^{-1}). The aquation of *fac*-$[Codpt(H_2O)Cl_2]^+$ was examined at two different wavelengths, 402 and 540 nm. For these wavelengths, the rate constants were in good agreement (to within 5%). For example, the rate constants determined in 1 M $HClO_4$ and 30 °C were 3.97×10^{-4} and 3.81×10^{-4} s^{-1} for 402 and 540 nm respectively. A series of spectral scans during the

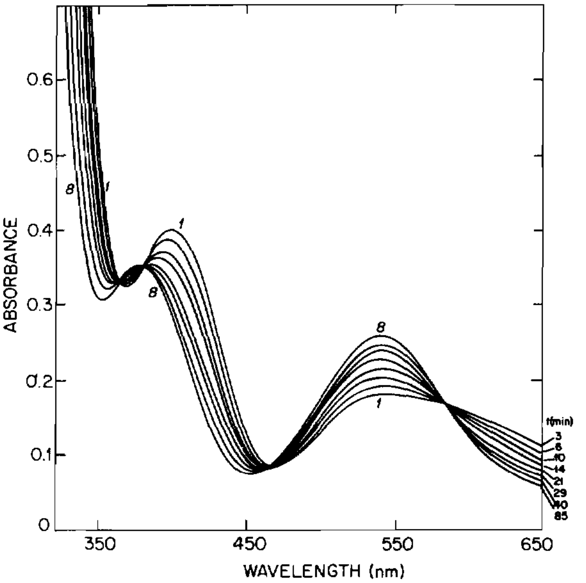

Fig. 3. Spectral changes as a function of time for the acid hydrolysis of *fac*-$[Codpt(H_2OCl_2]^+$ (5.0×10^{-3} M, 25.0 °C, μ = 0.5 M and 0.0904 M $HClO_4$).

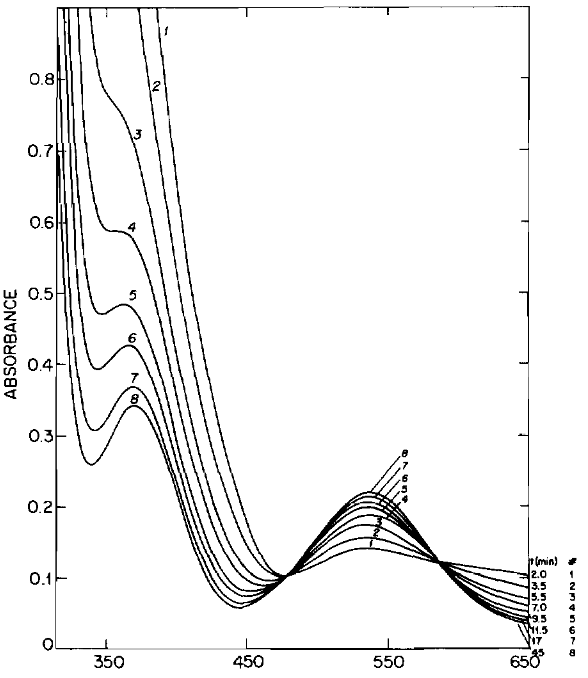

Fig. 4. Spectral changes as a function of time for the acid hydrolysis of *fac*-$[Codpt(H_2O)Br_2]^+$ (4.0×10^{-3} M, 25 °C, μ = 0.5 M and 0.0634 M $HClO_4$).

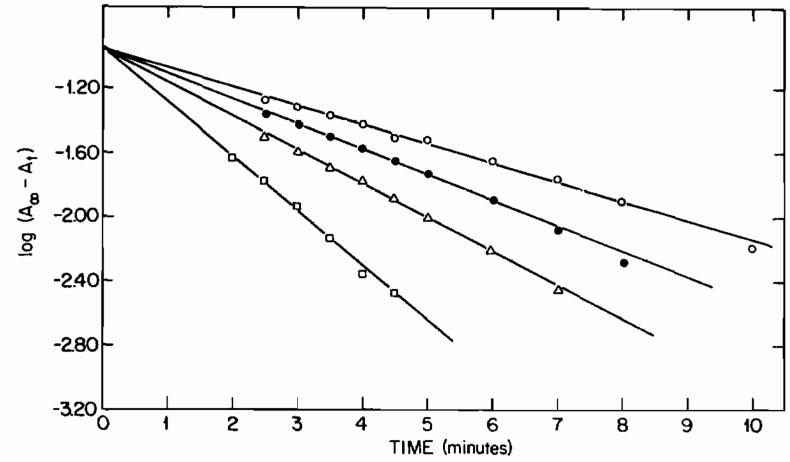

Fig. 5. First-order plot for $\log(A_\infty - A_t)$ *vs.* time for the aquation of *fac*-$[\mathrm{Codpt(H_2O)Cl_2}]^+$ ion (5.0×10^{-3} M, 38.9 °C, $\mu = 0.5$ M, $\lambda = 540$ nm) at different $[\mathrm{H_3O^+}]$ concentrations: ○, 0.0904; ●, 0.0633; △, 0.0452; □, 0.0225 M.

TABLE II. First-order Rate Constants and the Activation Parameters for the Reaction:

fac-$[\mathrm{Codpt(H_2O)Cl_2}]^+ + \mathrm{H_2O} \xrightarrow{k_2}$ *fac*-$[\mathrm{Codpt(H_2O)_2Cl}]^{2+} + \mathrm{Cl^-}$, in 1 M $\mathrm{HClO_4}$

Temperature (°C)	$k_2 \times 10^4$ ($\mathrm{s^{-1}}$)
25.0	1.79
30.0	3.81
35.0	7.53
40.0	14.9
$\Delta H^\ddagger$ (kJ $\mathrm{mol^{-1}}$)	106.7(±0.5)
$\Delta S^\ddagger$ (J $\mathrm{K^{-1}\,mol^{-1}}$)	41.8(±1.7)

loss of the first halide in $[\mathrm{Codpt(H_2O)X_2}]^+$ complexes are given in Figs. 3 and 4, for X = Cl and Br, respectively. For the aquation of the dichloroaqua species the scans show four isosbestic points at 364, 380, 467 and 585 nm (Fig. 3). In the case of the dibromoaqua species, two isosbestic points were observed at 482 and 587 nm (Fig. 4). These isosbestic points did not change during the course of the reaction, and the final spectrum shows no appreciable change over a period of approximately 2 h (1 M $\mathrm{HClO_4}$ and 25 °C). These observations indicate that the third aquation step does not interfere with or complicate the study. The back titration of the released halide ions with standard $\mathrm{NH_4SCN}$ (see 'Experimental') gave 1.02(±0.04) mol of $\mathrm{Cl^-}$ released/mol of $[\mathrm{Codpt(H_2O)Cl_2}]^+$ and 1.05(±0.05) mol of $\mathrm{Br^-}$ released/mol of $[\mathrm{Codpt(H_2O)Br_2}]^+$ (average of two determinations in each case).

The aquation of *fac*-$[\mathrm{Codpt(H_2O)Cl_2}]^+$ was studied in 1 M $\mathrm{HClO_4}$ at different temperatures. The pseudo first-order rate constants (k_2), collected in Table II, were obtained from the slope of a plot of $\log(A_\infty - A_t)$ *versus* t, where A_∞ is the final absorbance reading and A_t is the absorbance at time t. The plots gave straight lines for at least four half lives. The activation parameters were calculated using the Eyring equation from the plot of $\ln(k_2/T)$ *versus* $1/T$. In 1 M $\mathrm{HClO_4}$, the enthalpy and entropy of activation obtained are $\Delta H^\ddagger{}_2 = 106.7 \pm 0.5$ kJ $\mathrm{mol^{-1}}$ and $\Delta S^\ddagger{}_2 = 41.8 \pm 1.7$ J $\mathrm{K^{-1}\,mol^{-1}}$.

The aquation of $[\mathrm{Codpt(H_2O)X_2}]^+$ was also examined over the pH range 1–2 and at different temperatures. A typical first-order plot is shown in Fig. 5. The data for the second aquation step for the acid dependence are summarized in Tables III and IV, for X = Cl and X = Br, respectively. These data indicate that the aquation of *fac*-$[\mathrm{Codpt(H_2O)X_2}]^+$ is acid inhibited. Similar behavior has been found for the aquation kinetics of $[\mathrm{Cotren(H_2O)X}]^{2+}$ (X = Cl and Br) [6, 20], *trans*-$[\mathrm{Coen_2(H_2O)Cl}]^{2+}$ [8], *β-cis*-$[\mathrm{Cotrien(H_2O)Cl}]^{2+}$ [7], $[\mathrm{Cren(NH_3)(H_2O)_2Br}]^{2+}$ [21], $[\mathrm{Cren(H_2O)_3Br}]^{2+}$ [22] and $[\mathrm{Cr(NH_3)(H_2O)_4Cl}]^{2+}$ [23].

The acid inhibition for the dihaloaqua complexes has been attributed to an equilibrium between the dihaloaqua complex ion and the more rapidly reacting dihalohydroxo species ($k_2 \ll k'_2$). This equilibrium will lead to the following reaction scheme

$$\begin{tikzcd}
fac\text{-}[\mathrm{Codpt(H_2O)X_2}]^+ + \mathrm{H_2O} \arrow[r, shift left, "K_a"] \arrow[d, "k_2"] & fac\text{-}[\mathrm{Codpt(OH)X_2}] + \mathrm{H_3O^+} \arrow[l, shift left] \arrow[d, "\mathrm{H_2O}"', "k'_2"] \\
fac\text{-}[\mathrm{Codpt(H_2O)_2X}]^{2+} + \mathrm{X^-} & fac\text{-}[\mathrm{Codpt(OH)(H_2O)X}]^+ + \mathrm{X^-}
\end{tikzcd}$$

$$fac\text{-}[\mathrm{Codpt(OH)(H_2O)X}]^+ + \mathrm{H_3O^+} \overset{K'_a}{\rightleftharpoons} fac\text{-}[\mathrm{Codpt(H_2O)_2X}]^{2+} + \mathrm{H_2O}\ \text{(very fast)}$$

TABLE III. The Kinetic Data for the Loss of the First Chloride in *fac*-$[\mathrm{Codpt(H_2O)Cl_2}]^+$ (μ = 0.5 M)

T (°C)	$[H_3O^+]$ (mM)	$k_{obs} \times 10^3$ (s^{-1})	$1/[H_3O^+]$ (M^{-1})	$k_2 \times 10^4$ (s^{-1})	$k'_2K_a \times 10^5$ (M s^{-1})
25.0	22.6	3.07	44.3	1.70	6.40
	45.2	1.58	22.1		
	63.3	1.21	15.8		
	90.4	0.86	11.1		
	479	0.31	2.09		
30.0	22.6	5.30	44.3	3.80	11.1
	45.2	2.84	22.1		
	63.3	2.14	15.8		
	90.4	1.61	11.1		
	479	0.61	2.09		
35.0	22.6	8.13	44.3	7.82	19.0
	45.2	4.86	22.1		
	63.3	3.95	15.8		
	90.4	2.87	11.1		
	479	1.13	2.09		
38.9	22.6	13.7	44.3	11.9	31.4
	45.2	8.03	22.1		
	63.3	6.32	15.8		
	90.4	4.66	11.1		
	479	1.80	2.09		

TABLE IV. The Kinetic Data for the Loss of the First Bromide in *fac*-$[\mathrm{Codpt(H_2O)Br_2}]^+$ (μ = 0.5 M)

T (°C)	$[H_3O^+]$ (mM)	$k_{obs} \times 10^3$ (s^{-1})	$1/[H_3O^+]$ (M^{-1})	$k_2 \times 10^4$ (s^{-1})	$k'_2K_a \times 10^4$ (M s^{-1})
20.5	27.2	4.76	36.8	3.14	1.21
	45.3	2.67	22.1		
	63.4	1.91	15.8		
	90.6	1.65	11.0		
	479	0.567	2.09		
25.0	27.2	7.66	36.8	5.25	1.94
	45.3	4.71	22.1		
	63.4	3.67	15.8		
	90.6	2.83	11.0		
	479	0.824	2.09		
28.5	27.2	10.7	36.8	8.75	2.71
	45.3	6.79	22.1		
	63.4	5.34	15.8·		
	90.6	4.13	11.0		
	479	1.15	2.09		
32.0	27.2	14.6	36.8	13.1	3.71
	45.3	9.45	22.1		
	63.4	7.15	15.8		
	90.6	5.60	11.0		
	479	2.01	2.09		

According to this scheme, the acid hydrolysis rate is the combination of the rates for the dihaloaqua (k_2; acid-independent pathway) and the dihalohydroxo species (k'_2; acid-dependent pathway). Thus the rate of the secondary aquation can be represented by eqn. (3)

$$-\frac{d[\mathrm{Codpt(H_2O)X_2^+}]}{dt} = k_2[\mathrm{Codpt(H_2O)X_2^+}] + k'_2[\mathrm{Codpt(OH)X_2}] \quad (3)$$

The observed rate constant for the overall reaction is then given by eqn. (4)

$$k_{obs} = \frac{k_2 + k'_2K_a/[H_3O^+]}{1 + K_a/[H_3O^+]} \quad (4)$$

In highly acid medium $K_a/[H_3O^+] \ll 1$, and eqn. (4) can be written as

$$k_{obs} \simeq k_2 + \frac{k'_2K_a}{[H_3O^+]} \quad (5)$$

The acid dissociation constants for *fac*-$[\mathrm{Codpt(H_2O)_3}]^{3+}$ were determined at 25 °C and μ = 0.1 M. Such dissociations can be represented by the following equations

$$fac\text{-}[\mathrm{Codpt(H_2O)_3}]^{3+} + H_2O \overset{K_1}{\rightleftharpoons} fac\text{-}[\mathrm{Codpt(OH)(H_2O)_2}]^{2+} + H_3O^+ \quad (6)$$

$$fac\text{-}[\mathrm{Codpt(OH)(H_2O)_2}]^{2+} + H_2O \overset{K_2}{\rightleftharpoons} fac\text{-}[\mathrm{Codpt(OH)_2(H_2O)}]^{+} + H_3O^+ \quad (7)$$

$$fac\text{-}[\mathrm{Codpt(OH)_2(H_2O)}]^{+} + H_2O \overset{K_3}{\rightleftharpoons} fac\text{-}[\mathrm{Codpt(OH)_3}] + H_3O^+ \quad (8)$$

The values of pK_1 and pK_2 were found to be 3.98 and 7.3. The determination of pK_3 was not possible due to the formation of fine black particles at pH $\geqslant$ 9.5. Based on these results, the K_a value for *fac*-$[\mathrm{Codpt(H_2O)X_2}]^+$ is expected to be much smaller than 1×10^{-7}; consequently the approximation used in eqn. (5) will hold very well, and the plot of k_{obs} *versus* $1/[H_3O^+]$ would then give a straight line with a slope equal to the product k'_2K_a and an intercept equal to k_2. Typical plots are illustrated in Fig. 6, and the corresponding kinetic data are collected in Tables III and IV, for X = Cl and X = Br, respectively. Thus, at 25 °C and μ = 0.5 M, k_{obs} for the second aquation step, at a given $[H_3O^+]$ concentration, can be calculated by the expressions

$$X = Cl; \quad k_{obs}(s^{-1}) = 1.70 \times 10^{-4} + \frac{6.40 \times 10^{-5}}{[H_3O^+]} \quad (9)$$

$$X = Br; \quad k_{obs}(s^{-1}) = 5.25 \times 10^{-4} + \frac{1.94 \times 10^{-4}}{[H_3O^+]} \quad (10)$$

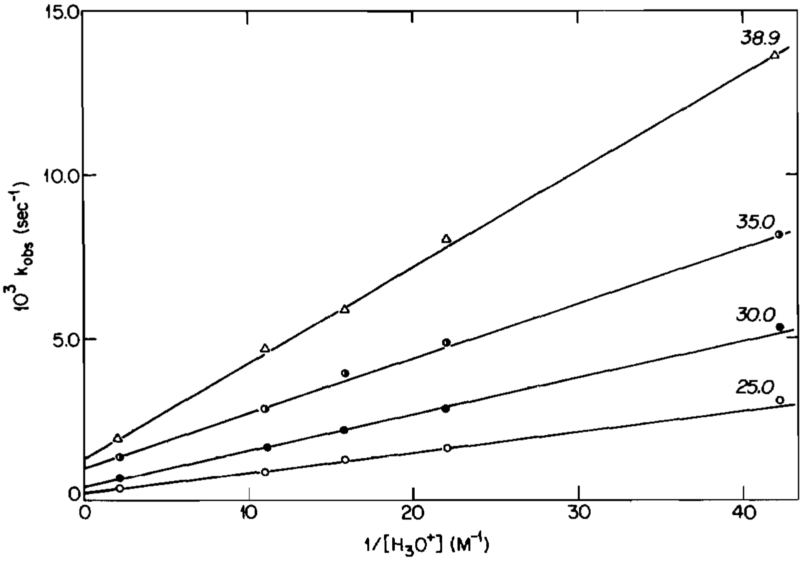

Fig. 6. Plot of the pseudo first-order rate constants (k_{obs}) for the aquation of *fac*-[Codpt(H_2O)Cl_2]$^+$ ion (μ = 0.5 M) at different temperatures: ○, 25.0; ●, 30.0, ◐, 35.0; △, 38.9 °C.

TABLE V. Variation of the Rate Constants with [H_3O^+] for the Tertiary Aquation Step at 25.0 °C and μ = 0.5 M

[H_3O^+] (mM)	k_{obs} × 10^3 (s^{-1})	
	X = Cl	X = Br
8.10	4.5	
22.4	1.6	6.3
33.9	1.3	3.9
60.3	0.72	2.4

TABLE VI. The Acid-independent Rate Constants for Acid Hydrolysis of Haloaminecobalt(III) Complexes with Different Net Charges at 25 °C

Complex	k (s^{-1})	Reference
Net charge 0		
fac-CodptCl$_3$	~2 × 10^{-2}	this work
fac-CodptBr$_3$	~2 × 10^{-2}	this work
Net charge 1+		
cis-[Coen$_2$Cl$_2$]$^+$	2.50 × 10^{-4}	24
[Cotren$_2$Cl$_2$]$^+$	2.96 × 10^{-3}	25
β-cis-[CotrienCl$_2$]$^+$	1.5 × 10^{-3}	26
cis-[Coen$_2$Br$_2$]$^+$	1.04 × 10^{-3}	27
[CotrenBr$_2$]$^+$	2.84 × 10^{-2}	28
fac-[Codpt(H_2O)Cl_2]$^+$	1.70 × 10^{-4}	this work
fac-[Codpt(H_2O)Br_2]$^+$	5.25 × 10^{-4}	this work
Net charge 2+		
cis-[Coen$_2$(H_2O)Cl]$^{2+}$	1.6 × 10^{-6}	8
[Cotren(H_2O)Cl]$^{2+}$	2.4 × 10^{-6}	20
β-cis-[Cotrien(H_2O)Cl]$^{2+}$	2.4 × 10^{-6}	7
[Cotren(H_2O)Br]$^{2+}$	3.3 × 10^{-6}	6
fac-[Codpt(H_2O)$_2$Cl]$^{2+}$	4.8 × 10^{-6}	this work
fac-[Codpt(H_2O)$_2$Br]$^{2+}$	2.5 × 10^{-5}	this work

The product k'_2K_a could not be separated into components without further information about the position of the equilibrium and/or the hydrolysis rate for the hydroxodihalo species. For the acid-independent pathway, the rate of aquation of the bromo species is 3 times faster than for the corresponding dichloro species. The activation parameters calculated from the plots of $\ln(k_2/T)$ *versus* $1/T$ yielded $\Delta H^{\ddagger}_2$ = 106.3 ± 0.4 kJ mol^{-1} and $\Delta S^{\ddagger}_2$ = 40.2 ± 1.7 J K^{-1} mol^{-1} for the chloro species, while for the bromo species, the values were 91.6 ± 0.4 kJ mol^{-1} for $\Delta H^{\ddagger}_2$ and 0.4 ± 1.7 J K^{-1} mol^{-1} for $\Delta S^{\ddagger}_2$. It can be noted that the rate constants and the activation parameters obtained in 1 M HClO$_4$ for the aquation of *fac*-[Codpt(H_2O)Cl_2]$^+$ (Table II) were found to be the same, within the experimental error, as those obtained for the acid-independent pathway for the same system. At relatively high [H_3O^+] the contribution of the hydroxodihalo species to the hydrolysis is negligible, since the equilibrium is shifted largely towards the aquadihalo species. For the acid-dependent pathway, the enthalpy and entropy of activation were found to be 85.4 ± 0.4 kJ mol^{-1} and −39.7 ± 2.1 J K^{-1} mol^{-1} respectively for the aquation of *fac*-[Codpt(H_2O)Cl_2]$^+$, and 70.3 ± 0.4 kJ mol^{-1} and −79.5 ± 1.3 J K^{-1} mol^{-1} for the corresponding aquation of *fac*-[Codpt(H_2O)Br_2]$^+$.

The third aquation step

The kinetics for the tertiary aquation step of CodptX$_3$ (or the loss of the halide in *fac*-[Codpt(H_2O)$_2$X]$^{2+}$) was studied over the hydrogen ion concentration range 0.02–0.06 M, at 25 °C and μ = 0.5

M. The study was performed by allowing the complex *fac*-$[Codpt(H_2O)X_2]^+$ to hydrolyze to *fac*-$[Codpt(H_2O)_2X]^{2+}$ for $\simeq 4\ t_{1/2}$ at the given acid concentration; then the conversion of the latter species into *fac*-$[Codpt(H_2O)_3]^{3+}$ was followed spectrophotometrically (see 'Experimental'). The final solution spectra were consistent with *fac*-$[Codpt(H_2O)_3]^{3+}$. The reaction proceeds according to the stoichiometric equation

$$fac\text{-}[Codpt(H_2O)_2X]^{2+} + H_2O \longrightarrow fac\text{-}[Codpt(H_2O)_3]^{3+} + X^- \qquad (11)$$

It has been found that the hydrolysis of *fac*-$[Codpt(H_2O)_2X]^{2+}$ is acid inhibited (Table V), and the mechanism used for the second aquation seems to hold in this case too. From the plot of the observed pseudo first-order rate constant *versus* $1/[H_3O^+]$, the acid-independent rate constant for the third aquation step (k_3) was calculated. These values were found to be 4.8×10^{-6} and 2.5×10^{-5} s^{-1}, for X = Cl and X = Br respectively, which indicates that $k_3(Br)/k_3(Cl) = 5$. Thus, at 25 °C, $\mu = 0.5$ M and at a given hydrogen ion concentration, the observed rate constant for the tertiary aquation step can be calculated by the expressions

$$X = Cl;\quad k_{obs}(s^{-1}) = 4.8 \times 10^{-6} + \frac{3.5 \times 10^{-5}}{[H_3O^+]} \qquad (12)$$

$$X = Br;\quad k_{obs}(s^{-1}) = 2.5 \times 10^{-5} + \frac{1.4 \times 10^{-4}}{[H_3O^+]} \qquad (13)$$

The relative rate of hydrolysis for the acid-independent pathway $k_1{:}k_2{:}k_3$ is 3100:35:1 for X = Cl and 720:20:1 for X = Br. The marked decrease in the labilization of the halide on going from the first to the second to the third aquation, can be attributed to the increase in the net positive charge of the complex. If bond breaking and separation of the halide ion is important in the rate determining step (for D or I_d mechanism), the reaction rates should decrease as a result of increasing the electrostatic attraction between the cobalt and the leaving halide.

The rate constants for the acid hydrolysis of $CodptX_3$, *fac*-$[Codpt(H_2O)X_2]^+$ and *fac*-$[Codpt(H_2O)_2X]^{2+}$, are summarized in Table VI, together with those for some related tetraamine complexes of *cis* geometry. Inspection of the data in Table VI reveals that for ions of the same net charge of 1+, the reactivity of the chloroamine complexes decreases in the order $[CotrenCl_2]^+$ > *β-cis*-$[CotrienCl_2]^+$ > *cis*-$[Coen_2Cl_2]^+$ > *fac*-$[Codpt(H_2O)Cl_2]^+$. On the other hand, the acid hydrolysis for ions of net charge 2+ seems to be different for the dpt ligand and the reactivity follows the order *fac*-$[Codpt(H_2O)_2Cl]^{2+}$ > *cis*-$[Cotren(H_2O)Cl]^{2+}$ ≃ *β-cis*-$[Cotrien(H_2O)Cl]^{2+}$ > *cis*-$[Coen_2(H_2O)Cl]^{2+}$. A parallel behavior was observed for the bromoamine species.

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