# **114.** *The Influence of Electrolytic Dissociation upon Rates of Reactions. Part III.* The Aquation of Chloropentamminecobalt*(III) *in Acidic Salt Solutions.*

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The rate of aquation of chloropentamminecobalt(III) in acidic media has been measured by following the rate of release of chlorine-36. Increased rates in the presence of nitrate, glycollate, sulphate, malonate, and phthalate are interpreted in terms of Davies's treatment wich ascribes the increases to the ion-pairs being more reactive than is the chloro-ion. Both the rate constant and the dissociation constant of such ion-pairs can be calculated from the kinetic data.

ALTHOUGH the rate of aquation of the chloropentamminecobalt(III) ion is independent of $[H^+]$ below [1] pH 7 and is not subject to wall or light effects,[2] it is affected by certain anions. This was demonstrated by Garrick [2,3] who found that the rate is slightly increased by chloride, nitrate, chlorate, formate, and acetate while sulphate caused a marked acceleration. These effects were considered to be independent of the cations of these salts and since the rate changes seemed to be related to the anion concentrations, [L], Garrick expressed his results in terms of

$$k_e = k_1 + k_L[L] \tag{1}$$

where $k_e$ is the experimental pseudo-unimolecular rate constant, $k_1$ its value in the absence of L, and $k_L$ is a catalytic coefficient, the value of which depends on the ionic strength $I$ in accordance with the relationship

$$\log (k_L/k_1) = 2Az_1z_2I^{\frac{1}{2}} \tag{2}$$

where $A$ is the Debye–Hückel constant while $z_1$ and $z_2$ are the valencies of the cobaltic ion and L, respectively.

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* Part II, *J.*, 1956, 1396.

[1] Lamb and Marsden, *J. Amer. Chem. Soc.*, 1911, **33**, 1882.

[2] Garrick, *Trans. Faraday Soc.*, 1937, **33**, 486.

[3] Garrick, *Trans. Faraday Soc.*, 1938, **34**, 1088.

The aquation rates of other cobalt(III) complex ions are also accelerated by certain anions; these have been reviewed by Basolo and Pearson.[4] Jones, Harris, and Wallace [5] have found that while chloride and bromide have little effect on the aquation rate of $Cr(NH_3)_5X^{2+}$ ($X^- = Cl^-, Br^-, I^-$), acetate, benzoate, various dicarboxylates, citrate, and sulphate cause distinct increases. Also, as Garrick [2] found, perchlorate retards slightly. They reported that plots of $k_e$ against [L] of univalent ligands are linear and extrapolate to a common $k_1$ at $[L] = 0$ while for multivalent ligands the plots are steep for low values of [L] and extrapolate to characteristic values of $k_1$. Such plots are empirical, which can account for $k_1$ appearing to depend on the ligand used. When $[L] > [Cr(NH_3)_5X^{2+}]$ the slopes of the latter plots are much shallower. It was concluded that the appropriate rate law is

$$\text{Rate} = C_1(k_1 + k_LK_A'C_L)/(1 + K_A'C_L) \qquad (3)$$

where $C_1$ and $C_L$ are the stoicheiometric concentrations of complex ion and ligand respectively and $K_A'$ is the association constant of the $Cr(NH_3)X,L$ ion-pairs. It was also stated that $K_A'$ can be estimated from (3) and that for L = citrate the answer agrees well with that obtained by direct means. Also there is a direct relationship between the characteristic $k_1$ and $K_A'$ values for a series of bivalent organic ligands.[6]

Clearer and wider concepts on the role of ion-pairs when ligands accelerate the rates of ionic reactions were suggested and illustrated by Wyatt and Davies.[7] For a second-order type their treatment can be expressed by

$$k_eC_1C_2 = \sum_1^n k_nC_aC_bf_af_b/f_x \qquad (4)$$

where $k_e$ as before is the experimental rate constant, $C_1$ and $C_2$ are the stoicheiometric concentrations of the two reactants, $C_a$ and $C_b$ are the actual concentrations of reacting ions or ion-pairs formed by $C_1$ and $C_2$ respectively which have a rate constant $k_n$, $n$ is the number of possible ion–ion, ion–ion-pair, or ion-pair–ion-pair reactions, and $f_af_b/f_x$ represents activity coefficients (charge on $x$ = sum of charges on $a$ and $b$). For example in the first system which they examined, $C_1$ = thiosulphate, $C_2$ = bromoacetate and since $M^{2+}$ ions were present the possible ion-pairs are $MS_2O_3$ and $MBrAc^+$, so there are four possible reactions each with its own rate constant. On electrostatic grounds the simple ion–ion reaction is the slowest, but since $[MBrAc^+]$ is very small most of the increased rate is due to the reaction of $MS_2O_3$ with $BrAc^-$. This scheme was developed quantitatively [7,8] and has since been used to interpret some other systems.[8,9] It also forms the basis of the present work.

Ion-pair effects on reaction rates were also studied by Olson and Simonson,[10] who expressed their findings in terms of an expression similar to (3) but considered that ion concentrations should be used instead of ionic strengths; Bell and Prue,[11] who, by assuming that the depolymerisations of diacetone by alkaline solutions is only effected by $OH^-$ ions, showed that the lower rates in the presence of $Ca^{2+}$, $Ba^{2+}$, $Na^+$, and $Tl^+$ (as compared with $K^+$ and $Rb^+$) could be attributed to these ions forming hydroxide ion-pairs; and Pedersen,[12] who found that decarboxylation of the nitroacetate ion is retarded by $Al^{3+}$ and a series of $M^{2+}$ ions. He attributed this to nitroacetate ion-pairs. In both this and the diacetone reaction it is assumed [8] that the ion-pairs have little or no reactivity.

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[4] Basolo and Pearson, " Mechanism of Inorganic Reactions," J. Wiley and Sons Ltd., New York, 1958.

[5] Jones, Harris, and Wallace, *Canadian J. Chem.*, 1961, **39**, 237.

[6] Peacock and James, *J.*, 1951, 2233.

[7] Wyatt and Davies, *Trans. Faraday Soc.*, 1949, **45**, 778.

[8] Davies, " Ion Association," Butterworths Publishing Co., London, 1962.

[9] Davies and Williams, *Trans. Faraday Soc.*, 1958, **54**, 1547.

[10] Olson and Simonson, *J. Chem. Phys.*, 1949, **17**, 1167.

[11] Bell and Prue, *J.*, 1949, 362.

[12] Pederson, *Acta Chem. Scand.*, 1949, **3**. 676.

Equations (1) and (3) can be related to (4). If $K_A'$ is the concentration association constant of a reacting ion-pair CpL formed by $C_1$, and $C_2 > C_1$,

$$K_A' = [\mathrm{CpL}]/[\mathrm{Cp}][\mathrm{L}] = [\mathrm{CpL}]/(C_1 - [\mathrm{CpL}])C_2 \quad (5)$$

Then from (4), if $k_1 \sim k_2$, for a pseudo-unimolecular reaction (*i.e.*, $C_2$ is constant)

$$\text{Rate} = k_eC_1 = C_1(k_1 + k_2K_A'C_2)/(1 + K_A'C_2) \quad (6)$$

Equations (3) and (6) are identical if the ionic strengths is constant, and $k_2 = k_L$. However this analysis shows (6) to be only approximate. Likewise if $K_A$ is the thermodynamic association constant of CpL, if $K_A'C_2$ is negligible, (6) gives

$$k_e = k_1 + k_2K_AC_2f_Mf_L/f_{ML} \quad (7)$$

which explains eqn. (1) when $k_L$ is substituted for $k_2K_A$, and also explains why $k_L$ also appears to depend on (2).

The significance of ion-pairs in a wide variety of kinetic preocesses is now widely accepted; numerous examples are reviewed in several monographs.[4,8,13,14]

We followed the rates of aquation of the chloropentamminecobalt(III) ion and its ion-pairs by measuring the rate of release of chlorine-36 from $Co(NH_3)_5{}^{36}Cl^{2+}$, separating the liberated chloride by filtration through cation-exchange papers. Rate constants were calculated by means of

$$k = (2{\cdot}303/t)\log\{(R_f - R_o)/(R_f - R_t)\} \quad (8)$$

where $R_o$, $R_t$, and $R_f$ are the count-rates of unit volume of filtrate at times $t = 0$, $t = t$, and $t_f$ refers to complete hydrolysis (on warming with excess of alkali) respectively. This expression disregards the effect of the reverse anation but since only a fraction of the aquation was followed, the appropriate corrections, as shown by Garrick[2] and by Adell,[15] are negligible. A typical run is illustrated by Tables 1 and 4 summarises all our results in the presence of salts at 35°. (All $R$ values are for 1000 sec.). These results assume that chloride exchange is insignificant. To examine this, a 0·004M solution of the inactive salt was aquated in the presence of [$H^{36}Cl$]. The count-rates did not change during a 10 hr. test, *i.e.*, exchange was negligible.

TABLE 1.

Aquation of the chloropentamminecobalt(III) ion at 35° with chlorine-36.

$10^5\,C_1 = 397$, $HClO_4 = 0{\cdot}01$M, $R_o = 4640$, $R_f = 49{,}850$

| | | | | | | |
|---|---|---|---|---|---|---|
| $R$ | 7655 | 9320 | 11,145 | 13,130 | 14,245 | 15,365 |
| $t$ (hr.) | 3·00 | 5·00 | 7·00 | 9·00 | 10·50 | 12·00 |
| $10^6k_e$ (min.$^{-1}$) | 384 | 363 | 369 | 384 | 379 | 376 |

The first seven runs of Table 4 are all within the range of $10^6k_e = 380 \pm 10$ and this is taken as $10^6k_1$. This figure and a few at other temperatures fit in well with some previous results (Table 2).

TABLE 2.

Summary of ion aquation rates at different temperatures ($10^6k_e$).

| | 20° | 25° | 30° | 35° | 50° | 52° |
|---|---|---|---|---|---|---|
| Present work | — | 96 ± 1 | — | 380 ± 10 | 2200 ± 20 | — |
| Previous results | 62 | 100 | 270 ± 8 | 400<br>(in 0·1M $HNO_3$) | — | 2530<br>(in 0·1M $HNO_3$) |
| Ref. | 17 | 3 | 17 | 16 | — | 18 |

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[13] Davies, " Progress in Reaction Kinetics," Vol. I, ed. G. Porter, Pergamon Press, Oxford, 1961.
[14] Monk, " Electrolytic Dissociation," Academic Press, London, 1961.
[15] Adell, *Z. anorg. Chem.*, 1941, **246**, 303.
[16] Pearson, Boston, and Basolo, *J. Phys. Chem.*, 1955, **59**, 304.
[17] Watkins and Jones, *J. Inorganic and Nuclear Chem.*. 1964, **26**, 469.
[18] Adamson and Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261.

Adamson and Basolo[18] obtained their rate constant from changes in the chloro-ion absorption band in the visible region. However the extinction coefficients of both chloro- and aquo-forms are small in this region so that high concentrations are needed to obtain reliable results.

The ultraviolet absorption bands are much stronger,[10] that of the chloro-ion starting at about 320 mμ and that of the aquo-ion at about 260 mμ. Some values of $k_1$ based on measurements at 260 mμ are given in Table 3; they were calculated from the usual expression, (8), by replacing $R$ by $D_c$, $R_0$ by $D_a$ and $R_t$ by $D_t$ where $D_c$ is the absorption of the chloro-ion, $D_a$ is that of the aquo-ion, and $D_t$ is the absorption at time $t$. An approximate value of $D_c$, 0·69, was obtained from $D$ at $t = 0$ but the actual value for calculating $k_1$ was obtained by selecting that value (0·687) which lead to constant $k_1$ values. The average is $10^6 k_1 = 385 \pm 7\%$ in good agreement with that given in Table 2. From the final figure of $D_t = 0{\cdot}050$, the fraction aquated at equilibrium is 0·95.

TABLE 3.

Aquation of the chloropentamminecobalt(III) ion at 35° in water from spectrophotometry.

$10^5 C_1 = 420$, $HClO_4 = 0{\cdot}01$M, $D_c = 0{\cdot}687$, $D_a = 0{\cdot}014$, 1 cm. cells, 260 mμ.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $D_t$ | 0·665 | 0·628 | 0·614 | 0·604 | 0·573 | 0·553 | 0·529 | 0·050 |
| $t$ (hr.) | 1·50 | 3·50 | 4·50 | 6·00 | 8·50 | 10·00 | 11·00 | ∞ |
| $10^6 k_1$ (min.$^{-1}$) | 370 | 435 | 425 | 365 | 365 | 370 | 375 | — |

## DISCUSSION

As shown by Table 4 chloride, acetate, and azide ions have no effect upon the aquation rate. The absence of rate-change by chloride agrees with the limited figures of Garrick[2] and with the more extended study of Jones, Harris, and Wallace[5] of the analogous chromium(III) chloro-ion. Nitrate and glycollate slightly raise the rate of aquation while sulphate, malonate, and phthalate are strong accelerators. The univalent ligands can be expected to have little influence since the dissociation constants of the ion-pairs are large (previous Paper), *i.e.*, the concentrations of these faster-aquating ion-pairs are small.

From equation (4), since $f_x = f_a f_b$ for both the chloro-ion and its ion-pairs CpL, we get

$$k_e C_1 = k_1(C_1 - [\mathrm{CpL}]) + k_2[\mathrm{CpL}] \tag{9}$$

[CpL] is calculated by approximations when L is a univalent ligand from ($K$ = dissociation constant)

$$\log K = \log (C_1 - [\mathrm{CpL}])C_1 - \log [\mathrm{CpL}] - \log f_a \tag{10}$$

since $C_L$-[CpL] $\sim C_L$ where $C_L$ is the initial true ligand molarity, and

$$-\log f_a = 4 \times 0{\cdot}51 \{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}3I)\} \tag{11}$$

The derived values of $k_2$ ($k_1$ taken from the mean of runs 1 and 2 of Table 4 and $K = 0{\cdot}03_5$ and 0·09 for the glycollate and nitrate ion-pairs,[19] respectively) are in Table 4. Some further figures for the nitrate, calculated from Garrick's[2,3] results at 25°, are in Table 5.

For the bivalent ligands the requisite equations are

$$\log K = \log (C_1 - [\mathrm{CpL}])(C_L - [\mathrm{CpL}] - [\mathrm{HL}]) - \log[\mathrm{CpL}] - \log f_a f_b \tag{12}$$

$$C_L = [\text{Total ligand}]/(1 + [\mathrm{H^+}]f_b/K_2) \tag{13}$$

where[14] $K_2$ is 0·0077 for $HSO_4^-$ and[20] $1{\cdot}85 \times 10^{-6}$ for HMal$^-$. For phthalate,

$$C_L = \text{Total acid} - [\mathrm{HL^-}] = m_2 - m_1 \tag{14}$$

since known molarities of acid ($m_1$) and sodium hydroxide ($m_2$) were taken. The values of $K$ were taken from the previous Paper,[19] namely 0·0032 (sulphate), 0·0050 (malonate),

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[19] Archer and Monk, preceding Paper.

[20] Hamer, Burton, and Acree, *J. Research Nat. Bureau Stds.*, 1940, **24**, 269.

0·0030 (phthalate). The resultant values of $k_2$ are given in Table 4 while further sulphate data based on some of Garrick's work [3] at 25° are shown in Table 5. Allowance has been made in both Tables for [8] $NaSO_4^-$(K = 0·2) and $KSO_4^-$($K$ = 0·1).

TABLE 4.

Summary of aquation results for chloropentamminecobalt(III) at 35° using chlorine-36

Gly = glycollate, Mal = malonate, Ph = phthalate. $10^6k_1$ taken as 380 in calculating $k_2$.

| Run | $10^5C_1$ | $10^3$ [$HClO_4$] | pH | $10^5$ [Salt] | $10^6k_e$ (min.$^{-1}$) | $10^5$ [CpL] | $10^5$ [L] | $10^4I$ | $10^6k_2$ (min.$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 397 | 10 | — | 0 | 376 ± 6 | 0 | — | — | — |
| 2 | 320 | 10 | — | 0 | 384 ± 3 | 0 | — | — | — |
| 3 | 411 | 10 | — | 10,000(NaCl) | 384 ± 5 | 0 | — | — | — |
| 4 | 387 | 2(HAc) | 5·60 | 1,800(NaAc) | 378 ± 5 | — | — | — | — |
| 5 | 398 | — | 5·74 | 5,000($NaN_3$) | 380 ± 3 | — | — | — | — |
| 6 | 399 | — | 5·80 | 15,000($NaN_3$) | 384 ± 6 | — | — | — | — |
| 7 | 401 | 10 | — | 10,000($NaNO_3$) | 393 ± 6 | 120 | — | 1100 | 420 |
| 8 | 398 | — | 5·21 | 7,600(NaGly) | 400 ± 2 | 185 | — | 880 | 425 |
| 9 | 398 | — | 5·30 | 11,970(NaGly) | 416 ± 3 | 215 | — | 1310 | 445 |
| 10 | 398 | 10 | — | 402($Na_2SO_4$) | 437 ± 2 | 62 | 210 | 285 | 750 |
| 11 | 394 | 10 | — | 1,004($Na_2SO_4$) | 501 ± 1 | 117 | 587 | 412 | 785 |
| 12 | 392 | — | 5·68 | 1,003($Na_2SO_4$) | 534 ± 3 | 153 | 811 | 349 | 775 |
| 13 | 402 | — | 5·60 | 2,005($Na_2SO_4$) | 577 ± 4 | 198 | 1672 | 610 | 780 |
| 14 | 398 | — | 5·43 | 3,007($Na_2$Mal) | 510 ± 2 | 123 | 1351 | 743 | 800 |
| 15 | 398 | — | 5·82 | 4,040($Na_2$Mal) | 565 ± 2 | 167 | 2748 | 1095 | 820 |
| 16 | 339 | — | 5·7 | 930($Na_2$Ph) | 682 ± 12 | 138 | 792 | 325 | 1110 |
| 17 | 395 | — | 5·7 | 1,860($Na_2$Ph) | 762 ± 12 | 201 | 1659 | 595 | 1130 |

TABLE 5.

Analysis of Garrick's results for the aquation of chloropentamminecobalt(III) at 25°.

$10^6k_1$ taken as 100, $K(CpNO_3^+)$ = 0·09, $K(CpSO_4)$ = 0·0032.

| $10^5C_1 = Cp(NO_3)_2$ | $10^4$ [Salt] | $10^7k_e$ (min.$^{-1}$) | $10^5$ [$CpNO_3^+$] | $10^5$ [$CpSO_4$] | $I$ | $10^6k_2$ | $10^6k_3$ |
|---|---|---|---|---|---|---|---|
| 1000 | 0 | 1019 | $10_5$ | — | 0·030 | 118 | — |
| 2089 | 0 | 1024 | $35_0$ | — | 0·065 | 114 | — |
| 1028 | 495($KNO_3$) | 1049 | $24_5$ | — | 0·080 | 120 | — |
| 1016 | 1740($NaNO_3$) | 1070 | $41_0$ | — | 0·205 | 120 | — |
| 995 | 770($HNO_3$) | 1057 | $28_5$ | — | 0·105 | 120 | — |
| 945 | 1920($HNO_3$) | 1074 ± 2 | $45_0$ | — | 0·220 | 115 | — |
| 1000 | 260($Lu(NO_3)_3$) | 1060 | $26_0$ | — | 0·185 | 123 | — |
| 1064 | 100($K_2SO_4$) | 1350 | 73 | 300 | 0·0485 | — | 218 |
| 1007 | 397($K_2SO_4$) | 1760 | 30 | 520 | 0·1134 | — | 245 |
| 982 | 260($Na_2SO_4$) | 1650 | 40 | 460 | 0·0843 | — | 235 |
| 1007 | 510($Na_2SO_4$) | 1820 | 30 | 575 | 0·1470 | — | 245 |

Since the sulphate results [3] were obtained with $Cp(NO_3)_2$, the expression required is

$$k_eC_1 = k_1[Cp] + k_2[CpNO_3^+] + k_3[CpSO_4]$$

where $k_2$ and $k_3$ are the ion-pair rate-constants of the two ion-pairs indicated. For this purpose $k_2$ was taken as $1{\cdot}2 \times 10^{-4}$, the average result in Table 5.

From this information we obtain:

| Ligand | Nitrate | Glycollate | Sulphate | Malonate | Phthalate |
|---|---|---|---|---|---|
| $k$(ion-pairs)/$k$(ion) | 1·1(35°), 1·2(25°) | 1·15(35°) | 2·05(35°), 2·35(25°) | 2·08(35°) | 2·95(35°) |
| $K$ | 0·09 | $0{\cdot}03_5$ | 0·0032 | 0·0050 | 0·0030 |

Although there is a rough general relationship between the $k$ ratios and $K$ it is apparent that two bivalent organic ligands have a greater effect than has sulphate.

If at least two rate constants are obtained for a particular ligand at distinctly different ligand concentrations, and $k_1$ is known, then it is possible to estimate both $k_2$ and $K$ of the ion-pair. This is illustrated by means of the sulphate runs of Table 4. Values of $K$ = 0·006 to 0·002 were taken and $k_2$ calculated for each $K$ by an iterative process on an IBM 1620 computer. The final figures are given in Table 6. The average deviations in

$k_2$ ($\Delta k_2$) pass through a minimum and from plots of $\Delta k_2$ against $K$, and of $k_2$(av.) against $K$, the minimum of the first indicates that $K = 0{\cdot}0035$ while from the second plot this corresponds to $10^6k_2 = 790$ min.$^{-1}$; these figures are slightly bigger than the determined values of $K$ given in the previous Paper (0·0032) and the average $k_2$ from Table 4 ($10^6k_2 = 773$ min.$^{-1}$). In the same way, for malonate, $K = 0{\cdot}0056$ and $10^6k_2 = 850$ while for phthalate $K = 0{\cdot}0034$, $10^6k_2 = 1180$.

It follows from (9) that it is easier to carry out the above process by selecting values of $k_2$, finding [CpL] and hence $K$, and continuing until $K$ is constant. In practice the order of $K$ is known or a reasonable guess can be made whereas $k_2$ can vary widely so the method used for Table 6 can have advantages.

TABLE 6.

Sulphate ion-pair rate constants for different $K$ values

Data from Table 4, $10^6k_1$ taken as 380 min.$^{-1}$.

| Run | $K =$ | 0·006 | 0·005 | 0·004 | 0·003 | 0·002 |
|---|---|---|---|---|---|---|
| 10 | $10^6k_2 =$ | 982 | 898 | 814 | 729 | 643 |
| 11 | $10^6k_2 =$ | 1014 | 932 | 850 | 768 | 684 |
| 12 | $10^6k_2 =$ | 959 | 891 | 822 | 753 | 683 |
| 13 | $10^6k_2 =$ | 938 | 878 | 819 | 759 | 699 |
| | Average | 973 | 900 | 826 | 752 | 677 |
| | $\Delta k_2$ ($\pm$%) | 2·55 | 1·79 | 1·43 | 1·55 | 2·53 |

## EXPERIMENTAL

Chloropentamminecobalt(III) chloride was prepared from cobalt carbonate by the method of Jorgensen [21] except that the reaction mixture was cooled before 3N-hydrochloric acid was added to precipitate the salt since, if the mixture is hot, some of the dichlorotetrammine salt forms.[22] The crude precipitate was converted into the aquo-form by warming on a water-bath with dilute ammonium hydroxide, then reconverted to crystals of the chloro-form by pouring it into concentrated hydrochloric acid. These crystals were washed several times with methanol and dried at 50°.

Chlorine-36 was introduced in two ways. In the first, about 3 g. of the chloro-salt, 1 g. of lithium chloride, 0·5 ml. of 2N-hydrochloric acid and 50 ml. of 0·001N-perchloric acid containing 20 μc of chlorine-36 were kept at about 80° for 4—5 hr. A portion of the salt dissolved and underwent exchange. The hot solution was decanted into a second beaker, cooled, and the mother liquor returned to the original beaker. The exchange, decantation, and cooling processes were continued until all the crystals had been transferred to the second beaker. About 100 ml. of methanol were added, the solution was filtered and evaporated to a small volume, and the filtrate reserved for further exchanges while the active crystals were dissolved in a little water at 35° and reprecipitated by 100 ml. of concentrated hydrochloric acid (to remove most of the chlorine-36 outside the complex ion). The crystals were separated by decantation, washed several times with methanol, and dried at 50°.

In the second method, about 3 g. of the aquo-salt were dissolved in the minimum of water at 80°, 20 μc of chlorine-36 in 2N-hydrochloric acid added and the solution kept at 80° for 4 hr. before the chloro-salt was precipitated with 10 ml. of concentrated hydrochloric acid and 100 ml. of methanol. The salt was recrystallised as above. The product had a higher activity than the product of the first method but the mother-liquor was useless for further conversion.

For a kinetic run a weighed quantity of complex salt (about 0·25 g.) in a conical flask and the reacting solution in a de-greased 250 ml. graduated flask were equilibrated in a bath kept to ±0·02°. The solution was added and the conical flask shaken in the bath. Tests showed that only about 0·2 ml. of solution were lost. At timed intervals, 10 ml. aliquot portions were withdrawn and filtered through a double layer of cation-exchange paper (Amberlite SA-2 in the $Na^+$ form). The first 4 to 5 ml. were rejected, and the rest retained for counting. Filtration took 1 to 1·5 min. When required, the papers were regenerated in 4M-$NaNO_3$, washed with water, and dried at room temperature. For counting, 1 ml. samples were mixed with 5 ml. of dioxan-based scintillator and the counts recorded with a scintillation counter (Ekco Ltd.).

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[21] Jorgensen, *Z. anorg. Chem.*, 1898, **17**, 462.

[22] King, " Inorganic Preparations," Allen and Unwin Ltd., London, 1950.

Sufficient counts were taken to keep the statistical error below 0·4%. Corrections were made for background and lost counts. The relative efficiences of the counting vials were found by means of a standard solution of [$H^{36}Cl$]. All counts were made in the same period. A " zero-time " sample was also taken while to obtain the total activity excess sodium hydroxide was added to 10 ml. of an unfiltered sample which was then warmed on a water-bath until the cobalt ppt. had coagulated. This was filtered off and washed on an ordinary paper into a 50 ml. flask, and 1 ml. samples of this solution counted.

The spectrophotometric measurements were made with a Hilger " Uvispek " instrument fitted with a temperature-controlled cell-holder and recorder.

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