Preparation and Characterization of μ-Amido-μ-acetato and μ-Amido-μ-formato Binuclear Ammine Complexes of Cobalt(III) and Related Kinetic Studies

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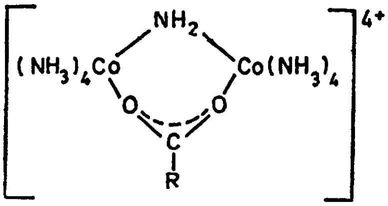
Chloride and perchlorate salts of μ-amido-μ-acetato-bis[tetra-amminecobalt(III)] (I) and μ-amido-μ-formato-bis-[tetra-amminecobalt(III)] (II) have been prepared from the μ-amido-μ-chloro-bis[tetra-amminecobalt(III)] complex. Evidence consistent with the structures indicated in (I) and (II) is considered. A kinetic study has been made of the reaction of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex with acetic acid in perchloric acid solutions, $I = 2{\cdot}0\text{M}$ ($LiClO_4$). Over the temperature range 25—40 °C and at hydrogen-ion concentrations 0·1—1·5M, the rate law is as in (i). Activation parameters have been determined and, at 25 °C,

$$-d\ln[(\mathrm{Co^{III}})_2]/dt = (k_1 + k_2[\mathrm{H^+}])[\mathrm{CH_3CO_2H}] \qquad \text{(i)}$$

$k_1 = (1{\cdot}4 \pm 0{\cdot}1) \times 10^{-6}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ and $k_2 = (6{\cdot}5 \pm 0{\cdot}1) \times 10^{-6}\ \mathrm{l^2\ mol^{-2}\ s^{-1}}$. The reverse reaction, the decomposition of the μ-amido-μ-acetato-complex, has been investigated briefly at 50 °C and the rate law is of the form (ii).

$$-d\ln[(\mathrm{Co^{III}})_2]/dt = a + b[\mathrm{H^+}] \qquad \text{(ii)}$$



(I) $R = CH_3$
(II) $R = H$

THE preparation and characterization of the μ-amido-μ-oxalato-bis[tetra-amminecobalt(III)] complex has been described previously.[1] We now report the preparation of μ-amido-μ-acetato-bis[tetra-amminecobalt(III)] and μ-amido-μ-formato-bis[tetra-amminecobalt(III)] (hereafter referred to as μ-amido-μ-acetato- and μ-amido-μ-formato-complexes respectively), and consider the possibility of extending the procedures described to the preparation of other μ-amido-μ-carboxylato binuclear cobalt(III) complexes.

Details of the preparation of chloride and perchlorate salts of both complexes are given in the Experimental section. The starting material is the μ-amido-μ-chloro-bis[tetra-amminecobalt(III)] complex which in solution rapidly forms μ-amido-[aquotetra-amminecobalt(III)] [chlorotetra-amminecobalt(III)],[2] the reactant in these preparations (Scheme 1). Conversion of the reactant into the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex is fairly fast,[3] and conditions had to be such as to minimize this side reaction. The reaction of the μ-amido-μ-hydroxo-complex with acetic acid is slow, and impractical as a preparative method. Although we have found that nitrate catalyses formation of the μ-amido-μ-acetato-complex, the product is impure, and the procedure less satisfactory (see details in Experimental section). The advantage of using the μ-amido-μ-chloro-bis[tetra-amminecobalt(III)] complex lies in the spontaneous cleavage of the chloride bridge in aqueous solution.[2]

RESULTS

The first five sections below are concerned with the characterization of the μ-amido-μ-acetato- and μ-amido-μ-

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[1] K. L. Scott, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3651.

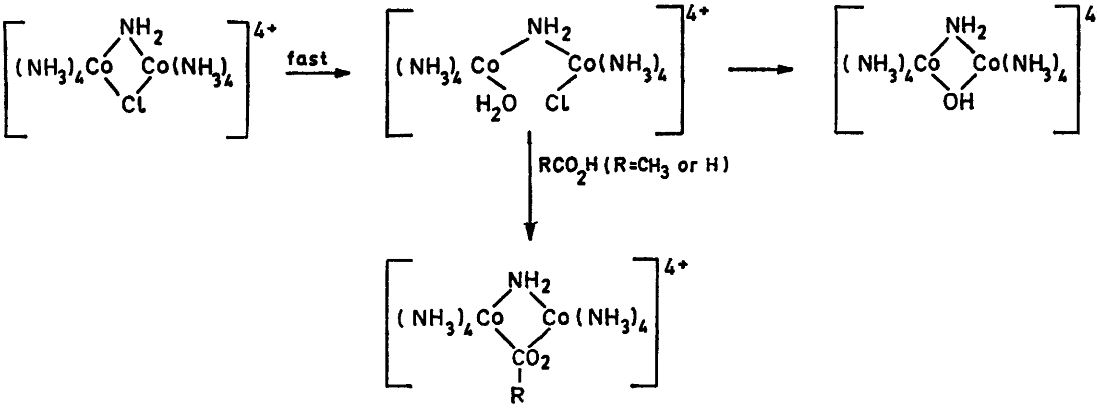
[2] A. G. Sykes and R. S. Taylor, *J. Chem. Soc.* (*A*), 1970, 1424.

[3] S. W. Foong, R. D. Mast, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1266.

formato-complexes. There follow two sections in which kinetic studies are reported.

Analyses.—Elemental analyses are consistent with the formulae given in the Experimental section. From the loss in weight after dehydration over P_2O_5 all the water molecules appear to be removed, and there is therefore no evidence consistent with the presence of co-ordinated water.

pH *Measurements.*—The pH of a 5×10^{-4}M solution of the μ-amido-μ-acetato-complex in 0·1M-$LiClO_4$ at 25 °C was initially 5·24, but after 10 min became 5·28 and after 40 h 6·42. The pH of the background 0·1M-$LiClO_4$ was *ca.* 5·3, where removal of carbon dioxide was not effected for this study. It is concluded that there are no co-ordinated water molecules, and that the acetate is initially bridging.[4] This structure is moreover retained for periods of up to 1 day. Subsequent increases in pH may result from a variety of decomposition processes including aquation of ammonia ligands[5] and/or the acetate bridge (see below).



SCHEME 1

TABLE 1

A comparison of asymmetrical and symmetrical C–O stretching frequencies (cm^{-1}) for acetate and formate ligands and the separation of these bands with different degrees of co-ordination

Compound	$\nu_{as}(CO)$	$\nu_s(CO)$	$\Delta\nu$	Reference
$CH_3CO_2^-$ (Na salt)	1578	1425	153	*a*
$[Co(NH_3)_5(CH_3CO_2)]^{2+}$	1603	1380	223	*b*
$(NH_3)_4Co{\cdot}\mu(NH_2,CH_3CO_2){\cdot}Co(NH_3)_4)^{4+}$	1530	1410	120	This work [c]
$(NH_3)_3Co{\cdot}\mu(OH,OH,CH_3CO_2){\cdot}Co(NH_3)_3{}^{3+}$	1535	1440	95	*e,f*
HCO_2^- (Na salt)	1590	1355	235	*d*
$[Co(NH_3)_5(HCO_2)]^{2+}$	1640	1345	295	*e*
$(NH_3)_4Co{\cdot}\mu(NH_2,HCO_2){\cdot}Co(NH_3)_4{}^{4+}$	1570	1365	205	This work [c]
$(NH_3)_3Co{\cdot}\mu(OH,OH,HCO_2){\cdot}Co(NH_3)_3{}^{3+}$	1550	1355	195	*e,f*

[a] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kabayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904 and ref. 6. [b] Perchlorate salt, M. Linhard and B. Rau, *Z. anorg. Chem.*, 1953, **271**, 121. [c] Chloride salt; KBr discs. [d] Ref. 6. [e] Bromide salt, ref. 6. [f] H. Siebert and G. Tremmel, *Z. anorg. Chem.*, 1972, to be published.

I.r. Spectra.—Free acetate has 15 i.r.-active fundamentals. Amongst these are the asymmetrical and symmetrical C–O stretching frequencies at 1578 and 1425 cm^{-1} respectively. The positions of the bands shift on co-ordination and the separation of the two is often indicative of the type of bonding. Table 1 summarizes available data including those obtained in the present study. The separation of the C–O stretching frequencies is consistent with that observed for the di-μ-hydroxo-μ-acetato-bis[triamminecobalt(III)] and analogous formato-complex.[6]

U.v.-visible Spectra.—Details of the peak positions of the *d–d* bands are almost identical for the μ-amido-μ-acetato-, μ-amido-μ-formato-, and μ-amido-μ-oxalato-bis[tetraamminecobalt(III)] complexes, as previously noted.[1] For the perchlorate salt of the μ-amido-μ-formato-complex we prefer a value of 360 instead of 353 l mol^{-1} cm^{-1} for the extinction coefficient at 515 nm. The spectrum of the μ-amido-μ-oxalato-complex is independent of $[H^+]$ over the 400—650 nm range, but below 400 nm significant absorbance differences are observed due to protonation. No similar effects are apparent for the μ-amido-μ-acetato- and μ-amido-μ-formato-complexes.

Cr^{2+} *Reductions.*—Rates of reduction with Cr^{2+} are consistent only with structures (I) and (II) as indicated in the abstract. A four-membered ring would possess a free carbonyl group and rate constants for Cr^{2+} reduction would be expected to be of the same order of magnitude as those for acetato- and formato-penta-amminecobalt(III) respectively. However, observed rate constants are 10^3—10^4 times slower.[7] An aquo-acetato-species present on dissolving the solid in water can also be ruled out since, on reduction with Cr^{2+}, an $[H^+]^{-1}$ dependence would be expected. Furthermore the existence of a kinetic path involving the

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[4] For examples of behaviour expected when an aquo-ligand is present see M. B. Stevenson, R. D. Mast, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 937.

[5] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1426.

[6] G. Tremmel, Inaugural Dissertation, Universität Heidelberg, 1970, p. 34. We thank Professor H. Siebert for providing us with the information therein.

[7] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 1832.

aquo-formato-species, which is produced over a long period by ring opening, proves conclusively that a formate bridge is present originally.

Kinetics of Formation of the μ-Amido-μ-acetato-complex.—The reaction of μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] with acetic acid was studied by conventional spectrophotometry, by following the increase in absorption due to the μ-amido-μ-acetato-complex at its 517 nm peak position ($\varepsilon = 3681\ \text{mol}^{-1}\ \text{cm}^{-1}$). Solutions of the μ-amido-μ-hydroxo-complex in acetic acid were diluted 1 : 1 with 4·0M-$HClO_4$–$LiClO_4$ solutions; no allowance was made for acetic acid in calculating the ionic strength, which was adjudged to be $I = 2{\cdot}0\text{M}$ ($LiClO_4$). Since decomposition of the reactant (and possibly also the product) ensures that OD_∞ is never reached, values of OD_∞ were obtained (*a*) from the known spectrum of the μ-amido-μ-acetato-complex, and (*b*) by taking OD_∞ readings from replicate runs with HNO_3–$LiClO_4$ for $HClO_4$–$LiClO_4$. The enhancement of the rate by nitrate ions (see below) enabled OD_∞ to be measured. Values obtained in (*a*) and (*b*) were in agreement to within 2%. Because of the slowness of the reaction it was necessary to work at high acetic acid concentrations. The effect of acetic acid on k_{obs} is indicated in Table 2. There is a slight non-linear dependence on the concentration of acetic acid $>1{\cdot}0$M (Figure 1) and it was therefore decided to work with acetic acid not exceeding 1·0M. Plots of log ($OD_\infty - OD_t$) against time were linear to >80% reaction at 25 °C, but only to *ca.* 60% at 40 °C (Figure 2). Pseudo-first-order rate constants, k_{obs}, obtained at $[H^+] = 0{\cdot}1$—$2{\cdot}0$M are given in Table 3, and their hydrogen-ion dependence illustrated in Figure 3. Within the $[H^+]$ range 0·1—1·5M the dependence is of the form (1). Rate constants (Table 4)

$$k_{obs} = (k_1 + k_2[H^+])[CH_3CO_2H] \qquad (1)$$

and activation parameters were obtained by a least-squares treatment in which each data point in the range $[H^+] = 0{\cdot}1$—$1{\cdot}5$M was given equal weighting.[8] The activation parameters for k_1 and k_2 respectively are $\Delta H_1^\ddagger =$

TABLE 2

The dependence of pseudo-first-order rate constants, k_{obs}, on acetic acid concentration for the formation of the μ-amido-μ-acetato-complex. Concentrations of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] reactant were in the range $1{\cdot}7 \times 10^{-4}$—$2{\cdot}6 \times 10^{-4}$M; $I = 2{\cdot}0$M ($LiClO_4$)

t/°C	$[H^+]$/M	$[CH_3CO_2H]$/M	10^6k_{obs}/s^{-1}
25	2·0	0·5	6·5
	2·0	0·75	9·2
	2·0	1·0	12·4
	2·0	1·0	13·5
	2·0	1·75	25·7
	2·0	2·0	29·0
	2·0	2·5	37·2
40	1·0	1·0	34·0
	1·0	1·5	53·7
	1·0	2·0	76·0
	1·0	2·5	104

TABLE 3

Pseudo-first-order rate constants, k_{obs}, for the formation of the μ-amido-μ-acetato-complex from μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] (perchlorate salt). $[CH_3CO_2H] = 1{\cdot}0$M except where otherwise stated; $I = 2{\cdot}0$M ($LiClO_4$)

t/°C	$[H^+]$/M	10^4[complex]/M	$10^6k_{obs}[CH_3CO_2H]^{-1}$/ l mol^{-1} s^{-1}
25·0	0·50	1·71	4·5
	0·50	1·72	4·6
	0·75	1·71	6·1
	1·25	1·69	9·6
	1·50	1·69	11·1
	1·50	2·74	11·4 [a]
	1·63	1·69	12·0
	1·75	1·69	12·0
	1·88	1·69	12·8
	2·00	1·69	12·4
	2·00	2·58	13·5 [a]
	2·00	2·60	13·0 [a,b]
32·5	0·50	1·71	9·8
	0·75	1·71	14·0
	1·00	1·71	16·0
	1·25	1·71	20·4
	1·50	1·71	22·0
	2·00	1·71	25·0
40	0·10	1·71	14·0
	0·25	1·71	17·7
	0·75	1·71	29·0
	1·00	1·69	34·0
	1·25	1·71	39·1
	1·50	1·69	45·1
	1·75	1·69	47·0
	1·75	1·71	48·0
	2·0	7·00	51·0
	2·0	1·56	50·0
	2·0	1·71	50·0

[a] Chloride salt of complex used. Rate constants are not noticeably different from those using perchlorate salt. [b] $[CH_3CO_2H] = 0{\cdot}5$M.

TABLE 4

A summary of k_1 and k_2 as defined in equation (1), for the formation of the μ-amido-μ-acetato-complex from μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)], $I = 2{\cdot}0$M ($LiClO_4$)

t/°C	10^6k_1/l mol^{-1} s^{-1}	10^6k_2/l^2 mol^{-2} s^{-1}
25	1·4 ± 0·1	6·5 ± 0·1
32·5	4·2 ± 1·1	12·1 ± 1·0
40	12·0 ± 0·3	22·0 ± 0·3

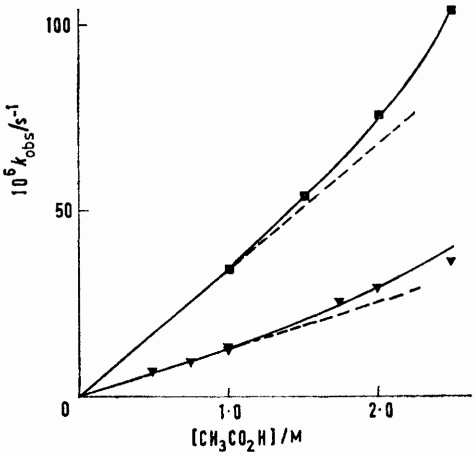

FIGURE 1 The dependence of pseudo-first-order rate constants, k_{obs}, on acetic acid concentration for the formation of the μ-amido-μ-acetato-complex, $I = 2{\cdot}0$M ($LiClO_4$). (■) At 40 °C, $[H^+] = 1{\cdot}0$M; (▼) at 25 °C, $[H^+] = 2{\cdot}0$M

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[8] Los Alamos Report LA 2367 1959 and Addenda by R. H. Moore and R. K. Zeigler. We are grateful to Dr. T. W. Newton for details of this program.

$26\cdot5 \pm 2\cdot3$ kcal mol^{-1}, $\Delta S_1^\ddagger = 3 \pm 7$ cal K^{-1} mol^{-1}, $\Delta H_2^\ddagger = 14\cdot3 \pm 0\cdot6$ kcal mol^{-1}, and $\Delta S_2^\ddagger = -34\cdot4 \pm 1\cdot9$ cal K^{-1} mol^{-1}. We are uncertain as to the reliability of the data at $[H^+] < 0\cdot1$M because of the slowness of the reaction and effectiveness of the decomposition of the μ-amido-μ-hydroxo-complex [5] under these conditions.

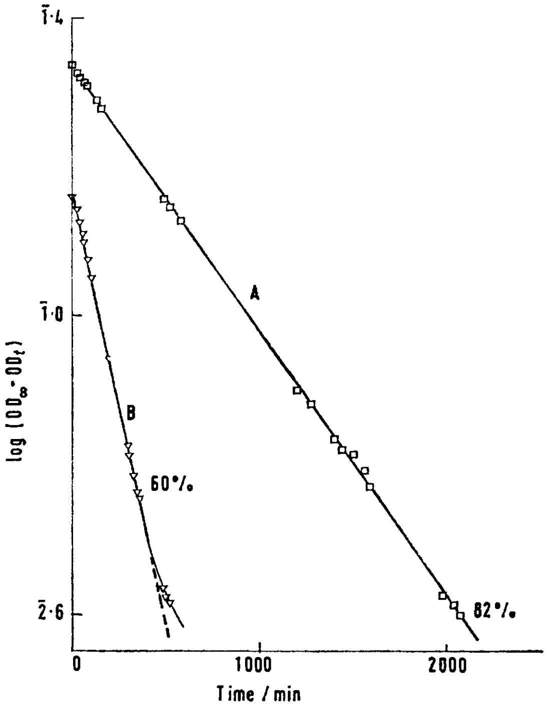
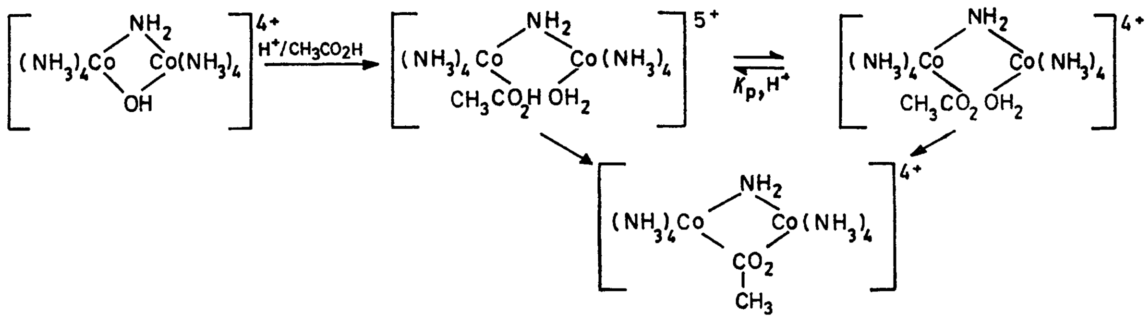


FIGURE 2 Pseudo-first-order plots for the reaction of μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] with acetic acid (1·0M), $I = 2\cdot0$M ($LiClO_4$). Run A: 25 °C, [complex] = $2\cdot58 \times 10^{-4}$M, $[H^+] = 2\cdot0$M; Run B: 40 °C, [complex] = $1\cdot69 \times 10^{-4}$M, $[H^+] = 1\cdot5$M



SCHEME 2

The curvature observed in Figure 3 at $[H^+] > 1\cdot5$M is probably due to protonation of the acetate ligand in an aquo-acetato intermediate, which has the net effect of reducing the rate of formation of the μ-amido-μ-acetato-complex since the protonated intermediate will not readily undergo bridge closure. The k_2 pathway for the formation of the μ-amido-μ-acetato-complex can thus be summarized as in Scheme 2. We have examined the possibility that protonation might manifest itself in other ways, such as the reduced linearity of first-order plots due to build-up of the aquo-intermediate. No such curvature was observed. An allowance for protonation of the aquo-complex (protonation constant K_p) can be made by plotting $k_{obs}(1 + K_p[H^+])$ against $[H^+]$, assuming that reaction of the protonated form makes negligible contribution. Linearity is observed at all temperatures with a K_p value of *ca.* 0·2 l mol^{-1}.

A brief study was made of the effect of nitrate ions on the reaction of the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex with acetic acid at $[H^+] = 2\cdot0$M, $I = 2\cdot0$M, procedure as before. A first-order dependence on nitrate was observed and there is a 10-fold catalytic effect with 2·0M-HNO_3.[9] The nitrate-catalysed path is first order in $[H^+]$ with curvature again incident at the higher $[H^+]$ values.

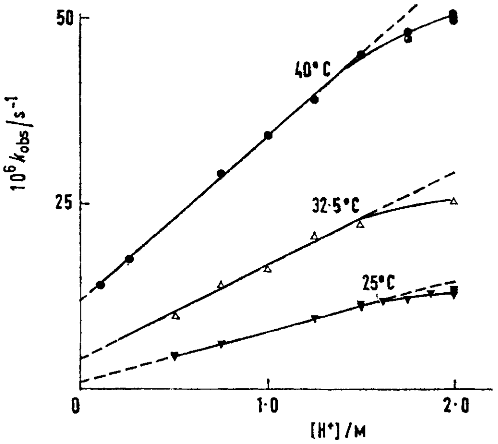


FIGURE 3 The dependence of k_{obs} on $[H^+]$ [equation (1)] for the reaction of μ-amido-μ-hydroxy-bis[tetra-amminecobalt(III)] with acetic acid, $I = 2\cdot0$M ($LiClO_4$)

Kinetics of the Reverse Reaction.—The kinetics of the release of acetate from the μ-amido-μ-acetato-complex were studied at 50 °C, $I = 2\cdot0$M ($LiClO_4$). The primary product is believed to be the μ-amido-μ-hydroxo-complex which subsequently decomposes, as reported elsewhere.[5] Plots of log ($OD_t - OD_\infty$) against time were linear to only *ca.* 10% reaction, values of OD_∞ being calculated on the assumption that the μ-amido-μ-hydroxo-complex is formed. Rate constants k_r (Table 5), obtained from these plots, are seen to fit a dependence of the form (2). At 50 °C, a =

$$k_r = a + b[H^+] \qquad (2)$$

$(5\cdot9 \pm 1\cdot7) \times 10^{-7}$ s^{-1} and $b = (9\cdot4 \pm 1\cdot2) \times 10^{-7}$ l mol^{-1} s^{-1},

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[9] Further details of rate constants can be obtained from K. L. Scott, Ph.D. Thesis, University of Leeds, 1972.

from an unweighted least-squares treatment. The catalytic effect of nitrate ions (last entry in Table 5) is again noted.

One run was carried out on the reverse reaction of the μ-amido-μ-formato-complex. At 50 °C, $[H^+] = 0{\cdot}25$M, [complex] $= 6{\cdot}7 \times 10^{-4}$M, and $I = 1{\cdot}0$M ($LiClO_4$), $k_r = 2{\cdot}73 \times 10^{-6}$ s^{-1}, which is larger than the value observed for the μ-amido-μ-acetato-complex.

TABLE 5

Rate constants for the reverse reaction, the decomposition of the μ-amido-μ-acetato-bis[tetra-amminecobalt(III)] complex at 50 °C, $I = 2{\cdot}0$M ($LiClO_4$). First-order plots were linear to only *ca.* 10% reaction at $\lambda = 510$ nm using a Unicam SP 800 recording spectrophotometer

$[H^+]$/M	10^4[complex] [a]/M	$10^7k_r/s^{-1}$
0·01	7·4	5·9
1·0	7·6	15·2
1·5	7·4	22·3
1·6	30·8	18·8
2·0	7·5	24·6
2·0	7·4	207 [b]

[a] Bromide salt of the μ-amido-μ-acetato-complex used. [b] Effect of 2·0M-HNO_3.

DISCUSSION

The reaction path k_2 which exhibits a first-order dependence on hydrogen-ion concentration, (1), is believed to correspond to the reaction of the protonated form of the μ-amido-μ-hydroxo-complex (*i.e.* the μ-amido-μ-aquo-form) with acetic acid. Similar hydrogen-ion dependent paths are observed in other bridge-cleavage reactions of this complex with a variety of incoming ligands including SO_4^{2-},[10] Cl^-,[3] and H_2O.[11] The rate constant k_2 ($6{\cdot}5 \times 10^{-6}$ l^2 mol^{-2} s^{-1} at 25 °C, $I = 2{\cdot}0$M) for the formation of the μ-amido-μ-acetato-complex is slow compared with values observed when SO_4^{2-} ($2{\cdot}15 \times 10^{-2}$ l^2 mol^{-2} s^{-1}) or X^- (*e.g.* $9{\cdot}6 \times 10^{-4}$ l^2 mol^{-2} s^{-1} for chloride) are the reactants. It resembles more closely the value observed for the formation of the bis-aquo-complex where H_2O is the incoming ligand ($k_2 = 7{\cdot}9 \times 10^{-5}$ l mol^{-1} s^{-1} at 25 °C, $I = 2{\cdot}0$M). The hydrogen-ion independent path ($k_1 = 1{\cdot}4 \times 10^{-6}$ l mol^{-1} s^{-1} at 25 °C) has been assigned to a reaction involving hydroxo-bridge cleavage where acetic acid is the incoming ligand. A similar pathway has been observed with chloride as the incoming ligand ($k_1 = 1{\cdot}2 \times 10^{-4}$ l mol^{-1} s^{-1} at 25 °C [3]). An alternative explanation is that a proton-assisted bridge-cleavage reaction occurs with acetate as the incoming ligand in which case we might write $k_1 = kK_a$, where K_a is the acid dissociation constant for acetic acid and k the rate constant for this path. Since k for a 1— reactant is expected to be of the order of magnitude of 10^{-4} l^2 mol^{-2} s^{-1} and K_a is small [pK_a 4·5 at 25 °C, $I = 0{\cdot}5$M ($LiClO_4$) [12]], it is unlikely that this path will contribute for the range of $[H^+]$ investigated (0·1—2·0M). Also for a run at 40 °C, with 2M-sodium acetate, 1M-acetic acid, and $1{\cdot}7 \times 10^{-4}$M-complex, no reaction was observed over 1 h.

The hydrogen-ion dependence for the reverse reaction, equation (2), has the same form as observed previously for the μ-amido-μ-sulphato-complex, and from similar investigations with the analogous μ-amido-μ-selenato- and μ-amido-μ-dihydrogenphosphato-complexes,[13] such a dependence appears to have general applicability. This and other features of these reactions we shall discuss more fully in a subsequent paper. The value $K = 53$ l mol^{-1} at 50 °C, $I = 2{\cdot}0$M ($LiClO_4$), is obtained for the equilibrium (3) from an extrapolated k_2 value of $5{\cdot}0 \times 10^{-5}$ l^2 mol^{-2} s^{-1} at 50 °C and the experimentally determined b value of $9{\cdot}4 \times 10^{-7}$ l mol^{-1} s^{-1}. An extrapolated value of k_1 at 50 °C is not considered to be of sufficient precision to enable K to be calculated from the quantity k_1/a.

$$\mu(NH_2,OH) + CH_3CO_2H \overset{K}{\rightleftharpoons} \mu(NH_2,CH_3CO_2) + H_2O \qquad (3)$$

We have also investigated the possibility that the procedure described here for the preparation of the μ-amido-μ-acetato- and μ-amido-μ-formato-complexes might be extended to other carboxylate ligands. Evidence has been obtained that formation of μ-amido-μ-malonato- and μ-amido-μ-maleato-complexes does indeed occur using this procedure. Providing the solubility of the carboxylic acid is sufficiently high in aqueous solution, no real difficulties are apparent; benzoic and fumaric acids were too insoluble for us to prepare, at first attempt, the μ-amido-μ-benzoato- and μ-amido-μ-fumarato-complexes.

EXPERIMENTAL

Samples of μ-amido-μ-chloro-bis[tetra-amminecobalt(III)] chloride $[(NH_3)_4Co{\cdot}\mu(NH_2,Cl){\cdot}Co(NH_3)_4]Cl_4,4{\cdot}5H_2O$ were prepared as described elsewhere.[8,14] Cleavage of the chloride bridge in aqueous solution occurs rapidly [2] and Scheme 1 is applicable.

Preparations.— *μ-Amido-μ-acetato-bis[tetra-amminecobalt*(III)] *chloride.* The μ-amido-μ-chloro-complex (1·0 g) was dissolved in 50% acetic acid (35 ml) at 50 °C and kept at this temperature for 50 min. The solution was then evaporated to dryness at 30—40 °C under reduced pressure using a rotary evaporator. The resulting solid was dissolved in a minimum amount of 4M-hydrochloric acid at 40 °C, cooled to room temperature, and left overnight at *ca.* 5 °C. The product was collected, washed with ethanol and ether, and dried by suction. To convert any remaining chloro-complex into the μ-amido-μ-acetato-complex, the solid was dissolved in a minimum amount of 50% acetic acid (*ca.* 2 ml) at 50 °C and kept at this temperature for 30 min. Dark red crystals were obtained after cooling overnight at 5 °C. These were dried by suction, washed with ethanol and ether, and then dried again. After wash-

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[10] M. B. Stevenson, A. G. Sykes, and R. S. Taylor, *J. Chem. Soc.* (*A*), 1970, 3214.

[11] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1991.

[12] See for example, M. Deneux, R. Meilleur, and R. L. Benoit, *Canad. J. Chem.*, 1968, **46**, 1383.

[13] S. W. Foong, Ph.D. Thesis, University of Leeds, 1971.

[14] M. B. Stevenson and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 2979.

ing the final product (0·35 g) was a lighter red *powder* {Found: C, 4·95; H, 6·75; N, 24·6; Cl, 28·1. Calc. for $[(NH_3)_4Co{\cdot}\mu(NH_2,CH_3CO_2){\cdot}Co(NH_3)_4]Cl_4,2H_2O$: C, 4·75; H, 6·50; N, 24·85; Cl, 28·0%. Loss in weight on dehydration over P_2O_5 for two weeks: 6·5 and 8·5 (two determinations). Calc. for $2H_2O$: 7·1%}. The anhydrous material is hygroscopic.

μ-Amido-μ-acetato-bis[*tetra-amminecobalt*(III)] *perchlorate*. A sample of the pure chloride salt (see above) was converted into the perchlorate salt as follows. The chloride (0·35 g) was first dissolved in a minimum of 0·1M-$HClO_4$ (*ca.* 1 ml). A slight excess of crystalline silver perchlorate was then added to the solution at 40 °C and the resulting silver chloride was filtered off. An equal volume of 72% $HClO_4$ was added to the filtrate which was then cooled overnight at 5 °C. The *crystals* obtained were collected, dried by suction (as well as possible), washed with ethanol and ether, and finally dried again; yield 0·1 g. A second crop of crystals was obtained after allowing the filtrate to evaporate in the atmosphere. These were treated in the same way as the first crop; total yield 0·25 g. The loss in weight after dehydration over P_2O_5 was 2·54 (Calc. for $1H_2O$: 2·42%). The formula $[(NH_3)_4Co{\cdot}\mu(NH_2,CH_3CO_2){\cdot}Co(NH_3)_4](ClO_4)_4,H_2O$ is also required to give an absorption coefficient at 517 nm in agreement with that for the chloride salt.

μ-Amido-μ-formato-bis[*tetra-amminecobalt*(III)] *chloride*. A sample of μ-amido-μ-chloro-bis[tetra-amminecobalt(III)] chloride (1 g) was dissolved in 50% formic acid (20 ml) previously heated to 50 °C. This temperature was maintained for 35 min after which the solution was evaporated to dryness under reduced pressure at 30—40 °C and a crude sample (*ca.* 1 g) of the μ-amido-μ-formato-complex (chloride salt) obtained. To prepare a pure sample, the crude material (1·0 g) was dissolved in a minimum of 4M-HCl (*ca.* 25 ml) at 50 °C and the hot solution was filtered. The solution was kept at 50 °C for only 2—3 min otherwise there is significant conversion of the complex into the aquochloro-form with loss of the formate ligand. The filtrate was kept at 0 °C for 5 h after which the first batch of crystals was collected. Subsequent batches contained the μ-amido-μ-chloro-complex as impurity. The pure *crystals* were collected, washed with ethanol and ether, and dried by suction (yield 0·5 g) {Found: C, 2·25; H, 6·65; N, 23·8; Cl, 27·2. Calc. for $[(NH_3)_4Co{\cdot}\mu(NH_2,HCO_2){\cdot}Co(NH_3)_4]Cl_4,4H_2O$: C, 2·25; H, 6·60; N, 23·8; Cl, 26·8. The loss in weight after leaving in a desiccator over P_2O_5 for 2 weeks was 14·0. Calc. for $4H_2O$: 13·6%}.

μ-Amido-μ-formato-bis[*tetra-amminecobalt*(III)] *perchlorate*. The crude salt of the μ-amido-μ-formato-complex (1 g) was dissolved in a minimum of 0·1M-$HClO_4$ (*ca.* 4 ml) at 40 °C and a slight excess of solid silver perchlorate was added. The resulting silver chloride which formed was filtered off. To the filtrate half the volume of 72% $HClO_4$ was added and the solution cooled overnight at 5 °C. The *crystals* obtained were collected, washed with ethanol, then ether, and dried by suction. The sample was recrystallized by dissolution in a minimum amount of 0·1M-$HClO_4$ at 40 °C and by addition of half the volume of 72% $HClO_4$ (yield 0·5 g). Dehydration over P_2O_5 gave 2·3% loss in weight. That calculated for the loss of H_2O from $[(NH_3)_4Co{\cdot}\mu(NH_2,HCO_2){\cdot}Co(NH_3)_4](ClO_4)_4,H_2O$ is 2·46%. Absorption coefficients compared with those obtained for the chloride salt were also consistent with this formula.

Alternative procedure. The kinetic studies referred to above indicated that nitrate has a strong catalytic effect on the conversion of the μ-amido-μ-hydroxo- into the μ-amido-μ-acetato-complex. Attempts to improve yields of the μ-amido-μ-acetato-complex, by dissolving the chloride salt of the μ-amido-μ-chloro-complex (1·0 g) in 50% acetic acid (43 ml) at 50 °C and adding conc. HNO_3 (6 ml) (temperature maintained for 30 min), did not on addition of bromide ions give a product of satisfactory purity.

The preparation of μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] perchlorate for kinetic studies was as described elsewhere.[5] Absorbance changes in kinetic runs were monitored on Unicam SP 500 and 800 spectrophotometers complete with thermostatted cell housings. Lithium perchlorate was prepared from lithium carbonate and perchloric acid, and was recrystallized until free from anion impurities. The acetic acid used was Fisons AnalaR Grade (*ca.* 17·4M).

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