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Exchange of Oxygen between Carboxylatoamminecobalt(III) Complexes and Water

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Half of the oxygen in $Co(en)_2C_2O_4^+$ exchanges at a rate which is first order in $[H^+]$. The half-life at 1 M H^+ and 25° is 3.0×10^4 sec. The half-life for exchange of the remaining oxygen is at least 500 times as long. In the oxygen exchange between oxalatopentaamminecobalt(III) and the solvent water at high $[H^+]$, three distinct kinds of oxygen can be observed, present in the ratio 1:2:1. The most labile of the oxygens is identified with the carbonyl adjacent to Co(III), and the least, with the oxygen attached to Co(III). At low acid the exchange rate decreases and a single exchange half-life is observed. Internal rearrangement is more rapid under these conditions than external exchange; analysis of the data suggests that the adjacent carbonyl oxygen carries the exchange for all the positions. The results, particularly at high acid, are difficult to reproduce, as they are for the formato and trifluoroacetato systems. For the latter two also, the exchange pattern varies with conditions, under some conditions two exchange half-lives being observed and under others only one. The exchange results are considered in relation to those on aquation, and the conclusion is reached that, with the exception of the trifluoroacetato and oxalato complexes aquating under the influence of acid, all the other aquation reactions proceed by Co–O bond rupture.

Introduction

A number of reports have appeared[1–4] recently dealing with oxygen exchange between coordinated oxalate and solvent water. We have accumulated some observations on the same process for carboxylate complexes of the cobalt–ammine series which we have, thus far, withheld from detailed publication[5] because of an element of irreproducibility in the results which we were unable to eliminate. We are prompted to present our results now because of the current interest in this subject as evidenced by the recent publications and because we feel that despite the irreproducibility referred to, useful and significant conclusions can be drawn from our observations. Moreover, the irreproducibility, which points to a curious catalysis of linkage isomerization, is itself a matter of interest. Bringing our results to public attention may motivate other work and lead to the discovery of the cause of the catalysis.

Experimental Section

The preparations of binoxalatopentaamminecobalt(III) perchlorate,[6] oxalatobis(ethylenediamine)cobalt(III) chloride,[7] and trifluoroacetatopentaamminecobalt(III) perchlorate[8] have been described elsewhere. The formato and acetato complexes were prepared by a procedure similar to that adopted for the trifluoroacetato. The analytical results are shown in Table I.

Stock Reagents.—The stock solution of sodium perchlorate was made up dissolving Fisher purified analytical reagent grade solid in distilled water. The concentration was determined by evaporating an aliquot to dryness, cooling in a desiccator, and weighing the residue.

Solutions containing $TlCl_6^{3-}$ were prepared by dissolving 25 g of purified Tl_2O_3 (Fisher) in 100 ml of concentrated HCl. A small amount of $KClO_3$ was added to ensure that thallium was fully oxidized.

Water used as solvent was redistilled from alkaline permanganate solution, taking precautions against entrainment of solids. Water enriched in ^{18}O (1.6 atom %) was obtained from Bio-Rad Laboratories, Richmond, Calif.

o-Phenylenediamine dihydrochloride, reagent grade, was purified by the method suggested in ref 9.

Isotopic Exchange between Complexes and Solvent.—The solutions were prepared by dissolving complex compounds of normal isotopic composition in water enriched in ^{18}O. The flasks containing the exchanging solution were covered with foil to exclude light and were immersed in a thermostated bath at 25 ± 0.05°. Samples were withdrawn at intervals, and the complex was separated by precipitation and eventually was treated so as to convert contained oxygen to CO_2, which was then analyzed for ^{18}O content. The methods of precipitation and subsequent handling differed from complex to complex and are described separately for each.

The isotopic composition at infinite time was taken to equal that of the solvent. In the plots, F represents the fraction of the oxygen in the complex which has reached isotopic equilibrium with the solvent.

$Co(en)_2C_2O_4^+$.—The precipitation was done by pouring 5 ml of the solution over 2 g of solid NaI. The crystals of $[Co(en)_2C_2O_4]I$ were washed twice with absolute methanol, then dried at 40° for 12 hr, and pumped on in a vacuum desiccator for 12 hr. Isotopic analysis was done by the Anbar–Guttmann method.[10]

$Co(NH_3)_5C_2O_4H^{2+}$.—When the Anbar–Guttmann method was used for isotopic analysis, the complex was precipitated by adding 5 ml of solution to 0.5 ml of hexachlorothallic acid solution. The salt $[Co(NH_3)_5C_2O_4H]_3(TlCl_6)_2$ was collected and then treated as described for $[Co(en)_2C_2O_4]I$. The method gave reproducible results but of limited accuracy above 80% exchange.

In a number of cases, the isotopic analysis was based on the clean quantitative reaction $Ag_2C_2O_4 \rightarrow 2Ag + 2CO_2$, but use of the reaction depends on releasing oxalate from the complex with minimal isotopic exchange. Relying on earlier results on oxygen exchange in the hydrolysis of the oxalate complex, the conditions of low base concentration (<0.1 M) and high temperature (100°) were chosen.[7] The complex was precipitated as the perchlorate by pouring 10 ml of solution onto 6 g of $NaClO_4 \cdot H_2O$. It was collected and was dried by pumping in a vacuum desic-

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[1] C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4615 (1964).

[2] J. E. Teggins and R. M. Milburn, *Inorg. Chem.*, **4**, 793 (1965).

[3] L. Damrauer and R. M. Milburn, *J. Am. Chem. Soc.*, **90**, 3884 (1968).

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[5] Some of the conclusions appear in R. B. Jordan, C. Andrade, and H. Taube, Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964.

[6] C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966).

[7] C. Andrade and H. Taube, *J. Am. Chem. Soc.*, **86**, 1328 (1964).

[8] R. B. Jordan and H. Taube, *ibid.*, **88**, 4406 (1966).

[9] E. L. Martin, *Org. Syn.*, **19**, 70 (1939).

[10] M. Anbar and S. Guttmann, *Intern. J. Appl. Radiation Isotopes*, **5**, 233 (1959).

TABLE I

ANALYTICAL RESULTS

Compoud	Co		ClO_4^-		$C_2O_4^{2-}$		N	
	Theoret	Obsd	Theoret	Obsd	Theoret	Obsd	Theoret	Obsd
$[Co(NH_3)_5C_2O_4H][ClO_4]_2$[a]	...	...	46.04	45.90	20.37	20.33	16.21	16.20
$[Coen_2C_2O_4]Cl\cdot 3H_2O$[b]	16.49	16.52	...	...	...	...	...	...
$[Co(NH_3)_5O_2CH][ClO_4]_2$[c]	14.6	14.5	51.2	50.51	11.6[f]	11.7	...	...
$[Co(NH_3)_5O_2C_2F_3](ClO_4)_2$[d]	12.9	12.7	43.5	43.4	...	...	17.4	17.5
$[Co(NH_3)_5O_2C_2H_3](ClO_4)_2$[e]	14.6	14.5	49.4	49.0	...	...	...	...

[a] ε 74.0 at 507 nm (ε 74.1 in *g*). [b] ε 114 at 498 nm, 146 at 356 nm (ε 113 and 145, respectively, in *g*). [c] ε 69.4 at 500 nm, 55.8 at 350 nm. [d] ε 63.5 at 500 nm, 51.0 at 350 nm (ε 63.0 and 49.8 in *h*). [e] ε 77.1 at 500 nm, 60.3 at 350 nm. [f] Analysis for formate by MnO_4^- titration. [g] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29,** 311 (1956). [h] K. Kuroda and P. Gentile, *ibid.*, **38,** 2154 (1965).

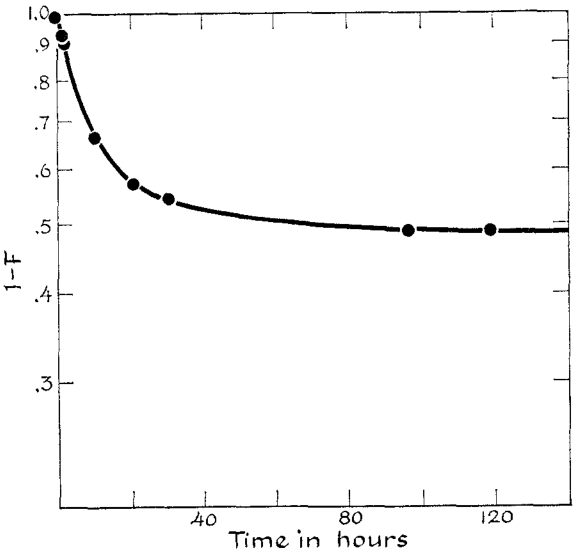

Figure 1.—Oxygen exchange between $(en)_2CoC_2O_4^+$ and H_2O, at 25°, [HCl] = 1.0 *M* and $[(en)_2CoC_2O_4^+]$ = 0.02 *M*. *F* is the fraction of oxygen in the complex which has equilibrated with the solvent.

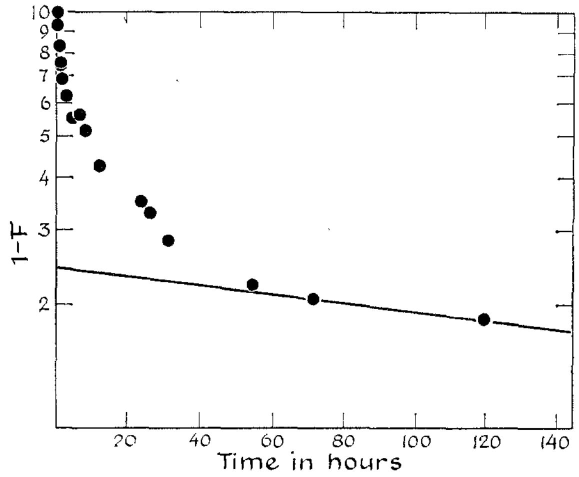

Figure 2.—Oxygen exchange between $(NH_3)_5CoC_2O_4^+$ and H_2O at 25°, [HCl] = 1.0 *M* and $[(NH_3)_5CoC_2O_4^+]$ = 0.03 *M*. *F* is defined in Figure 1.

cator for 24 hr. The solid was then added to 20 ml of 0.05 *M* NaOH heated at 100°. After allowing 5 min to elapse to complete the hydrolysis, the liquid was cooled to room temperature, and cobalt oxide was separated by filtration. The filtrate was neutralized with concentrated $HClO_4$, added slowly with stirring, then 1 drop excess was added, and the $Ag_2C_2O_4$ was precipitated by adding 0.5 g of $AgNO_3$. The handling and decomposition of $Ag_2C_2O_4$ are described elsewhere.[6]

$Co(NH_3)_5O_2CH^{2+}$.—The $TlCl_6^{3-}$ salt was precipitated and washed as described above. It was dried at 40–60° under high vacuum for 3–4 hr and was then heated to 110° for 4–5 hr to release CO_2 from the complexed formate. The CO_2 was collected by distillation from a Dry Ice–methanol bath into the sample tube which was cooled by liquid air. Further purification was found to be unnecessary.

$Co(NH_3)_5O_2C_2F_3^{2+}$.—The salt $[Co(NH_3)_5O_2C_2F_3]_3[TlCl_6]_2$, obtained by treating the reaction solution with one containing $TlCl_6^{3-}$, was heated with *o*-phenylenediamine dihydrochloride at 300° for 4 hr in a sealed tube to convert contained oxygen to H_2O.[11] The sample was cooled in a Dry Ice–methanol bath, and volatile impurities were removed by pumping. The sample was then warmed to room temperature, and water was distilled into a break-seal tube containing $HgCl_2$–$Hg(CN)_2$. The conversion of water to CO_2 took place at 400° (3–4 hr) and the CO_2 was purified by gas chromatography prior to isotopic analysis.

$Co(NH_3)_5O_2C_2H_3^{2+}$.—Initially, the $TlCl_6^{3-}$ salt was precipitated, and this was then treated by the Anbar–Guttmann method.[10] In the second, preferred method, the perchlorate salt was precipitated using solid $NaClO_4$. This salt was redissolved in 0.1 *M* $Ba[OH]_2$ at 90°. After 3 min the mixture was cooled in ice water, filtered to remove cobalt oxide and other solids, and neutralized with NH_4NO_3. An equal volume of 5 *M* $AgNO_3$ was added to the neutralized filtrate and the solution was cooled. The precipitate of $AgO_2C_2H_3$ proved to be too fine to collect by filtration so that 0.1 ml of 1 *M* NaCl was added, and the mixed precipitate was collected, washed with methanol, and vacuum dried. The solid was heated at 200° with pyridinium tribromide[12] in a sealed evacuated bulb. Samples were purified by gas chromatography and then analyzed spectrophotometrically.

It should be noted that since the solvent is in great excess, the exchange results are not affected by the partial aquation of the complex except insofar as the aquation products are incorporated into the complexes subjected to isotopic analysis. Incorporation of $Co(NH_3)_5H_2O^{3+}$ is a factor when the $TlCl_6^{3-}$ salts are precipitated, but nevertheless will hardly affect the results for the carbonyl oxygen which, as will appear, exchanges rather rapidly for the formato and binoxalato systems. Any influence of the aquation products is avoided by the use of $Ag_2C_2O_4$ or $AgO_2C_2H_3$ in the respective systems. This superior method of isotopic analysis for the oxalato system, as will be pointed out, did not circumvent the difficulties encountered in the exchange studies.

Results

Exchange of Oxygen between Oxalatobis(ethylenediamine)cobalt(III) and Solvent.—The exchange profile for a typical experiment with Co $(en)_2C_2O_4^+$ is shown in Figure 1. In this, as in the other experiments done with the chelate, it is clear that half of the contained oxygens exchange rapidly compared to the remaining half. The results on the rate of exchange for the more

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(11) H. Dohn, M. Moll, and R. Menasse, *Helv. Chim. Acta*, **42,** 1225 (1954).

(12) R. B. Jordan and A. L. Odell, *Anal. Chem.*, **39,** 681 (1967).

TABLE II

EXCHANGE OF THE LABILE OXYGEN IN $Co(en)_2C_2O_4^+$ WITH THE SOLVENT[a]

[HCl], *M*	10^5k_{ex}, sec^{-1}	$10^5k_{ex}/[H^+]$, M^{-1} sec^{-1}
0.40	0.92 ± 0.03	2.3
0.70	1.61 ± 0.05	2.3
1.00	2.30 ± 0.1	2.3

[a] Temperature 25°; μ = 1.0 (NaCl); [complex] = 0.02 or 0.03 *M*.

labile oxygens as a function of acidity are shown in Table II.

It follows from the data that the important term in the rate law for the exchange in the range of acid concentration covered shows the rate to be first order in $[H^+]$. An exchange specific rate for the chelate is defined by the rate law

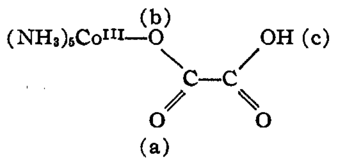
$$\frac{d[O]}{dt} = k_c[O][H^+] \qquad (1)$$

where the term on the left represents the total rate of the reaction carrying the exchange. When [O] is expressed in gram-atoms per liter, then $k_c = k_{ex}/[H^+] = 2.3 \times 10^{-5}\ M^{-1}\ sec^{-1}$ at 25°.

In one experiment, which was a continuation of the second of Table II, an attempt was made to measure the rate of exchange of the less labile oxygens. These exchange studies are complicated by the aquation reaction. The aquo product also responds to the method of isotopic analysis, and because the aquo ion is in isotopic equilibrium with the solvent, the measurements made represent upper limits on the rate of exchange of the less labile half of the oxygen. For the experiment in question, the upper limit for k_{ex} is $1.7 \times 10^{-8}\ sec^{-1}$.

Oxygen Exchange between Oxalatopentaamminecobalt(III) and Solvent.—Exchange profiles are shown in Figures 2–4, which illustrate the diversity of the exchange behavior and its variability. The data displayed in Figure 2 refer to a strongly acidic medium. Under these conditions the exchange behavior corresponds to the presence of more than one kind of exchanging oxygen. Figure 3, on the other hand, displaying data for less acidic solution, shows that all of the oxygens under these conditions are equivalent with respect to the exchange process. The conditions for the experiment which provided the results shown in Figure 4 were identical with those of the experiment of Figure 2, but the exchange pattern is clearly quite different.

At most, three kinetically different oxygens can be expected for the species



where (a) signifies the adjacent carbonyl, (b) the bridging oxygen, and (c) the terminal group, but fewer will be observed in the exchange process if internal exchanges are rapid compared to the external. The exchange curves can be decomposed into segments corresponding to the different half-lives. Where composite exchange behavior was observed, the decomposition was done by drawing straight lines to correspond to the different segments and using one straight line as the basis for deducing the half-life for the oxygen with the next shorter half-life. For the most part, the half-lives for successive oxygens differed by a factor of at least 10, and the method suffices to the accuracy justified by the data to define the several half-lives and also to fix the fraction of the total represented by each kinetically distinguishable component. The results obtained by analyzing the exchange data for the monodentate complex are summarized in Table III.

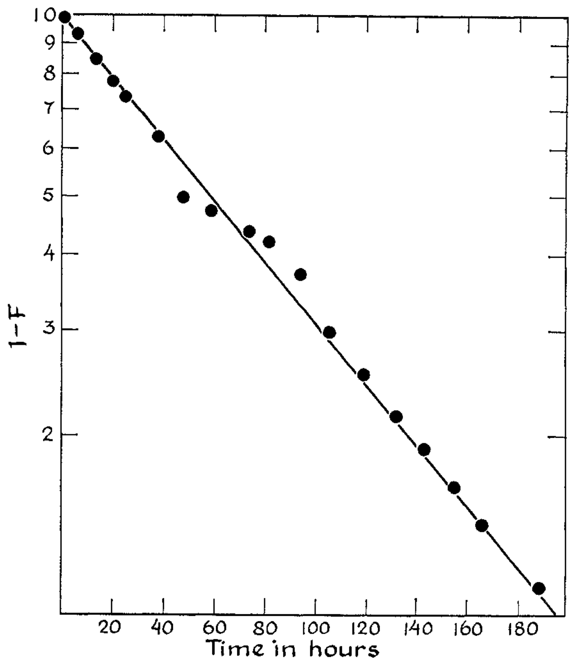


Figure 3.—Oxygen exchange between $(NH_3)_5CoC_2O_4^+$ and H_2O at 25°, [HCl] = 0.03 *M*, $[(NH_3)_5CoC_2O_4^+]$ = 0.03 *M*, and μ = 1.0 (NaCl). See Figure 1 for the definition of *F*.

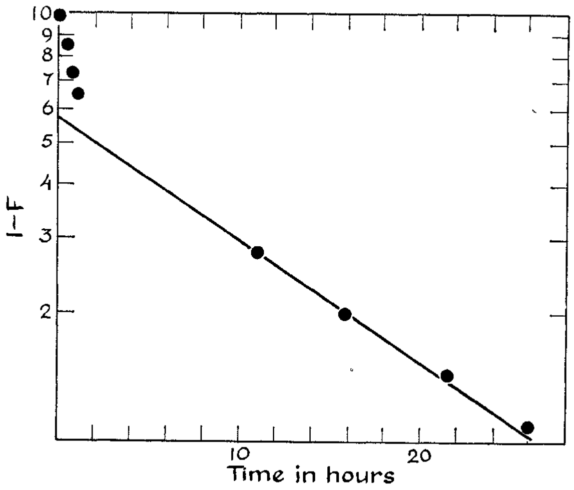


Figure 4.—Oxygen exchange between $(NH_3)_5CoC_2O_4^+$ and H_2O at 25°, [HCl] = 1.0 *M*, and $[(NH_3)_5CoC_2O_4^+]$ = 0.02 *M*. *F* is defined in Figure 1. Conditions are the same as in Figure 2, but the exchange profile is clearly different illustrating the irreproducibility of the exchange kinetics.

TABLE III[a]

OXYGEN EXCHANGE FOR $Co(NH_3)_5C_2O_4H^{2+}$ AS A FUNCTION OF ACIDITY

Expt	[Acid], *M*	$t_{1/2}$ (hr) for First	Second	Third	Remarks
1	2.0^b	0.19 (0.25)	7.8 (0.5)	>2 × 10^2 (0.25)	μ = 2.0
2	1.0^b	0.40 (0.25)	10 (0.5)	1.8 × 10^2 (0.25)	
3	1.0^b	...	...	1.9 × 10^2 (0.25)	Only last oxygen followed; $HClO_4$; [complex] = 3 × 10^{-3} *M*
4	1.0^c	0.40 (0.25)	8 (0.5)	>3 × 10^2 (0.25)	
5	1.0^c	0.41 (0.4)	9.5 (0.6)	...	
6	1.0^c	0.50 (0.4)	10 (0.6)	...	
7	$1.0^{b,d}$	... (0.45)	8.5 (0.55)	...	0.04 *M* $CoCl_2$ added
8	$1.0^{b,d}$	0.5 (0.45)	9.8 (0.55)	...	Complex recrystd 3 times; new HCl
9	$1.0^{b,d}$	0.56 (0.45)	10 (0.55)	...	Solvent redistilled
10	$1.0^{b,d}$	0.40 (0.4)	7.5 (0.60)	...	Solvent pretreated with Cl_2; Cl_2 present during reaction
11	$1.0^{b,d}$	0.55 (0.49)	12.4 (0.51)	..	HCl prepd from H_2SO_4 + NaCl
12	$1.0^{b,d}$	0.48 (0.41)	10.5 (0.59)	...	HCl prepd from $HClO_4$ + KCl; polyethylene reaction vessel
13	$1.0^{b,d}$	0.58 (0.45)	10.5 (0.55)	...	HCl as above. New prepn of complex
14	$1.0^{b,d}$	... (0.5)	15 (0.5)	...	HNO_3; triply distilled solvent; original complex
15	$1.0^{c,d}$	... (0.5)	14 (0.5)	...	New complex; solvent triply distilled
16	$1.0^{b,d}$	... (0.25)	7 (0.5)	125 (0.25)	New complex at 2.5 × 10^{-3} *M*; $HClO_4$
17	0.40^b	0.98 (0.25)	9.0 (0.50)	0.7 × 10^2 (0.25)	
18	0.40^b	1.0 (0.25)	10 (0.50)	1.1 × 10^2 (0.25)	
19	0.40^b	1.6 (0.25)	16 (0.50)	~1.3 × 10^2 (0.25)	μ = 0.7
20	0.30^c	1.8 (0.4)	22 (0.6)	...	...
21	0.10^b	6 (0.25)	47 (0.75)	...	...
22	0.10^b	5 (0.27)	44 (0.73)	...	...
23	0.10^b	4.7 (0.28)	48 (0.78)	...	[Complex] = 7.5 × 10^{-3} *M*; μ = 2.1
24	0.10^c	4 (0.25)	32 (0.75)	...	...
25	0.030^c	59 (1.00)	...	...	...
26	0.010^b	1.45 × 10^2 (1.00)	...	...	...

[a] Temperature 25.0°, HCl as acid, μ = 1.0–1.1, and complex at 0.03–0.04 *M*, but with exceptions to each of these conditions as noted under Remarks. NaCl was used to maintain ionic strength in chloride media; $NaClO_4$ in perchlorate media. The figures in parentheses following the half-lives represent the fractions of the total oxygen showing the particular exchange rate. [b] Anbar–Guttmann method of isotopic analysis. [c] $Ag_2C_2O_4$. [d] These experiments were done by R. B. J. (others by C. A.) in an effort to trace the source of the irreproducibility. This series was done after the others reported in the table.

Formatopentaamminecobalt(III).—In Figure 5 are shown exchange profiles for 0.05 *M* HCl and 0.05 *M* $HClO_4$. It is apparent from the graphs that under these conditions two kinetically distinct oxygens are observed, present in equal amounts. As in the case of the oxalatopentaammine complex, the exchange patterns change with conditions, but in contrast to the behavior noted there, in the present case the two oxygens become equivalent at higher acid concentration where a single half-life or exchange is observed. The results obtained in treating the data for the formato complex, by the method outlined for the monodentate oxalato, are summarized in Table IV.

TABLE IV

EXCHANGE BEHAVIOR OF $Co(NH_3)_5CO_2H^{2+}$

[Acid], *M*	1st oxygen[a]	2nd oxygen[a]
0.50 HCl	13 (1.0)	...
0.50 HCl	12 (1.0)	...
0.20 HCl	30 (1.0)	...
0.20 HCl	30 (1.0)	...
0.20 $HClO_4$	34 (1.0)	...
0.05 HCl	74 (0.5)	250 (0.5)
0.05 HCl	56 (0.5)	750 (0.5)
0.05 $HClO_4$	62 (0.5)	350 (0.5)

[a] The meanings of the entries correspond to those in Table III. μ = 0.60 (NaCl when HCl is used and $NaClO_4$ when $HClO_4$ is used); temperature 25.0°; fraction of total oxygen is given in parentheses.

Trifluoroacetatopentaamminecobalt(III).—Experiments were done at a single acidity (0.49 *M* HCl) and at ionic strength of 0.60 *M* (NaCl), and though the conditions were as much as possible kept constant, variability in exchange behavior was observed in this system also. The results are summarized in Table V.

TABLE V

OXYGEN EXCHANGE FOR THE TRIFLUOROACETATO COMPLEX IN 0.49 *M* HCl AND 0.60 *M* NaCl

Sample age, weeks	[Complex], *M*	$t_{1/2}$, hr 1st oxygen	2nd oxygen
1	0.013	45 (1.0)	...
1[a]	0.020	45 (1.0)	...
7	0.014	33 (0.5)	240 (0.5)
14	0.010	25 (0.5)	550 (0.5)
14[b]	0.010	25 (0.5)	550 (0.5)
51	0.025	48	~1500

[a] NH_4Cl rather than NaCl used to build up ionic strength. [b] In D_2O (99%).

Duplicates performed at the same time agree satisfactorily (compare expt 1 with 2 and 4 with 5) but experiments done as the age of the sample increases show a change with time in the sense that the discrimination between the two kinds of oxygen increases. It needs to be stressed, however, that the extinction coefficients and absorbance maxima of solutions made up after 1 year were identical with those made earlier.

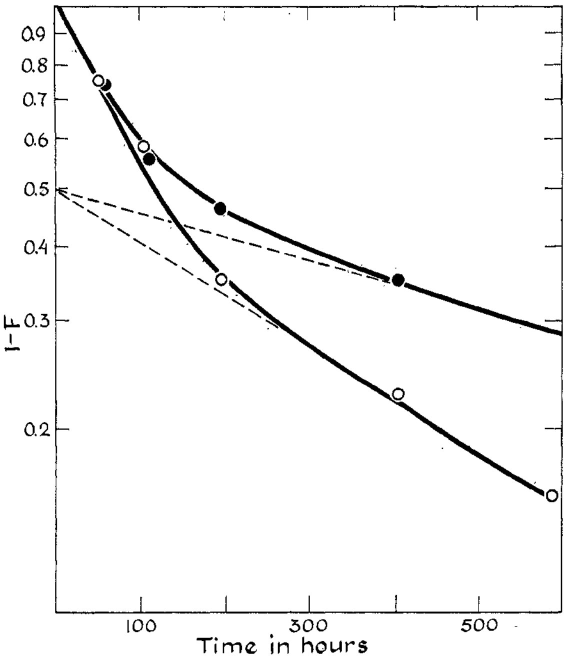


Figure 5.—Oxygen exchange between $(NH_3)_5CoO_2CH^{2+}$ and H_2O at 25°: ○, 0.05 M $HClO_4$, $\mu = 0.60$ ($NaClO_4$); ●, 0.05 M HCl, $\mu = 0.60$ (NaCl). F is defined in Figure 1.

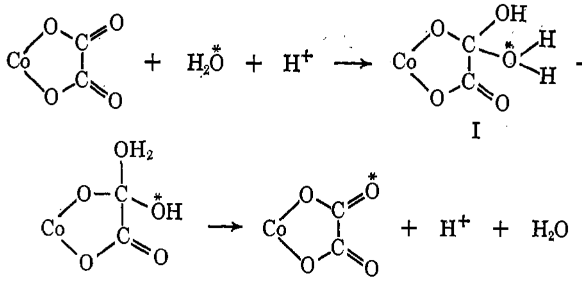
An attempt was made to measure the exchange of the bridging oxygen alone. This is feasible in principle because, in strong alkali and reduced temperature,[8] hydrolysis takes place with essentially only C–O bond cleavage. At intervals, the reaction was quenched by adding saturated $NaClO_4$(aq). The solid complex perchlorate was dissolved in water of normal isotope composition, cooled to ice temperature, and hydrolyzed in 1 M NaOH. The resulting hydroxy complex was converted to $[Co(NH_3)_5OH_2]Br_3$[13] and the isotopic composition was determined as described previously. The first sample was taken after *ca.* 80 hr; the results when plotted show straight-line behavior but extrapolate to somewhat more than 50% exchange for zero time. On the basis of all the other experiments, the carbonyl oxygen is expected to be largely exchanged by the time the first sample is taken. Thus, the results indicate that the two oxygens of the carboxyl group become interequilibrated in the precipitation process. The exchange half-time observed was *ca.* 170 hr; considering that the sample was used 10 months after preparation, the agreement with the entries in Table V is by no means satisfactory.

Acetatopentaamminecobalt(III).—Exchange of oxygen between the acetato complex and solvent is extremely slow. In an experiment at 25° with [HCl] = 0.50 M and $\mu = 0.60$, exchange had proceeded $\ll 2\%$ after 190 hr, and this would correspond to $k_{ex} \ll 3 \times 10^{-8}$ sec^{-1}. The first-order specific rate governing aquation[14] under the same conditions is $\sim 1.7 \times 10^{-6}$ sec.

Discussion

$Co(en)_2C_2O_4$.—The results for the chelated complex seem to be quite straightforward: two of the four oxygens exchange rather readily at a rate which is first order in [H^+], and the remaining two at a very much slower rate. The differentiation in rate is in contrast to the behavior observed for $C_2O_4^{2-}$ coordinated to Cr(III)[1] but resembles that described[8] for $Rh(C_2O_4)_3^{3-}$.

Two distinct mechanisms for the exchange of the more labile oxygen in $Co(en)_2C_2O_4^+$ may be considered, as given by the reactions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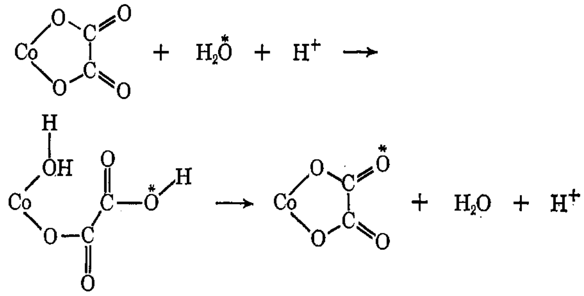
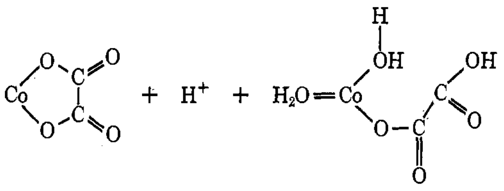

(3)

In reaction 3, C–O bond breaking must be assumed for the mechanism to be consistent with the result that only half of the oxygens exchange. It should be noted that because proton transfer is rapid, the two remote oxygens shown in eq 3 become equivalent.

The equilibrium constant for reaction 4 has been


(4)

estimated[6] as 0.1. If the rate for the reverse of (4) is assumed to be governed by the rate of exchange of water in the *cis*-aquo complex, the specific rate of ring opening is calculated to be 6×10^{-7} M^{-1} sec^{-1}. This is enough slower than the exchange (2.8×10^{-5}) to exclude the ring-opening mechanism, even making liberal allowance for error in estimating K for reaction 4 and in estimating the rate of water exchange in the cobalt complex (this was taken to be the same as in $Co(NH_3)_5H_2O^{3+}$).[15]

Short of a comparison of the kind which has been made in eliminating reaction 3 as a path for the exchange reaction it can, of course, be argued that once a configuration such as I in eq 2 is reached—this con-

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(13) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

(14) F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

(15) A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 825 (1952).

figuration is presumably reached also on the way to ring opening—there is no reason to invoke ring opening for exchange, because exchange can be achieved by a simple proton shift in the intermediate (I).

Pentaammines.—For the remaining systems studied, the overriding observation is that the rates of exchange are irreproducible and are puzzling in important respects. Some conclusions will be drawn, but in the interests of a fair evaluation of the data, before discussing the conclusions, it seems desirable to consider the irreproducibility.

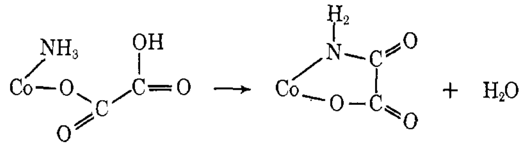
Experiments 1, 2, 4, 17, 18, and 19 of Table III show behavior which, though complex, is reasonable for oxalate as a ligand, namely, that there are three kinetically distinct oxygens in thd ratio of 1:2:1. Experiments 21–24 also show reasonable exchange behavior, namely, two kinetically distinct oxygens in the ratio 1:3. Finally, it is noted that the behavior observed in expt 25 and 26 is also reasonable: only one kind of exchangeable oxygen is featured at low acidity. These experiments were all done fairly early in the life of a particular preparation of the oxalato complex.

At a certain stage in the investigation, the exchange pattern changed; thus compare the results of expt 5 with those of expt 1 and 2. In expt 5, under conditions identical with those arranged for in expt 2, only two kinds of exchangeable oxygen are observed. In addition to the irreproducibility referred to, there is also the disturbing observation that in expt 5 and several others the two kinds of exchangeable oxygens are apportioned according to their exchange lability in the ratio of 2:3. Considering that four exchangeable oxygens are in question, a ratio such as this is, at first sight, not compatible with the concept of stoichiometry; however, it can arise if the oxygens are exchanging successively rather than independently.

Experiments 7–16 were done in an intensive but unrewarding effort to gain control of the exchange behavior for the binoxalato complex. The variations in conditions introduced were changes in solvent, in container, in the complex, in the identity of the acid, and also of the experimenter. The experiments included a test of the possibility that Co^{2+} is responsible for what must be regarded as anomalous behavior (*cf.* expt 7 and 8) and that free oxalate may be responsible (*cf.* expt 8 and 10). The experiment with Cl_2 present also covers the possibility that Fe^{2+} or other such reducing impurity is the cause of the anomaly.

Returning to the results at high acid concentration, we conclude that those which feature three distinct kinds of oxygens come closest to describing the intrinsic behavior of the system. This decision is made on the basis of the principle that an intrinsic reaction path cannot be eliminated, short of eliminating one of the components of the activated complex, but new paths can always be introduced. The change from the results of expt 2 to those of expt 5 can be understood in general terms if a catalyst for the internal exchange of the slowest oxygen of expt 2 with the more labile oxygens develops or is introduced. That a catalyst is developed in the system is suggested by the fact that on aging, the preparation began to show the anomalous behavior. Even if this proposition is accepted, further *ad hoc* assumptions must be made to account for the fact that a sample which in HCl(aq) exhibited exchange behavior that we regard as anomalous (*cf.* expt 13 and 15) showed normal behavior in $HClO_4$(aq) (*cf.* expt 16). Moreover, it must be admitted that even a new preparation can contain the catalyst (expt 13–15).

The possibility that the intrinsic nature of the complex changes with time was dealt with by spectrophotometric means. No differences were detected in solutions made up from a given solid, even after this had been stored for several months. Other properties such as the rates of aquation likewise are insensitive to storage time and in fact showed none of the anomalies recorded for the exchange behavior. A possible change is that of oxalate to oxamide



(5)

Application of the isotopic dilution method of analysis to a sample in the anomalous phase of the exchange behavior showed, however, that the complex had retained its full complement of four oxygens.

The data for the formato complex appear to be normal except for the fact that the slower of the two oxygens revealed at low acid shows variable rates. The variability in rate can be ascribed, as in the case of binoxalate, to catalysis of internal exchange. The exchange behavior for the formato does differ from that of the binoxalato complex in an important respect: the discrimination between the oxygens for the former decreases at high acid, whereas for the former it decreases at low acid.

In the studies with the trifluoroacetato complex, a single preparation was used, and with it a continuous progression in behavior as a function of time was observed, but in contrast to the behavior suggested for the binoxalato complex, the discrimination between the two oxygens for the trifluoroacetato complex increases as the time increases.

It has been shown by the X-ray diffraction studies[16] that the oxygens in acetatopentaamminecobalt(III) chloride perchlorate are nonequivalent. The present studies extend this conclusion also to three carboxylatopentaamminecobalt(III) complexes in solution. The fact that under certain conditions each of the complexes shows only a single half-life for oxygen exchange does not gainsay this conclusion. Nonequivalent atoms can appear to be equivalent with respect to exchange, but equivalent atoms cannot show disparate half-lives.

$Co(NH_3)_5C_2O_4H^{2+}$.—The 1:2:1 exchange pattern observed for the binoxalato complex at high acid identifies the terminal oxygen atoms as those having the intermediate half-life (9 hr). For these oxygens, the

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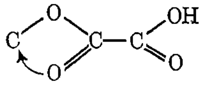
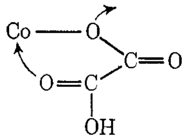
(16) E. B. Fleischer and R. Frost, *J. Am. Chem. Soc.*, **87**, 3998 (1965).

rate is independent of acid concentration. A half-life of 9 hr corresponds to a specific rate of 2.1 × 10^{-5} sec^{-1}, when the concentration of exchangeable oxygen is expressed in gram-atoms per liter. The corresponding specific rate for oxygen exchange in oxalic acid by the acid-independent path is 3.1 × 10^{-5} sec^{-1}.[17] The oxygens in the two cases are expected to be quite similar, and the agreement in the values of the rate constants supports the identification which has been made. It moreover suggests that an intrinsic rate of exchange was measured for the terminal oxygens. The exchange rate for oxalic acid can be expected to be somewhat higher because the extra proton opens up paths not available for the binoxalate complex.

The oxygen referred to in Table III as the "first" is seen by comparing the entries for expt 1, 2, 4, and 17–24 to exchange at a rate which is first order in $[H^+]$. Taking the mean of the results at 0.4 and 1.0 M H^+, k for this process is calculated as 4.5 × 10^{-4} M^{-1} sec^{-1}. The oxygen in question can reasonably be identified as the carbonyl oxygen adjacent to Co(III). At high acid, exchange of the carbonyl oxygen with H_2O is rapid compared to interequilibration of oxygens in the complex, but at low acid the reverse is true, and a single half-life is observed. It will be shown that at low acid the rates of oxygen exchange can be accounted for by assuming that the exchange is carried by the carbonyl oxygen, this oxygen then interchanging with the others by the "linkage isomerization" reactions indicated below.



(6)



(7)

To make the identification, account must be taken of the fact that at the low acidities a substantial fraction of the Co(III) exists as $Co(NH_3)_5C_2O_4^+$, while at 1.0 M H^+ $Co(NH_3)_5C_2O_4H^{2+}$ is by far the more abundant form. Using for K_{diss} the value[6] 8.8 × 10^{-3}, the fraction of the Co(III) present in 0.03 and 0.01 M external acid in the protonated form is 0.80 and 0.68, respectively, while the concentrations of H^+ are 3.60 × 10^{-2} and 1.95 × 10^{-2} M, respectively. (Note that total complex concentration in these experiments was 0.030 M.) Applying these values, allowing for the fact that exchange at the carbonyl position carries the exchange for all four oxygens and assuming that the exchange rate remains first order in $[H^+]$, the measured exchange half-lives at 0.03 and 0.01 M lead to calculated values for the specific rate of exchange at the carbonyl position of 4.5 × 10^{-4} and 4.0 × 10^{-4} M^{-1} sec^{-1}. These are in good agreement with the value of 4.5 × 10^{-4} M^{-1} sec^{-1} measured directly at high acidity.

The fact that simple exchange behavior is observed at lower acidity sets lower limits on the rate of the internal linkage isomerization reaction 7. Its half-life at 0.03 M must be substantially less than the half-life for exchange, namely, 59 hr. However, we can by no means be certain that intrinsic rates for these processes are being dealt with, and it is possible that the lower limit in rate referred to applies to the process as catalyzed by some unknown ingredient. This suspicion is reinforced by the fact, already referred to, that the disparity in exchange rate for the structurally different oxygens in the case of the formato complex decreases with increasing acidity while for the oxalato complex the reverse behavior is observed. Furthermore, the exchange half-life for the slowest oxygen in the oxalato system is observed to vary erratically, and it is likely that since this is the bridging oxygen, its exchange is governed by internal exchange with the carbonyl oxygen.

$Co(NH_3)_5O_2CH^{2+}$.—The average values for the first-order specific rates of exchange of the carbonyl oxygen in the formato complex are calculated as 3.1 × 10^{-5}, 1.25 × 10^{-5}, and 3.0 × 10^{-6} sec^{-1} at 0.50, 0.20, and 0.05 M H^+, respectively, on the assumption again that when only a single half-life is observed, the exchange is carried by the carbonyl oxygen. As in the case or the oxalato complex, the rate of exchange is first order in $[H^+]$. The second-order specific rates corresponding to the first-order rates given above are 6.2 × 10^{-5}, 6.3 × 10^{-5}, and 6.0 × 10^{-5} M^{-1} sec^{-1}, the mean value being 6.2 × 10^{-5} M^{-1} sec^{-1}.

$Co(NH_3)_5O_2CF_3^{2+}$.—The last experiment of Table V is so much at variance with the others that the possibility of an error in the composition of the solutions must be admitted. Excluding this result and assuming that also for the trifluoroacetate the rate of exchange of the carbonyl oxygen is first-order in $[H^+]$, the value of the specific rate as 1.5 × 10^{-5} M^{-1} sec^{-1} is calculated from the data.

General Comments

In Table VI rate data on related reactions of carboxylate complexes are summarized. Attention has already been directed[5] to the slowness of aquation of carboxylatocobaltammine complexes compared to the hydrolysis of the corresponding esters. If consideration is limited to the path involving C–O rather than Co–O bond rupture, the comparison can be understood in a qualitative way. Oxygen in $Co(NH_3)_5OH^{2+}$ is much more nucleophilic than in CH_3OH (the pK values of the conjugate acids are approximately 6 and −1, respectively) and the former is thus a much poorer leaving group than is the latter.

The data in Table VI do show that the carbon esters are not invariably more labile than cobalt esters. Thus, for ethyl acetate compared to acetatopentaamminecobalt(III) hydrolyzing or aquating by the k_0 path, these rates are 1.5 × 10^{-10} and 2.4 × 10^{-8} sec^{-1}, respectively. The greater rate for the latter can be ascribed to the intervention of a mechanism involving Co–O rather than C–O bond breaking. The observa-

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[17] R. M. Milburn and H. Taube, *J. Am. Chem. Soc.*, **81**, 3515 (1959).

TABLE VI

SUMMARY OF AQUATION, HYDROLYSIS, AND EXCHANGE DATA FOR CARBON AND COBALT–AMMINE ESTERS

Substance	Process	k_0[a]	k_h[a]	Ref
$H_2C_2O_4$	Exchange	3.1×10^{-5}	1.8×10^{-4}	*h*
$(CH_3)_2C_2O_4$	Hydrolysis	0.5×10^{-5} [b]	3.5×10^{-5} [b]	*i*
$(CH_3)_2C_2O_4$	Exchange	...	1.6×10^{-5}	*j*
$Co(NH_3)_5C_2O_4H^{2+}$	Aquation	2.4×10^{-8}	2.3×10^{-7}	*k*
$Co(NH_3)_5C_2O_4H^{2+}$	Exchange	2.1×10^{-5} [c]	4.5×10^{-4} [d]	*l*
$Co(en)_2C_2O_4^+$	Aquation–chelate ring opening	...	1×10^{-7}	*m*
$Co(en)_2C_2O_4^+$	Exchange (external O)	...	2.3×10^{-5}	*l*
$HO_2C_2H_3$	Exchange	$<1 \times 10^{-7}$	5.6×10^{-4}	*n*
$C_2H_5O_2C_2H_3$	Hydrolysis	1.5×10^{-10}	1.1×10^{-4}	*o*
$Co(NH_3)_5O_2C_2H_3^{2+}$	Aquation	2.4×10^{-8}	2.8×10^{-6}	*p*
$Co(NH_3)_5O_2C_2H_3^{2+}$	Exchange	$<3 \times 10^{-9}$	$<5 \times 10^{-9}$	*l*
$HO_2C_2F_3$	Exchange	7.7×10^{-4} [e]	1.4×10^{-3} [e]	*q*
$CH_3O_2C_2F_3$	Hydrolysis[f]	5.5×10^{-5}	4.7×10^{-4}	*r*
$Co(NH_3)_5O_2C_2F_3^{2+}$	Aquation	2.9×10^{-7}	1.5×10^{-6}	*s*
$Co(NH_3)_5O_2C_2F_3^{2+}$	Exchange	...	1.5×10^{-5}	*l*
CH_3O_2CH	Hydrolysis[g]	...	1.0×10^{-3}	*t*
$Co(NH_3)_5O_2CH^{2+}$	Exchange	...	6.2×10^{-5}	*l*

[a] The general rate law is: rate = $[\text{subs}](k_0 + k_h[H^+])$. For the chemical changes, [subs] represents the concentration of the species shown in the first column. For the exchange processes, the rate is expressed in gram-atoms of oxygen per liter per second and [subs] represents the concentration in gram-atoms per liter of exchangeable oxygen. [b] The specific rates reported have been divided by 2 to allow for the fact that a molecule of the ester contains two hydrolyzable groups. [c] Remote oxygen. [d] Adjacent carbonyl oxygen. [e] The specific rates reported in *o* have been multiplied by 55.5 to make them commensurate with others in the table. [f] In 60:40 water–dioxane (by volume) at 0°. According to the results of a single measurement of rate at 25°, a factor of *ca.* 6 can be introduced to yield values of rate at 25°. The change to water on solvent will increase the rates still further. [g] In 40:60 water–acetone (by volume). [h] See ref 2 and 17. [i] A. Skrabal, *Monatsh. Chem.*, **38,** 29 (1917). [j] C. Andrade, Ph.D. Thesis, University of Chicago, Chicago, Ill., 1964. [k] See ref 6. [l] This work. [m] See text. [n] D. R. Llewellyn and C. O'Connor, *J. Chem. Soc.*, 545 (1964). [o] A. Skrabal and M. Rückert, *Monatsh Chem.*, **50,** 369 (1928). [p] See ref 14. [q] D. R. Llewellyn and C. O'Connor, *J. Chem. Soc.*, 4400 (1964). [r] C. A. Bunton and T. Hardwick, *J. Chem. Soc.*, 3248 (1958). [s] See ref 14. [t] W. B. S. Newling and C. N. Hinshelwood, *J. Chem. Soc.*, 1357 (1936).

tions by Monacelli, *et al.*,[14] on the relative rates of aquation of carboxylato complexes of $Co(NH_3)_5^{3+}$, $Rh(NH_3)_5^{3+}$, and $Ir(NH_3)_5^{3+}$ bear on this issue. The range in rate of aquation for the acetato complexes exceeds 20 by the k_0 path. With the individuality of the metal ion being so strongly felt in the reaction rate, it seems likely that substitution takes place at the metal ion at least for the more labile systems. This behavior is to be contrasted to the rates of aquation by the k_h path for the trifluororacetato complexes where the range in rates is only a factor of 2 and where it therefore seems safe to conclude that C–O rupture takes place. For the acetato complexes aquating by the k_h path and for the trifluoroacetato complexes aquating by the k_0 path, the range in rates is 40 and 50, respectively. Even though the cobalt and rhodium complexes react at the same rate,[18] because the iridium complexes react much less rapidly, it is hard to escape the conclusion that the rates of aquation for the iridium complexes set upper limits on the rates of C–O bond cleavage. Thus we conclude that, in the aquation of the acetato- and trifluoracetatocobaltammine complexes, it is only for the latter reacting by the k_h path that C–O bond cleavage is involved. This conclusion is at variance with that reached by Monacelli, *et al.*,[14] who consider the C–O bond-breaking mechanism to be of much greater generality, but the conclusion is necessary to make some of our present results understandable.

In view of the similar inductive effects of the CF_3 and CO_2H groups, it seems likely that the binoxalatocobaltammine complex, when it aquates by the k_h path, does so by C–O bond rupture; by the k_h path Co–O bond rupture is again presumed to take over.

Assuming different mechanisms for the k_0 and k_h aquation reactions of the binoxalato and trifluoroacetato complexes helps explain why oxygen exchange by a path zero order in [H+] is not observed. The data in Table VI show that exchange by the k_h path for the binoxalato complex is much more rapid than aquation by the same path. It is reasonable to suppose that a similar relationship would obtain in considering the k_0 path for two processes, but only for that component of the aquation reaction which involves C–O bond rupture. However, as we have already concluded, aquation by Co–O bond rupture takes over for the k_0 path, and it is not surprising, therefore, that the exchange reaction, involving as it does C–O bond rupture, is too slow to be observable in comparison to the aquation rate.

The rapidity of exchange by the k_h path compared to aquation referred to in the previous paragraph, contrasting as it does with the behavior of carbon esters, merits further comment. It will be considered with reference to a mechanism in which a common intermediate for aquation and exchange is assumed. The fact that exchange and aquation proceed by activated complexes of the same composition does not, of course, constitute proof that a common intermediate is involved. Whether or not a common intermediate is

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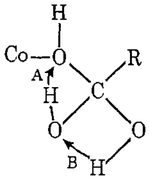
[18] Recent work (F. Monacelli and E. Viel, *Inorg. Chim. Acta*, **1,** 467 (1967)) has shown that the rate of water exchange in $Rh(NH_3)_5H_2O^{3+}$ is much the same as that observed[15] for $Co(NH_3)_5H_2O^{3+}$. Water exchange involves metal–oxygen bond cleavage, and thus the agreement of rates of aquation of the carboxylato complexes of $Co(NH_3)_5^{3+}$ and $Rh(NH_3)_5^{3+}$ cannot be used as evidence for C–O bond cleavage.

actually involved, such an intermediate is a useful high-energy reference state to which the stabilities of the two activated complexes for reaction can be compared. In the equilibrium distribution for the assumed high-energy intermediate composed of the cobalt complex, H_2O, and H^+ each of the oxygens presumably bears a proton



The entities CH_3^+ (or $C_2H_5^+$) and $Co(NH_3)_5^{3+}$ can both be regarded as Lewis acids, and it is interesting to compare their effects in promoting addition of water to the carbonyl double bond. It is likely that proton redistribution reactions (shown by the arrows A and B) in the intermediate are rapid compared to C–O bond rupture, and thus, except for a minor statistical factor, each time water is added to the carboxyl oxygen, exchange or aquation (hydrolysis) follows. On this basis, the sum of the exchange rate and aquation or hydrolysis rate will be taken as a measure of the rate of hydration of the carbonyl group. The vibrational frequencies of the carboxyl group as observed[19] in the infrared spectrum suggest that the contrast in bond order for the two C–O bonds in a carbon ester is much greater than in a cobalt ester, so that the π bond is much more completely localized in the carbonyl oxygen for the carbon ester. It is to be expected that addition to the double bond will take place the more readily the more completely the π bond is localized, and on this basis the sum of the exchange and aquation rates is expected to be greater for the carbon than for the cobalt ester. This relationship holds for the k_0 paths for $(CH_3)_2C_2O_4$ compared to $Co(NH_3)_5C_2O_4H^{2+}$, despite the fact that we are dealing with upper limits on the rates of aquation by C–O bond cleavage for the cobalt esters. (Most of the reaction, it has already been concluded, proceeds by Co–O bond rupture.) It also holds for the k_h paths for the trifluoroacetate and formate cases, but it does not hold for the k_h path when binoxalate is the ligand. The remarkably high value of k_h for carbonyl exchange for the latter system seems quite anomalous, particularly in comparison with the trifluoroacetate and formate systems. The unusual exchange lability of the adjacent carbonyl in the binoxalate case may be a consequence of participation in the activation by the proton on the remote carboxyl. This proton is in addition to that added from solution in making up the activated complex.

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[19] M. J. Schmelz, I. Nakagawa, S. Mizushimi, and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 287 (1959).

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Absorption and Circular Dichroism Spectra of Oxalatobis(aminoacidato)cobaltate(III) Complexes

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Oxalatobis(L-serinato)cobaltate(III) complex has been prepared and completely separated into the six configurationally optically active isomers by an ion-exchange chromatographic method and isolated as their potassium salts: they are Δ- and Λ-*trans*(N)-Co(ox)(L-ser)$_2^-$, Δ- and Λ-C_2-*cis*(N)-Co(ox)(L-ser)$_2^-$, and Δ- and Λ-C_1-*cis*(N)-Co(ox)(L-ser)$_2^-$. These isomers have been characterized by their absorption and circular dichroism spectra in the visible wavelength region being compared with the data of the corresponding three isomers of oxalatobis(glycinato)cobaltate(III) complex, of which the C_2-*cis*(N) and C_1-*cis*(N) isomers have been newly resolved. The additivity of configurational and vicinal contributions to the optical activity has been substantiated.

Introduction

Amino acid complexes of cobalt(III) have been recognized as interesting in relation to the electronic absorption and circular dichroism (CD) spectra and to the stereospecificity of the complexes.[1-11] In a previous paper dealing with the preparation of mixed amino acid complexes,[12] we characterized the three geometrical isomers (*trans*(N), C_2-*cis*(N), and C_1-*cis*-

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