

manganate and was collected in 6 *M* hydrochloric acid. The potassium pentachloroaurate(III) was prepared from this solution by the method of Charronat.¹⁰ The ethyl acetate used was Baker and Adamson Analyzed Reagent Grade. All other chemicals used were reagent grade.

(E) **Equipment.**—All spectra were recorded on a Cary Model

(10) R. Charronat, *Ann. Chim. (Paris)*, **16**, 52 (1931).

14 recording spectrophotometer. The freeze drying was done on a VirTis micro freeze dryer.

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Kinetics of Aquation of *cis*-Dibromobis(ethylenediamine)cobalt(III) Cation

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The kinetics of aquation of *cis*-[Co(en)₂Br₂]⁺ has been studied in 0.1 *F* HNO₃ at 15.0, 20.0, and 25.0°. The pseudo-first-order rate constant for the loss of one bromide at 25.0 ± 0.03° was found to be (10.4 ± 0.4) × 10⁻⁴ sec.⁻¹. The rate is independent of initial concentration of the complex over the range 2.0–8.0 *mF*, of pH from 1.0 to 3.0, and of ionic strength 0.014 to 0.304. Added sulfate ion accelerates the aquation. The Arrhenius activation energy is 23.8 ± 0.9 kcal./mole and Δ*S*^{*} is +5.0 ± 3 cal./deg.

In the present study, we have investigated the first-step aquation of *cis*-dibromobis(ethylenediamine)-cobalt(III) cation under various conditions of added electrolytes. A considerable amount of kinetic data has been reported for the aquation of *cis*- and *trans*-dihalobis(ethylenediamine)cobalt(III) cations of the type [Co(en)₂X₂]⁺ where X = F or Cl.² The only cobalt(III) dibromo analog whose aquation has been studied kinetically is *trans*-[Co(en)₂Br₂]⁺ ion.^{3,4} Therefore, this study completes the *cis*- and *trans*-dihalobis(ethylenediamine)cobalt(III) series and permits comparisons to be made within the series. It is also of interest to compare these results with those of the corresponding chromium(III) analogs insofar as data are available.

Experimental

***cis*-Dibromobis(ethylenediamine)cobalt(III) Bromide.**—Carbonatobis(ethylenediamine)cobalt(III) bromide was prepared according to the method of Pfeiffer.⁵ This compound was treated with alcoholic hydrogen bromide according to the method of Werner⁶ to produce *cis*-[Co(en)₂Br₂]Br·H₂O. Purification was effected by quickly dissolving 4 g. of the crude material in 1 l. of ice-cold H₂O and suction filtering the solution onto 110 g. of NaBr. The resulting precipitate was washed with three 20-ml. portions of cold H₂O, then with four bed volumes of absolute alcohol, and dried over H₂SO₄. *Anal.* Calcd. for *cis*-[Co(en)₂Br₂]Br·H₂O: C, 11.00; H, 4.15; Br, 54.87; N, 12.83; Co, 13.49. Found: C, 10.91; H, 4.08; Br, 54.70; N, 12.82; Co, 13.04. It was found that this monohydrate could be stored over H₂SO₄ up to 7 weeks without dehydration. The anhydrous salt was ob-

tained by heating the monohydrate at 125° for 12 hr. and then at 130° for an additional 3.5 hr. *Anal.* Calcd. for *cis*-[Co(en)₂Br₂]Br: C, 11.47; H, 3.85; Br, 57.23; N, 13.38; Co, 14.07. Found: C, 11.43; H, 4.07; Br, 57.30; N, 13.47; Co, 13.86.

***cis*-Dibromobis(ethylenediamine)cobalt(III) Nitrate.**—This compound was prepared according to the method of Werner⁶ by recrystallizing the crude bromide with NaNO₃ in place of NaBr in the salting-out step. *Anal.* Calcd. for *cis*-[Co(en)₂Br₂]NO₃: C, 11.98; H, 4.02; Br, 39.86; N, 17.47; Co, 14.70. Found: C, 12.12; H, 4.18; Br, 40.07; N, 17.18; Co, 14.20. All other reagents used in this study were commercially available materials of reagent grade and were used without further purification.

Analytical Methods.—Nitrogen was determined in this laboratory by Kjeldahl microanalysis. Bromide analyses were performed by dissolving the sample in excess 1 *F* NaOH and digesting on a steam bath for 30 min. The resulting solution was then allowed to cool, acidified with a twofold excess of 1 *F* HNO₃, diluted by a factor of ten, and titrated to a potentiometric end point with standard AgNO₃ in the presence of a nonionic detergent. The remaining elements were determined by microanalysis.⁷

Kinetic Measurements.—Titrimetric runs were begun by placing a sample of the complex sufficient to give the desired concentration in a glass-stoppered actinic glass flask. This flask and a separate container of reaction solvent were placed in a thermostatic bath whose temperature was controlled to ±0.03°. After the establishment of thermal equilibrium, 100 ml. of the solvent was withdrawn from the solvent container and discharged into the sample flask by means of a volumetric pipet. As soon as the pipet was drained the flask was removed from the bath, wiped dry (to prevent evaporative cooling), shaken vigorously for 30 sec., and returned to the bath. As soon as was convenient, an aliquot (ordinarily 10 ml.) was withdrawn and discharged into a quenching solution which consisted of an acidified acetone solution of a nonionic detergent at about -20° and titrated to a potentiometric end point with standard AgNO₃. The temperature at the end of the titration was -2 to -5°. Further ali-

(1) Taken from the M.S. thesis submitted by William F. Cain to the University of Detroit, 1965.

(2) For a review see D. R. Stranks in J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers Inc., New York, N. Y., 1960, p. 78.

(3) F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4883 (1956).

(4) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).

(5) P. Pfeiffer, S. Golther, and O. Angern, *Chem. Ber.*, **60**, 308 (1927).

(6) A. Werner, *Ann.*, **386**, 114 (1912).

(7) Microanalysis by Weiler and Strauss; Microanalytical Laboratory, Oxford, England.

quots were withdrawn, quenched, and titrated at intervals which corresponded to approximately one-fourth of a half-life.

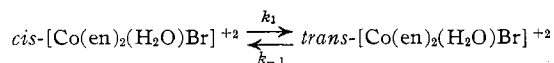
Spectrophotometric data were obtained *in situ* using a Beckman DU spectrophotometer equipped with matched 1-cm. quartz cells. The reaction temperature was maintained constant within $\pm 0.03^\circ$ with a thermostatically controlled temperature bath. Reactant solutions were made in the same manner described for the titrimetric runs; the cell was filled and the reaction followed by observing the decrease in the optical density at 605 $m\mu$. The solutions for runs which involved added electrolytes were prepared in the same way except that the desired concentration of additional salt in a thermostated solution of HNO_3 was added to the complex. Readings were taken at constant intervals over three half-lives and the final reading, D_∞ , was recorded at a time corresponding to six half-lives.

Light Sensitivity.—The cover of the cell compartment of the Beckman DU spectrophotometer was replaced with a transparent plastic cover. Runs were made with a 100-watt incandescent bulb supported 10 in. above the thermostated cell compartment. At 3-min. intervals the light was extinguished for 1.5 min. while readings were taken.

Results and Discussion

The pseudo-first-order rate constant for the aquation of *cis*- $[\text{Co}(\text{en})_2\text{Br}_2]^+$ has been determined by two independent methods. Potentiometric titration data were plotted as $\log C_0/C_t$ vs. t , where C_0 and C_t are the complex concentration at zero time and time t , respectively. Data in that form gave a straight line up to about 57% reaction. Spectrophotometric data were plotted as $\log (D_t - D_\infty)$ vs. t where D_t is the optical density at time t and D_∞ was recorded at a time corresponding to six half-lives. These plots were linear over 87% reaction. The initial slopes of the rate plots obtained by both experimental methods show a positive deviation from linearity, after the percentage reaction indicated above. This deviation is assumed to arise from interference by the slower second aquation reaction. Table II shows that data obtained from both of these methods are in excellent agreement. In most cases triplicate runs agreed within $\pm 2\%$, and in no case did the discrepancy exceed $\pm 4\%$. Attempts were made to observe the rate of aquation of the anhydrous bromide, but these were unsuccessful due to the low solubility of this compound in the reactant solvent ($< 10^{-3} M$). Since the solubility of the nitrate is considerably greater ($> 2.0 \times 10^{-3} M$), it represented a more suitable choice to compare aquation rates of the anhydrous and hydrated compounds.

Spectrophotometric studies of the aquation of *cis*- $[\text{Co}(\text{en})_2\text{Br}_2]^+$ are complicated by the isomerization of the bromoaquo product. Chan and Tobe⁴ made spectrophotometric studies of 0.01 *F* nitric acid solutions initially containing only *cis*- or *trans*- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Br}]^{+2}$ and observed that the reaction



occurs at a rate which is inversely proportional to the hydrogen ion concentration. At equilibrium the solution was found to contain 76% of the *cis* isomer and $(k_1 + k_{-1})$ at 25.0° is $2.13 \times 10^{-4} \text{ sec.}^{-1}$. Fortunately, the spectrum of a mixture of these bromoaquo isomers exhibits an isosbestic point at 605 $m\mu$.⁸ The spectrum

of *cis*- $[\text{Co}(\text{en})_2\text{Br}_2]^+$ is well-known.⁹ There is sufficient difference between the molar absorptivity indices of the reactant (~ 75) and the products (~ 32) at 605 $m\mu$ to allow the aquation reaction to be studied spectrophotometrically without interference from the subsequent isomerization reaction. The possibility that the reaction may proceed by isomerization of *cis*- $[\text{Co}(\text{en})_2\text{Br}_2]^+$ before aquation can be ruled out because the aquation rate of the *trans* isomer is known to be considerably slower than the observed rate for the *cis* isomer.^{3,4}

Arrhenius parameters for this study were calculated from a linear plot of $\log k$ vs. $1/T$ over the range 15.0–25.0°. The rate constants determined over this range are given in Table I. The activation energy calculated from these data is $23.8 \pm 0.9 \text{ kcal./mole}$ and the entropy of activation is $+5.0 \pm 3 \text{ cal./deg}$.

TABLE I

EFFECT OF TEMPERATURE ON THE RATE CONSTANT^a

Temp., °C.	$10^4 k$, sec. ⁻¹
15.0	2.6 ± 0.1
20.0	5.5 ± 0.2
25.0	10.5 ± 0.4

^a At pH 1.0 and initial complex concentration 4.0 *mF*.

Table II gives the rate of aquation at 25° as determined spectrophotometrically in nitric acid under various conditions of pH, complex concentration, and added electrolyte. It is apparent from Table II that the rate is independent of the initial complex concentration, pH, and ionic strength over the range at which these

TABLE II

RATES OF AQUATION OF *cis*- $[\text{Co}(\text{en})_2\text{Br}_2]^+$ UNDER VARIOUS CONDITIONS AT 25.0° IN HNO_3

Concn. of complex, <i>mF</i>	pH	Added electrolyte or other condition	μ	$10^4 k$, sec. ⁻¹
4	2	None	0.014	10.3
4	1	None	0.104	10.5 ^a
2	1	None	0.102	10.4 ^{a,b}
2	1	None	0.102	10.5
4	1	None	0.104	10.4
8	1	None	0.108	10.4
4	1	100-w. bulb 10 in. from reaction vessel	0.104	10.5
4	2	0.090 <i>M</i> NaNO_3	0.104	10.5
4	3	0.099 <i>M</i> NaNO_3	0.104	10.4
4	1	0.01 <i>M</i> NaNO_3	0.114	10.4
4	1	0.10 <i>M</i> NaNO_3	0.204	10.4
4	1	0.20 <i>M</i> NaNO_3	μ .304	10.5
4	1	0.0033 <i>M</i> Na_2SO_4	0.114	10.3
4	1	0.033 <i>M</i> Na_2SO_4	0.204	11.6
4	1	0.067 <i>M</i> Na_2SO_4	0.304	12.3
4	1	0.100 <i>M</i> Na_2SO_4	0.404	12.6

^a Rate followed by bromide release. ^b Complex as nitrate salt.

variables were investigated. The fact that the rate is independent of ionic strength was not unexpected, since this behavior is typical for the reaction between a uni-

(8) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4533 (1962).

(9) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **271**, 107 (1952).

valent cation and a neutral water molecule in dilute solutions.¹⁰ Solubility limitations precluded the extension of the study to higher ionic strengths in the case of added nitrate ion. It is clear that sulfate ion in concentrations 8-fold or greater than the initial complex concentration tends to accelerate the aquation reaction. This observation can be explained by assuming that the *cis*-dibromobis(ethylenediamine)cobalt(III) cation forms ion pairs with the sulfate anion which promotes removal of the coordinated bromide ion by an SN1 dissociation type mechanism. Light was routinely excluded in this study since the aquation rates of some cobalt complexes are accelerated by light.¹¹ However, the control experiment does not indicate that the reaction is affected by light from an incandescent lamp.

Tobe, *et al.*,^{4,12} have investigated the steric course of a large number of octahedral aquation reactions of the type $[\text{Co}(\text{en})_2\text{AX}]^{+n}$ where X represents the ligand being replaced and A is the orienting ligand. In every case it was found that the aquation of the *cis* complexes appears to be stereospecific and only the *cis* isomer of the product is obtained. On the other hand, *trans* complexes are aquated with steric change if the orienting ligand can exhibit an electropositive conjugative effect, *i.e.*, transfer electrons to the metal in the transition state. Since these conditions prevail in most reactions which have been studied, steric change is usually

observed in the aquation of *trans* complexes of Co(III). Quinn and Garner¹³ have reported similar results for *cis* isomers of Cr(III) complexes, but the relatively small number of *trans* isomers, which have been examined thus far, were found to give predominantly or wholly *trans* product. The configuration of the aquation product in the present study was not determined but no evidence was obtained to indicate that the stereospecific rule for *cis* complexes is violated here. Chan and Tobe⁴ also observed a 5- to 6-fold increase in the aquation rate when X is changed from Cl to Br. However, these authors noted that the *trans*-dibromo complex aquates about 4 times faster than the *trans*-dichloro complex at 25°. This latter observation is consistent with the results obtained in the present study. Moreover, these results are in accord with the observation² that in comparison with the *trans* isomers, the rates of aquation of the *cis* isomers of Co(III) complexes are often about an order of magnitude greater.

The aquation rate of *cis*- $[\text{Cr}(\text{en})_2\text{Br}_2]^+$ at 25° is about three times greater than the aquation rate of the Co(III) analog studied here. Crystal field theory predicts a lower activation energy for the Cr(III) d³ system compared to the Co(III) d⁶ system when solvent effects are ignored.¹⁴ However, Arrhenius activation parameters are not available for the Cr(III) complex and one is not justified in drawing further conclusions concerning the relative rates of these two complexes.

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(11) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956).

(12) C. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960).

(13) L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

(14) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 123.

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The Donor Properties of Pyrophosphate Derivatives. II. Complexes of Octamethylpyrophosphoramidate with Nontransition Metals¹

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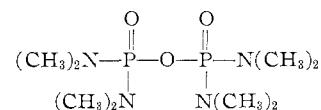
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New complexes of octamethylpyrophosphoramidate (OMPA) with alkali metal salts, alkaline earth salts, $\text{Al}(\text{ClO}_4)_3$, $\text{Pb}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, and SbCl_5 have been prepared. The following compounds have been synthesized: $\text{LiClO}_4 \cdot 2\text{OMPA}$, $\text{LiNO}_3 \cdot \text{OMPA} \cdot 3\text{H}_2\text{O}$, $\text{LiCl} \cdot \text{OMPA} \cdot 2\text{H}_2\text{O}$, $\text{NaClO}_4 \cdot \text{OMPA}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{OMPA}$, $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{OMPA} \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 2\text{OMPA} \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{ClO}_4)_2 \cdot 3\text{OMPA}$, $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{OMPA}$, $\text{CaCl}_2 \cdot \text{OMPA} \cdot 4\text{H}_2\text{O}$, $\text{Ba}(\text{ClO}_4)_2 \cdot 2\text{OMPA}$, $\text{Al}(\text{ClO}_4)_3 \cdot 3\text{OMPA}$, $\text{Cd}(\text{ClO}_4)_2 \cdot 3\text{OMPA}$, $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{OMPA}$, and $2\text{SbCl}_5 \cdot \text{OMPA}$. Elemental analyses, infrared spectra, conductivity measurements, and X-ray powder patterns were used to characterize the complexes.

Introduction

The first paper of this series⁴ reported the formation of coordination compounds of several transition metal

ions with the ligand octamethylpyrophosphoramidate (OMPA). The structure of OMPA is



The present work is concerned with OMPA complexes of nontransition elements, especially the alkali and

(1) Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) Partly abstracted from the M.A. thesis of C. J. Popp.

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(4) M. D. Joesten and K. M. Nykerk, *Inorg. Chem.*, **3**, 548 (1964).