sumption that the change in geometry is so large that $V_{\mathrm{Cu,Cu}}$ actually increases as an electron is removed from this axis is any difficulty encountered. Similar arguments can be made for the other possible arrangements which show that the observed effects would not be expected to arise from this source.

Thus the results seem to be consistent only with order B of the levels given above.

Experimental

The crystal used was a cylinder approximately 10 mm. in diameter and 20 mm. long oriented with respect to the unit cell so that the Cu–Cu axes of both sites were normal to the cylinder axis. Since the orientation of the crystal was not critical, it was simply oriented manually using the external faces of the crystal and a protractor. The diameter was chosen to give a slip fit in the probe insert.

The spectra were taken with a Varian DP-60 spectrometer operating at 4.3 Mc./sec. The probe was fitted with a Varian 4331-TWL dewar probe insert cooled with liquid nitrogen. The only modification of the instrument was the replacement of the receiver gain control with a continuously variable resistor to permit operation at as high a gain as possible consistent with a reasonable base line. The spectra were recorded at maximum transmitter power, the sweep frequency was 40 c.p.s., and the scan rate was approximately 25 gauss/min.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE PENNSYLVANIA STATE UNIVERSITY,
UNIVERSITY PARK, PENNSYLVANIA 16802

Stereospecific Reactions of Various *cis*- and *trans*-Bromobis(ethylenediamine)cobalt(III) Complexes with Chlorine[1a]

BY JOSEPH F. REMAR, DAVID E. PENNINGTON,
AND ALBERT HAIM[1b]

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It has been shown[2] that the reaction of $\mathrm{Co(NH_3)_5Br^{+2}}$ with $\mathrm{Cl_2}$ is rapid and results in the quantitative formation of $\mathrm{Co(NH_3)_5Cl^{+2}}$

$$\mathrm{Co(NH_3)_5Br^{+2} + {}^1/_2Cl_2 = Co(NH_3)_5Cl^{+2} + {}^1/_2Br_2}$$

In order to determine the stereochemistry of this type of reaction, the studies have been extended to complexes of the class *cis*- and *trans*-$\mathrm{Co(en)_2XBr^{+n}}$ (X = $\mathrm{NH_3}$, Cl, Br), and the results obtained are reported in the present paper.

Experimental

Preparation of Complexes.—*trans*-$\mathrm{[Co(en)_2Cl_2]Cl}$ was prepared according to the method of Bailar[3] and was used as the starting material for the preparation of the other complexes. The following compounds were prepared as described in the references cited: *cis*-$\mathrm{[Co(en)_2NH_3Br]Br_2}$,[4] *trans*-$\mathrm{[Co(en)_2NH_3Br]S_2O_6}$,[5] *cis*-$\mathrm{[Co(en)_2Br_2]Br}$,[6] *trans*-$\mathrm{[Co(en)_2Br_2]Br}$,[7] *trans*-$\mathrm{[Co(en)_2Br]ClO_4}$,[8] *cis*-$\mathrm{[Co(en)_2BrCl]Br}$,[9] and *trans*-$\mathrm{[Co(en)_2BrCl]ClO_4}$.[10] *cis*-$\mathrm{[Co(en)_2BrCl]ClO_4}$ was obtained by treating a concentrated solution of the bromide salt with concentrated perchloric acid.

The purity of the complexes was ascertained by comparing the absorption spectra measured in the present work with the spectra reported in the literature. Table I lists the wave lengths of the first absorption maximum and the corresponding molar absorbancy indexes for the complexes investigated.

TABLE I

SPECTRAL DATA FOR $\mathrm{Co(en)_2XBr^{+n}}$ COMPLEXES[a]

Complex	λ, mμ[b]	A[c]	Ref.
cis-$\mathrm{Co(en)_2NH_3Br^{+2}}$	540	81.3[d]	This work
	540	81	*e*
trans-$\mathrm{Co(en)_2NH_3Br^{+2}}$	545	51.6[f]	This work
	545	50	*g*
cis-$\mathrm{Co(en)_2Br_2^+}$	550	115[h,i]	This work
	552	110	*j*
trans-$\mathrm{Co(en)_2Br_2^+}$	655	51.6[h,k]	This work
	658	53.8	*j*
	648	45	*l*
	656	48.5	*m*
cis-$\mathrm{Co(en)_2BrCl^+}$	542	98.2[h,i]	This work
	550	100	*n*
	548	96.3	*m*
trans-$\mathrm{Co(en)_2BrCl^+}$	634	42.2[h,k]	This work
	640	41	*n*
	635	41.4	*m*

[a] Measurements at room temperature, unless otherwise indicated. [b] Wave length for first absorption maximum. [c] Molar absorbancy index at maximum. [d] Average of fourteen measurements. [e] R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956). [f] Average of four measurements. [g] M. L. Tobe, *ibid.*, 3776 (1959). [h] Measured at 13 ± 1°. [i] Single measurement. [j] M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **271**, 101 (1952). [k] Average of two measurements. [l] J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956). [m] Ref. 8. [n] Ref. 10.

Resolution of *cis*-$\mathrm{[Co(en)_2NH_3Br]Br_2}$ was achieved by precipitation as the D(+)-α-bromocamphor-π-sulfonate, as described by Werner.[11] Only the least soluble diastereoisomer, *d*-*cis*-$\mathrm{[Co(en)_2NH_3Br]}$D(+)-$\mathrm{C_{10}H_{14}O_4BrS)_2}$, was isolated. Four resolutions were carried out, but in no case was an optically pure material obtained. This was shown by a comparison of observed values of $[M]_D$ (for example +991, +940) with the value $[M]_D$ = +1058, calculated from the contributions of the cation[12] and anion.[13] However, since we were only interested in the question of retention or loss of optical activity upon reaction, the polarimetric studies were carried out with the partially resolved materials.

Hypochlorous acid solutions were prepared and standardized as described elsewhere.[2] All other chemicals were reagent grade.

Procedure.—Acidified (HCl or $\mathrm{HClO_4}$), standard solutions of the complexes were prepared, and their absorption spectra were recorded. The oxidant was then added, $\mathrm{Cl_2}$ as a gas and HOCl in solution. Visual observation indicated that, under the experimental conditions used, the reactions proceeded to completion within 1 min. However, in most instances the solutions were allowed to stand for 5 min. ($\mathrm{Cl_2}$ experiments) or 15 min. (HOCl experiments). For the experiments with $\mathrm{Cl_2}$, the excess oxidant was removed by a stream of nitrogen. For the experiments with HOCl, the excess oxidant was reduced with NaBr or NaCl, and the $\mathrm{Br_2}$ or $\mathrm{Cl_2}$ formed was removed by a stream of nitrogen.

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[1] (a) This work was supported in part by a grant from the National Science Foundation, GP-2001; (b) Fellow of the Alfred P. Sloan Foundation.

[2] A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 3108 (1963).

[3] *Inorg. Syn.*, **2**, 222 (1946).

[4] A. Werner, *Ann.*, **386**, 176 (1912).

[5] Ref. 4, p. 181.

[6] Ref. 4, p. 112.

[7] Ref. 4, p. 111.

[8] P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).

[9] Ref. 4, p. 118.

[10] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).

[11] A. Werner, *Ber.*, **44**, 1887 (1911).

[12] J. P. Mathieu, *Bull. soc. chim. France*, **3**, 476 (1936).

[13] M. B. Thomas and H. O. Jones, *J. Chem. Soc.*, **89**, 280 (1906).

Following this treatment, the resulting solutions were examined spectrophotometrically to determine the identity of the products.

The studies were carried out at room temperature (*ca.* 25°), except in the cases of *cis*- and *trans*-$Co(en)_2Br_2^+$ and *cis*- and *trans*-Co-$(en)_2BrCl^+$, where the rates of aquation of the starting materials and products are appreciable at 25°. In these cases, the treatment with the oxidant and the removal of the excess oxidant were carried out at 0°, and the spectra were recorded at 13 ± 1°.

Solutions of *d*-*cis*-$[Co(en)_2NH_3Br]Cl_2$ were obtained from the corresponding α-bromocamphor-π-sulfonate by an ion-exchange procedure whereby the organic anion was replaced by the Cl^- of a Dowex 1-X8 resin. Following the ion-exchange step, the solutions were treated as described above, with the exception that the optical activities of the reactant and product solutions were also measured. Blank experiments with ammonium D(+)-α-bromocamphor-π-sulfonate demonstrated that exchange of the organic ion for Cl^- in the resin was complete.[14]

Measurements.—Absorption spectra were obtained using a Cary Model 14 or 15 recording spectrophotometer. Optical rotations at the sodium D line were obtained using a Rudolph 200 photoelectric polarimeter.

Results and Discussion

The results of the spectrophotometric studies designed to determine the steric course of the reactions of *cis*- and *trans*-$Co(en)_2XBr^{+n}$ with Cl_2 are summarized in Table II. The reasonably good agreement between the values listed in columns 4 and 5 (wave lengths for absorption maxima and corresponding molar absorbancy indexes of the products observed) and columns 6 and 7 (corresponding values of the products expected for reactions proceeding with retention of geometry) demonstrates that for each bromo complex investigated, the reaction with Cl_2 (in the presence of Cl^-) produces the corresponding chloro complex with retention of geometry. For *cis*- or *trans*-$Co(en)_2Br_2^+$, the formation of *cis*- or *trans*-$Co(en)_2Cl_2^+$, respectively, can be interpreted on the basis of the following two successive reactions: *cis*- or *trans*-$Co(en)_2Br_2^+$ → *cis*- or *trans*-Co-$(en)_2BrCl^+$ → *cis*- or *trans*-$Co(en)_2Cl_2^+$. If this interpretation is correct, the observed retention of geometry for the reactions of *cis*- and *trans*-$Co(en)_2Br_2$ and of *cis*- and *trans*-$Co(en)_2BrCl^+$ implies that retention of geometry also occurs in the first step of the postulated sequence.

Studies with *cis*- and *trans*-$Co(en)_2NH_3Br^{+2}$ were also carried out in the absence of Cl^-, and under these conditions mixtures of $Co(en)_2NH_3Cl^{+2}$ and $Co(en)_2$-$NH_3OH_2^{+2}$ are obtained (*cf.* second and fourth entries of Table II). It is reasonable to assign the formation of $Co(en)_2NH_3OH_2^{+3}$ to the reaction of $Co(en)_2NH_3Br^{+2}$ with HOCl generated by the hydrolysis of Cl_2. The ratio of $Co(en)_2NH_3Cl^{+2}$ to $Co(en)_2NH_3OH_2^{+3}$ will depend, according to the present interpretation, upon the relative rates of reaction of Cl_2 and HOCl with $Co(en)_2$-NH_3Br^{+2} and upon the concentrations of H^+ and Cl^-. Apparently, at 0.12 *M* HCl the hydrolysis of Cl_2 is sufficiently suppressed and $Co(en)_2NH_3Cl^{+2}$ is the principal product, whereas at 0.24 *M* $HClO_4$ for the *cis* complex and at 0.96 *M* $HClO_4$ for the *trans* complex chlorine hydrolysis is sufficiently important and the aquo products can be readily detected.[15] Independent support for this interpretation was obtained from a study of the reactions of *cis*- and *trans*-$Co(en)_2NH_3Br^{+2}$ with HOCl. As shown by the last two entries of Table II, these reactions yield more than 80% of the corre-

TABLE II

SPECTROPHOTOMETRIC DATA FOR THE REACTIONS OF *cis*- AND *trans*-$Co(en)_2XBr^{+n}$ WITH CHLORINE[a]

Complex	[Complex], $M \times 10^4$	$[H^+]$, M[b]	λ, mμ[c]	A[d]	λ, mμ[e]	A[f]	Product
cis-$Co(en)_3NH_3Br^{+2}$	7.27–9.82	0.12–0.96	525	74.6[g]	525	72[h]	*cis*-$Co(en)_2NH_3Cl^{+2}$
			360	78.5[g]	360	78[h]	
cis-$Co(en)_2NH_3Br^{+2}$	5.77–10.5	0.24[i]	505	67.1[j]	...	...	58% *cis*-$Co(en)_2NH_3Cl^{+2}$ [k]
			355	71.7[j]	...	...	42% *cis*-$Co(en)_2NH_3OH_2^{+2}$
trans-$Co(en)_2NH_3Br^{+2}$	10.7–11.1	0.12–0.24	525	48.9[l]	525	48[h]	*trans*-$Co(en)_2NH_3Cl^{+2}$
			360	55.7[l]	360	52[h]	
trans-$Co(en)_2NH_3Br^{+2}$	12.8	0.96[i]	502	44.6[m]	...	...	83% *trans*-$Co(en)_2NH_3C^{+2}$ [k]
			350	52.6[m]	...	...	17% *trans*-$Co(en)_2NH_3OH_2^{+3}$
cis-$Co(en)_2Br_2^+$	5.45	0.12	533	89.9[m,n]	536	89.3[o]	*cis*-$Co(en)_2Cl^{2+}$
trans-$Co(en)_2Br_2^+$	10.3–15.7	0.12–1.2	615	38[l,n]	620	40.8[o]	*trans*-$Co(en)_2Cl_2^+$
cis-$Co(en)_2BrCl^+$	7.52	1.2	532	91.6[m,n]	536	89.3[o]	*cis*-$Co(en)_2Cl_2^+$
trans-$Co(en)_2BrCl^+$	10.8	0.12–1.2	613	36[l,n]	620	40.8[o]	*trans*-$Co(en)_2Cl^{2+}$
cis-$Co(en)_2NH_3Br^{+2}$	9.36–18.5[p]	0.01–0.015[i]	485	65.1[q]	r	r	82% *cis*-$Co(en)_2NH_3OH_2^{+3}$ [k]
			351	65.0[q]	r	r	18% *cis*-$Co(en)_2NH_3Cl^{+2}$
trans-$Co(en)_2NH_3Br^{+2}$	17.8[p]	0.015[i]	480	46.9[m]	480	48[h]	*trans*-$Co(en)_2NH_3OH_2^{+3}$
			345	54.3[m]	340	54[h]	

[a] Room temperature unless otherwise indicated. [b] Hydrochloric acid unless otherwise indicated. [c] Observed wave lengths for absorption maxima of product solutions. [d] Observed molar absorbancy indexes at maxima of product solutions. [e] Wave length for absorption maxima of products listed in column 8, literature values. [f] Molar absorbancy indexes at maxima of products listed in column 8, literature values. [g] Average for six experiments. [h] Ref. *e* of Table I. [i] Perchloric acid. [j] Average for three experiments. [k] Calculated using observed absorbancies at 550 and 450 mμ. [l] Average for two experiments. [m] Single experiment. [n] Spectrophotometric measurement at 13 ± 1°. [o] Ref. *j* of Table I. [p] Oxidant is HOCl. [q] Average for four experiments. [r] Values for *cis*-$Co(en)_2NH_3$-OH_2^{+3} are 480 (65) and 340 (60), ref. *e* of Table I.

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(14) It was also observed that 3–5% of the cobalt was retained in the anion-exchange resin. This loss of cobalt did not affect the quality of the results since the studies on retention or loss of optical activity were carried out on solutions *after* the ion-exchange step.

(15) This situation is in contrast with that reported for $Co(NH_3)_5Br^{+2}$, where even at 0.01 *M* $HClO_4$ the principal product of the reaction with Cl_2 is $Co(NH_3)_5Cl^{+2}$, but conforms to the results reported for $Cr(NH_3)_5Br^{+2}$.[2] Small differences in the reactivities of Cl_2 and HOCl toward a bromo complex can affect appreciably the relative yields of chloro and aquo complexes.

sponding aquo complexes.[16] In this context, it is necessary to note that the reaction of *cis*-$Co(en)_2NH_3Br^{+2}$ with HOCl does *not* proceed *via* formation of a *cis*-$Co(en)_2NH_3Cl^{+2}$ intermediate, which then reacts with HOCl to yield the observed aquo product. A solution of *cis*-$Co(en)_2NH_3Cl^{+2}$ treated with HOCl under the same conditions as *cis*-$Co(en)_2NH_3Br^{+2}$ showed no detectable change in light absorption over a period of 30 min.[17]

TABLE III

POLARIMETRIC DATA FOR THE REACTIONS OF *d-cis*-$Co(en)_2NH_3Br^{+2}$ WITH CHLORINE AND HYPOCHLOROUS ACID (ROOM TEMPERATURE)[a]

Oxidant	[M]D, reactant	[M]D, product	[M]D, calcd.[b]	% retention
Cl_2	+273[c]	+328[c]	+327	100
Cl_2	+412[d]	+487[d]	+495	98
Cl_2	+460[c]	+543[c]	+552	98
HOCl[e]	+438[f]	+377[f]	. . .	92[g]

[a] Hydrochloric acid (0.12 *M*) unless otherwise stated. [b] Calculated using the values [M]D = +500 for *d-cis*-$Co(en)_2NH_3Br^{+2}$ (ref. 12), [M]D = +600 for *d-cis*-$Co(en)_2NH_3Cl^{+2}$ (ref. 12) and J. G. Brushmiller, E. L. Amma, and B. E. Douglas, *J. Am. Chem. Soc.*, **84,** 3227 (1962), and [M]D = +432 for *d-cis*-$Co(en)_2NH_3OH_2^{+3}$ (ref. 18). [c] Single experiment; [Co(III)] = 1.11×10^{-3} *M*. [d] Average for two experiments; [Co(III)] = 8.14×10^{-4} *M* and 1.11×10^{-3} *M*. [e] Perchloric acid (0.015 *M*). [f] Average for three experiments; [Co(III)] varied from 1.11 to 1.78×10^{-3} *M*. [g] Calculated for the reaction which results in the formation of *cis*-$Co(en)_2NH_3OH_2^{+3}$; see text.

The polarimetric studies carried out with *d-cis*-$Co(en)_2NH_3Br^{+2}$ are summarized in Table III and provide the most conclusive evidence for the retention of both geometry and optical configuration in the reaction with Cl_2. Within experimental error the retention of optical activity is 100%, a result which provides further support for the rearrangement mechanism postulated to account for the quantitative formation of $Co(NH_3)_4Cl^{+2}$ by the reaction of $Co(NH_3)_5Br^{+2}$ with Cl_2.[2]

Polarimetric studies of the reaction between *d-cis*-$Co(en)_2NH_3Br^{+2}$ (bromide salt) and HOCl were also carried out. A comparison of columns 3 and 4 of Table III shows that retention of optical activity is a major feature of the reaction. However, the quantitative interpretation of the results is complicated because of the formation of mixtures of chloro and aquo products. If it is assumed that the chloro product is formed with retention of optical activity, it is possible to calculate from the observed value of [M]D (+377), the known product distribution (18% *cis*-$Co(en)_2NH_3Cl^{+2}$ and 82% *cis*-$Co(en)_3NH_3OH_2^{+3}$), and the value of [M]D for *d-cis*-$Co(en)_2NH_3OH_2^{+3}$ (+432)[18] that the reaction which results in the formation of *cis*-$Co(en)_2NH_3OH_2^{+3}$ proceeds with 92% retention of optical activity. In view of the complications in this system, and of the accumulation of experimental errors in the calculation, it is reasonable to conclude that this reaction also proceeds with complete retention of optical activity.

If the retention of geometry and optical configuration proves to be a general feature of reactions of the present type, it is possible that such reactions will be useful in syntheses and in the determination of geometries and optical configurations of related complexes.

Acknowledgment.—A. H. is indebted to Dr. A. M. Sargeson for helpful discussions regarding the optical activity of *cis*-$Co(en)_2NH_3OH_2^{+3}$ and for the measurement of the value of [M]D for this complex.

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(16) For *trans*-$Co(en)_2NH_3Br^{+2}$ the reaction with HOCl yields, apparently, only *trans*-$Co(en)_2NH_3OH_2^{+3}$. However, for the corresponding reaction of the *cis* complex some *cis*-$Co(en)_2NH_3Cl^{+2}$ is detected in addition to the principal product *cis*-$Co(en)_2NH_3OH_2^{+3}$. Part of the *cis*-$Co(en)_2NH_3Cl^{+2}$ may arise from the reaction of *cis*-$Co(en)_2NH_3Br^{+2}$ with the Cl_2 generated in the system by Br^- (inner and outer sphere) reduction of HOCl to Cl^-, followed by HOCl oxidation of Cl^-. Some attempts were made to investigate this point further, but the situation appears to be complicated. A solution of *cis*-$[Co(en)_2NH_3Br](ClO_4)_2$ was prepared from the corresponding Br^- salt by an ion-exchange technique, and aliquots were treated with a 5-fold excess of HOCl in the presence of 0.015 or 0.96 *M* $HClO_4$. The yields of *cis*-$Co(en)_2NH_3OH_2$ were 91 and 85%, respectively. Furthermore, visual observation indicated that the rate of the reaction increases markedly with increasing $[H^+]$.

(17) A similar observation was made previously. $Co(NH_3)_5Cl^{+2}$ does not react with HOCl within 10 min. at room temperature.[2]

(18) A. M. Sargeson, private communication.

CONTRIBUTION NO. 1770 FROM THE INSTITUTE FOR ATOMIC
RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

A Kinetic Study of the Reaction of Iodine and Iodochromium(III) Ion in Acidic Solution[1]

BY JAMES H. ESPENSON

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In the course of a previous kinetic study[2] of the formation of iodine in the reaction of iodate ion with iodide ion in an inert metal ion complex, $Cr(H_2O)_5I^{2+}$, the rate equation suggested that the oxidation reaction might proceed through a mechanism where iodine catalyzed the removal of iodide ion from the primary coordination sphere of chromium(III), followed by rapid oxidation of the liberated iodide ion. The present work constitutes a kinetic study of the reaction of iodine and iodopentaaquochromium(III) ion

$$Cr(H_2O)_5I^{2+} + I_2 + H_2O = Cr(H_2O)_6^{3+} + I_3^- \qquad (1)$$

and an examination of its role in the mechanism of oxidation of coordinated iodide ion.

Experimental

Reagents.—Iodochromium(III) ion was prepared by reaction of solutions of chromium(II) perchlorate and iodine and was isolated and purified by ion exchange on Dowex 50W-X8 cation-exchange resin as described by Swaddle and King.[3] During this procedure, water at 0° was circulated through the column jacket to prevent aquation of the complex

$$Cr(H_2O)_5I^{2+} + H_2O = Cr(H_2O)_6^{3+} + I^- \qquad (2)$$

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(1) This work was performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission.

(2) J. H. Espenson, *Inorg. Chem.*, **3**, 968 (1964).

(3) T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).