and also maxima in their molar susceptibilities as x is decreased below 2.5. These maxima may be symptomatic of the occurrence of electron trapping sites at oxygen defects. The greater the trapping energy, the more firmly bound the electron and the bigger its contribution to the paramagnetic susceptibility. The sketchy data that are available, particularly for the series VO_x, NbO_x, TaO_x and CrO_x, MoO_x, WO_x, suggest a decreasing maximum in the susceptibility *vs.* composition curves near 2.4 and 2.8, respectively. Otherwise, the susceptibilities can be interpreted at least qualitatively in terms of a partially-delocalized-electron model on either side of the maxima. It would be most useful to have additional magnetic data on other non-stoichiometric oxides and also electrical conductivity measurements over the range of composition.

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Kinetics and Products of Aquation of *cis*- and *trans*-Dichlorobis-(ethylenediamine)-chromium(III) Cations[1a,b]

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The products of the first-stage aquation of *trans*-$[Cr(en)_2Cl_2]^+$ in 0.10 *f* HNO_3 at 35.0° in the absence of light were found to be *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$, *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ and a dichloro complex tentatively identified as *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$ (*i.e.*, 1,6-dichloro-2,3-diaquo-ethylenediamine-chromium(III) cation). These previously unisolated or unreported chloroaquo complexes have been isolated in solution and their visible absorption spectra determined. Pseudo first-order rate constants for formation of these products are $(6.90 \pm 0.41) \times 10^{-5}$, $(1.12 \pm 0.40) \times 10^{-5}$ and $(0.78 \pm 0.05) \times 10^{-5}$ sec.$^{-1}$, respectively. The only detectable first-stage aquation product of *cis*-$[Cr(en)_2Cl_2]^+$ in 0.10 *f* HCl at 35.0° in the dark was *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$, formed directly with a pseudo first-order rate constant of $(1.11 \pm 0.02) \times 10^{-3}$ sec.$^{-1}$. Isomerization of *cis*-$[Cr(en)_2Cl_2]^+$ and of *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ to the *trans* isomers was not detected, conservative upper limits thus established for the *cis*-to-*trans* isomerization rate constants being 5×10^{-6} and 2×10^{-5} sec.$^{-1}$, respectively. The possibility of *trans*-to-*cis* isomerization of these two complexes could be neither confirmed nor ruled out, but $k \leqslant 1.12 \times 10^{-5}$ sec.$^{-1}$ for isomerization of *trans*-$[Cr(en)_2Cl_2]^+$ and $k < 1 \times 10^{-5}$ sec.$^{-1}$ for isomerization of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$.

This investigation began in a study of the kinetics of production of ionic chloride from *trans* - dichlorobis - (ethylenediamine) - chromium(III) cation in acidic aqueous solution,[2] as part of a program of comparing the reaction kinetics of analogous chromium(III) and cobalt(III) complexes. At first it was thought that a simple two-step process such as

$$trans\text{-}[Cr(en)_2Cl_2]^+ + H_2O \longrightarrow trans\text{-}[Cr(en)_2(OH_2)Cl]^{+2} + Cl^-$$

$$trans\text{-}[Cr(en)_2(OH_2)Cl]^{+2} + H_2O \longrightarrow trans\text{-}[Cr(en)_2(OH_2)_2]^{+3} + Cl^-$$

might account for the production of ionic chloride (*i.e.*, chloride ions displaced from the complex) during aquation, but the experimental kinetic data on the secondary aquation soon revealed that the actual process must be more complicated. Therefore we undertook to separate and identify the reaction products at various reaction times during the aquation of both *trans*- and *cis*-$[Cr(en)_2Cl_2]^+$. Combination of the chromatographic separation data with determinations of the total rate of loss of the reactant complex ion and the rate of production of ionic chloride, together with spectral observations, have enabled us to evaluate or place upper limits on nine rate constants for reactions occurring in the primary aquation of *trans*- and *cis*-$[Cr(en)_2Cl_2]^+$ and the rearrangements of these two cations and their first-stage aquation products. In favorable cases, this approach can provide a knowledge of the steric course of the aquation, needed for a full understanding of the reaction mechanism, and can lead to the discovery of reaction paths which are not revealed by studies of the rate of production of ionic chloride alone. Earlier kinetic studies[3,4] of the aquation of *trans*- and *cis*-$[Cr(en)_2Cl_2]^+$, including our own,[2] were based solely on measurement of the rate of chloride-ion release, and as is true of many previous kinetic studies of the aquation of coördination complexes, did not include identification of the product complexes.

Experimental

***trans*-Dichlorobis-(ethylenediamine)-chromium(III) Nitrate.**—This compound was prepared and characterized as described in a previous paper.[2]

***cis*-Dichlorobis-(ethylenediamine)-chromium(III) Chloride Hydrate.**—Violet powdered anhydrous chromium(III) chloride, donated by the Diamond Alkali Company, was suspended in technical ethyl ether and mixed with a 20% excess (in 20% ethereal solution) of Eastman Kodak "White Label" ethylenediamine (dried by distillation from sodium hydroxide). After ~2 hr. on the steam-bath, the mixture formed yellow-brown fluffy tris-(ethylenediamine)-chromium(III) chloride, which was washed with ethyl ether and dried overnight at ~100°; yield ~100%. This crude product was recrystallized with half its weight of ammonium chloride from 1 *f* HCl. The crystals were filtered, rinsed with ethyl ether, then thermally decomposed[5] in an Abderhalden drier at the temperature of refluxing methyl salicylate (b.p. 220–224°); concd. H_2SO_4 was used to absorb the ethylenediamine evolved. The resulting crude *cis*-dichlorobis-(ethylenediamine)-chromium(III) chloride was recrystallized twice from 3–6 *f* HCl solution; yield ~20%.

(1) (a) Based on a portion of the doctoral dissertation of D. J. MacDonald, University of California, Los Angeles, January, 1960. (b) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University. (c) California Research Corp., Richmond, Calif.

(2) D. J. MacDonald and C. S. Garner, *J. Inorg. Nuclear Chem.*, **18**, 219 (1961).

(3) J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **79**, 4285 (1957).

(4) R. G. Pearson, R. A. Munson and F. Basolo, *ibid.*, **80**, 504 (1958).

(5) C. L. Rollinson and J. C. Bailar, Jr., "Inorganic Syntheses," Vol. II, W. C. Fernelius, ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 201.

Anal. Calcd. for $[Cr(en)_2Cl_2]Cl \cdot H_2O$: Cr, 17.54; Cl, 35.9; C, 16.20; N, 18.90. Found: Cr, 17.43; Cl, 35.5; C, 16.34; N, 18.64.

All other chemicals were C.P. or reagent grade.

Cation-exchange Chromatographic Procedure.—Separations were achieved with 40-mm. × 9-mm. diam. columns of Dowex AG50W-X8 cation-exchange resin (100–200 mesh, in hydrogen-ion form). Appropriate reaction solutions, usually 0.1 *f* in hydrogen ion, were forced down through a column by compressed air at a controllable rate of 5–50 ml. per minute, resulting in complete adsorption of all chromium species on the resin. The various complex cations were selectively displaced from the resin by eluents of successively increasing acid concentration, the progress of each colored band down the column being followed visually. Eluents used were such that each would, in most cases, entirely elute a particular complex species while leaving the remaining bands of other species almost undisplaced; some overlap of the tail of the third fraction with the head of the fourth fraction below occurred in processing samples from *trans*-$[Cr(en)_2Cl_2]^+$ aquation at later reaction times. Typical volumes and concentrations of HNO_3 eluent appropriate to elution of the following complexes were found to be: *trans*-$[Cr(en)_2Cl_2]^+$, 200 ml., 0.3 *f*; *cis*-$[Cr(en)_2Cl_2]^+$ and a species formed in low yield in *trans*-$[Cr(en)_2Cl_2]^+$ aquation (tentatively identified as *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$), 250 ml., 0.6 *f*; *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$, 200 ml., 1.4 *f*; *cis*-$[Cr(en)_2(OH)_2Cl]^{+2}$ (plus one or more chloride-free species formed in <10% yield at 4 hr. in *trans*-$[Cr(en)_2Cl_2]^+$ aquation), 250 ml., 2.0 *f*.

Preparation of 1,6-Dichloro-2,3-diaquo-ethylenediamine-chromium(III) Cation in Solution.—A solution of what is tentatively considered to be this substance (hereinafter called *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$) was prepared by chromatographic separation from a mixture resulting from reaction of *trans*-$[Cr(en)_2Cl_2]NO_3$ in 0.1 *f* HNO_3 for 12 hr. at 35°. After elution with 0.3 *f* HNO_3 to remove any unreacted *trans*-$[Cr(en)_2Cl_2]^+$ and bring the second band down near the bottom of the resin column, the resin containing the upper bands was removed with a dropper and discarded. Elution with 2 *f* HNO_3 then brought the dichlorodiaquoethylenediamine species off the resin in ~0.01 *f* concentration.

Analytical Methods.—Visible absorption spectra were measured with a Cary Model 11 recording spectrophotometer, using matched quartz cells. Titrations of chloride released in aquation of *cis*-$[Cr(en)_2Cl_2]^+$ were performed as described earlier for the *trans* isomer.[2] Chloride analyses were performed by digesting the complex with excess NaOH solution on a steam-bath, then reacidifying and titrating to a potentiometric end-point with standard silver nitrate solution in the presence of a non-ionic detergent. Chromium was oxidized with hot alkaline peroxide and the resulting chromate spectrophotometrically determined at 372 mμ with a Beckman DU spectrophotometer. Nitrogen was determined in 1,6-dichloro-2,3-diaquo-ethylenediamine-chromium(III) cation in $HClO_4$ solution by the Van Slyke volumetric method.

Kinetic Measurements.—Freshly prepared solutions of pure *cis*- or *trans*-$[Cr(en)_2Cl_2]^+$ (usually 1–10 m*f*) in 0.10 *f* acid (HCl for the *cis*, HNO_3 or HCl for the *trans* isomer) were allowed to react at 35.00 ± 0.05° in the absence of light. Spectrophotometric observations were made at 35.0° on some solutions. Chloride released was determined by titration of other solutions. The various components in aliquots of the reaction mixture taken at given reaction times were separated by cation-exchange chromatography and the amount of chromium in each fraction determined. Contact with the resin was shown to have no detectable effect on the course or rate of the reactions. The rate of disappearance of the starting material was obtained by plotting the natural logarithm of the ratio of the initial concentration of *cis*- or *trans*-$[Cr(en)_2Cl_2]^+$ reactant to its concentration at reaction time *t* *vs.* *t*. The slope of the resulting linear plot is the desired first-order rate constant. The rate constants for production of the individual products were determined by extrapolating to zero reaction time the data obtained by cation-exchange chromatography at short reaction times and making use of the relation that, in the limit of $t = 0$, $k_{ij} = dX_j/dt$, where k_{ij} is the first-order rate constant for formation of product j from reactant i, and X_j is the mole-fraction of total Cr found as product j. The rate of production of the postulated dichlorodiaquo-ethylenediamine species was determined from data at long reaction times by numerical integration of the set of differential rate equations representing this reaction scheme, using a FORTRAN program developed for the IBM-709 electronic computer of the Western Data Processing Center at U.C.L.A. The results of these calculations are not significantly affected by aquation of *cis*- and *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$, the rate constants for which have been found by preliminary observations at 35° to be at most ene-tenth as large as the rate constants for production of these chloroaquo species from their parent dichloro species.

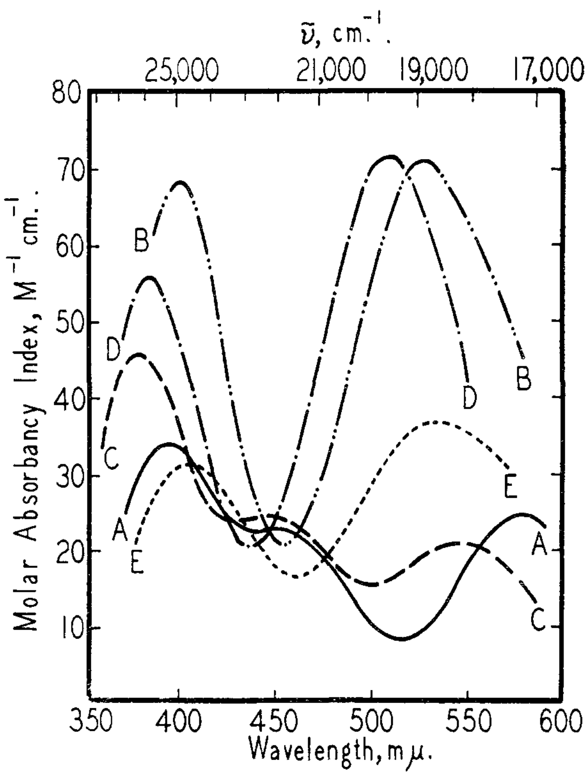


Fig. 1.—Visible absorption spectra of chromium(III) complexes at 25°: A, *trans*-$[Cr(en)_2Cl_2]^+$, 0.1 *f* HNO_3; B, *cis*-$[Cr(en)_2Cl_2]^+$, 0.1 *f* HCl; C, *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$, 0.2 *f* HNO_3 or 1.2 *f* HCl; D, *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$, 2 *f* HCl; E, *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$(?), 3 *f* $HClO_4$; the molar absorbancy index a_M is defined by the relation $\log (I_0/I) = a_M cl$.

Results

Products and Rates of Aquation of *trans*-$[Cr(en)_2Cl_2]^+$.—Three products were found arising from the first-stage aquation of *trans*-$[Cr(en)_2Cl_2]NO_3$ in 0.10 *f* HNO_3 at 35.0°: (1) A species eluted by 0.6 *f* HNO_3 (which would be expected to elute cations of only unipositive charge), having an absorption spectrum as shown in Fig. 1 (curve E) with an absorption peak-height ratio (blue/red) of 0.855 (*vs.* 0.960 for *cis*-$[Cr(en)_2Cl_2]^+$ which has a somewhat similar spectrum), a Cl/Cr atom ratio of 2.0 and a N/Cr atom ratio of ~2, corresponding to one ethylenediamine per Cr. On the basis of this evidence we have tentatively identified this substance as *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$ (*i.e.*, 1,6-dichloro-2,3-diaquo-ethylenediamine-chromium(III) cation), apparently formed by loss of an ethylenediamine molecule from *trans*-$[Cr(en)_2Cl_2]^+$ with replacement by two water molecules. Tentative assignment to a *trans*-dichloro-*cis*-diaquo configuration is based partly on the *cis*-type spectrum with

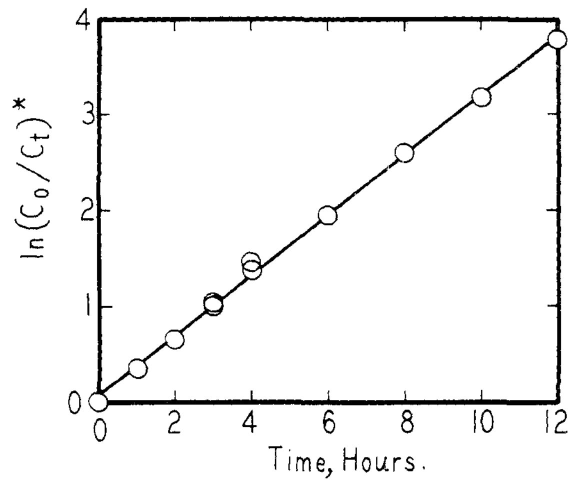


Fig. 2.—Total rate of reaction of *trans*-$[Cr(en)_2Cl_2]NO_3$ in 0.10 *f* HNO_3 at 35.0°: $^*C_0$ and C_t are concentrations of *trans*-$[Cr(en)_2Cl_2]^+$ at zero time and time *t*, respectively.

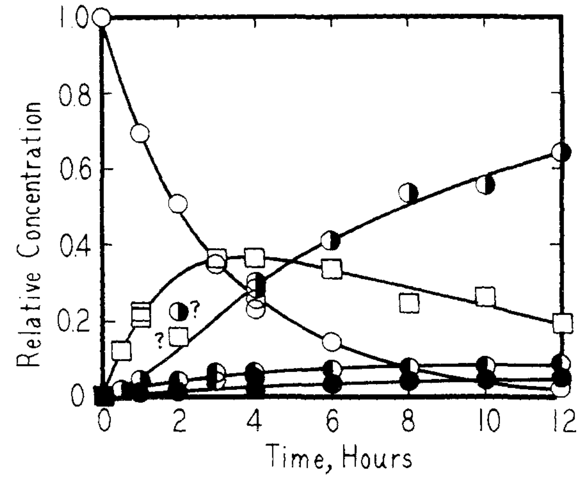


Fig. 3.—Products of aquation of *trans*-$[Cr(en)_2Cl_2]NO_3$ in 0.10 *f* HNO_3 at 35.0°: O, *trans*-$[Cr(en)_2Cl_2]^+$; ◐, *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$(?); □, *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$; ◑, *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ (at reaction times beyond ~2 hr., this fraction becomes increasingly impure, probably due to formation of chloride-free complexes); ●, all other chloride-free complexes.

absorption-peak molar absorbancy indices only about half those of *cis*-$[Cr(en)_2Cl_2]^+$. This fact suggests both a more symmetrical configuration about the chromium atom in the unknown complex and a *cis* configuration of the two monodentate ligands of greatest crystal-field strength (H_2O), *i.e.*, a *trans*-dichloro structure. This configuration would require no rearrangement in the substitution of the two water molecules for the ethylenediamine ligand lost from the parent *trans* complex and is also in accord with a possible hydrogen-bond stabilization of the complex (*vide infra*). This dichlorodiaquo species does not appear to undergo further significant reaction even over a period of 12 hr. at 35°. (2) A species eluted by 1.4 *f* HNO_3, with a Cl/Cr atom ratio of 0.9–1.12, and a three-peak visible absorption spectrum (curve C, Fig. 1). This species is *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$. (3) A species eluted by 2.0 *f* HNO_3, with a Cl/Cr atom ratio of ~0.9, and a *cis*-type two-peak visible absorption spectrum (curve D, Fig. 1). This species is *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$, the assignment of which to the *cis* isomer is based not only on the spectrum but also on the greater difficulty of elution from the cation-exchange resin (characteristic of *cis* isomers of octahedral complexes in general when compared with the behavior of the corresponding *trans* isomers) and on the sole formation of this species in the primary aquation of *cis*-$[Cr(en)_2Cl_2]^+$ (*vide infra*). These two chloroaquo species and the postulated *trans*-dichloro-*cis*-diaquo species have apparently not been previously isolated or characterized. The chromatographic separation results are given in Table I.

The total rate of disappearance of *trans*-$[Cr(en)_2Cl_2]^+$ in 0.10 *f* HNO_3 at 35.0° in the dark was found from chromatographic separations to be first-order in that complex, with a rate constant of $(8.75 \pm 0.05) \times 10^{-5}$ sec.$^{-1}$. A typical rate plot is given in Fig. 2. The plotted points do not significantly depart from a straight line even after 95% reaction, showing that the reactions involved are essentially irreversible first-order reactions under the conditions used. Figure 3 shows the rate of growth and decay of the various chromium species formed in the aquation of *trans*-$[Cr(en)_2Cl_2]^+$. At one half-life (~2 hr.) for the disappearance of this *trans* complex, it is seen that ~66% of the reacted complex has gone to *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$, ~20% to *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$, ~10% to the species tentatively identified as *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$ and ~4% to chloride-free complexes (diaquobis-(en) species, etc.). The rate constants involved in the formation of these products are given in Table II.

TABLE I

AQUATION KINETICS OF *trans*-$[Cr(en)_2Cl_2]^+$: RATIO OF CHROMIUM IN CHROMATOGRAPHIC FRACTION TO TOTAL CHROMIUM IN REACTION MIXTURE

35.00 ± 0.05°; 0.10 *f* HNO_3; 5-6 m*f* in complex initially; ionic strength 0.10; no light

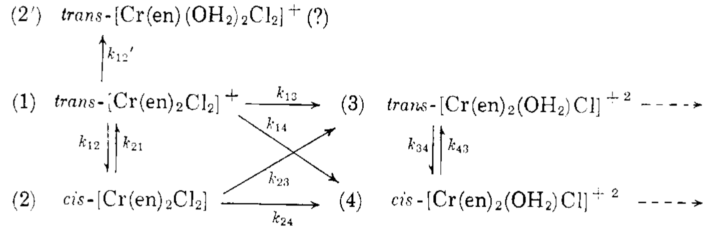
Reaction time, hr.	Chromatographic fraction[a] F1	F2	F3	F4	F5
0.00	(1.000)	(0.000)	(0.000)	(0.000)	(0.000)
0.50	...	...	.126	.021	...
1.00	0.695	0.035	.219	.040	.011
2.00	.509	.045	.160?[b]	.228?[c]	.015
3.00	.358	.058	.368	...	...
4.00	.242	.067	.330	.295	.035
6.00	.142	.073	.336	.410	.039
8.00	.074	.080	.249	.539	.044
10.00	.0412	.0814	.262	.556	.0486
12.00	.0226	.0906	.191	.645	.046

[a] F1, *trans*-$[Cr(en)_2Cl_2]^+$; F2, *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$ (?); F3, *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$; F4, *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ plus undetermined chloride-free complexes at longer reaction times (<10% at 4 hr.); F5, all other chloride-free complexes. [b] Value apparently too low. [c] Value apparently too high.

Aquation of *cis*-$[Cr(en)_2Cl_2]^+$.—The only product detectable chromatographically and spectrophotometrically in the primary aquation of *cis*-$[Cr(en)_2Cl_2]Cl$ in 0.10 *f* HCl at 35.0° in the dark

TABLE II

AQUATION AND *cis–trans* ISOMERIZATION RATE CONSTANTS IN 0.10 *f* ACID AT 35.0° IN THE DARK



Reaction	Acid	Method[a]	10^6 × rate constant, sec.$^{-1}$ Cr complexes[b]	Co complexes
$k_{12} + k_{13} + k_{14} + k_{12}'$	HNO_3	Chr. sep. (1)	8.75 ± 0.05	
$k_{12} + k_{13} + k_{14}$	HNO_3	Cl^- titr. (1)	8.02 ± .07[c]	16[f]
$k_{12} + k_{13} + k_{14}$	HNO_3	Cl^- titr. (1)	(14)[d]	
k_{12}'	HNO_3	Chr. sep. (1)	0.78 ± .05	
k_{12}''	HNO_3	Difference	(0.73 ± .09)	
$k_{12} + k_{14}$	HNO_3, HCl	Chr. sep. (1)	1.12 ± .40	
k_{13}	HNO_3	Difference	6.90 ± .41	
k_{13}	HNO_3, HCl	Chr. sep. (1)	(7.2 ± .6)	
k_{24}	HCl	Chr. sep. (2)	111 ± 2	
$k_{23} + k_{24} \cong k_{24}$	HNO_3, $HClO_4$	Cl^- detm. (2)	104[e]	
$k_{23} + k_{24} \cong k_{24}$	HCl	Cl^- titr. (2)	(109 ± 6)	
k_{24}	$HClO_4$	Spectro. (2)	(100 ± 10)	85[g]
k_{23}	$HClO_4$	Spectro (2)	<1	
k_{21}	$HClO_4$	Spectro (2)	<0.5	12(?)[h]
k_{34}	HNO_3	Spectro. (1)	<0.6	~34[i]
k_{43}	HCl	Spectro. (2)	<2	<9[j]

[a] Chr. sep. refers to chromatographic separations; numbers inside parentheses refer to chromium complex present initially. [b] Errors given are standard deviations, in most cases from a least-squares procedure; where two or more values of a given k appear, values considered less reliable are here enclosed in parentheses. [c] Rate constant for production of ionic chloride from *trans*-$[Cr(en)_2Cl_2]^+$, ref. 2. [d] Calcd. from 25° k of ref. 4 using E_a of ref. 2. [e] Calcd. from 30° k of ref. 3, using their E_a. [f] Value from Pearson, Boston and Basolo.[6] [g] Calcd. from spectrophotometric 25° k in 0.1 f HNO_3 from Pearson, Boston and Basolo,[7] using E_a from Mathieu.[8] [h] Value from Haworth, Neuzil and Kittsley[9]; value appears not to have been corrected for competing aquation and base hydrolysis; presence of added acid and absence of light unreported. [i] Actually ($k_{34} + k_{43}$), estimated from results of Tobe reported by Staples and Tobe[10]; acid not reported. [j] Based on rate of loss of optical activity of *l*-*cis*-$[Co(en)_2Cl_2]^+$ in 0.01 f acid at 30° from Mathieu,[11] which has been shown by Pearson, Meeker and Basolo[12] to involve *cis*-to-*trans* rearrangement of the *l*-*cis*-$[Co(en)_2(OH_2)Cl]^{+2}$ product.

was *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$. Aquation occurred with a pseudo first-order rate constant of (1.11 ± 0.02) × 10^{-3} sec.$^{-1}$, determined by the chromatographic separation method. A typical rate plot is shown in Fig. 4. A spectrophotometric study of the aquation in 0.1 f $HClO_4$ at 35.0° gave no indication of any primary product other than the *cis*-chloroaquo species; measurements over one reaction half-time at 400 mμ (see curves B and D, Fig. 1), calculating A_∞ (the absorbancy at infinite time) from the known spectrum of *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$, gave (1.0 ± 0.1) × 10^{-3} sec.$^{-1}$ for the aquation rate constant.

Discussion

It is possible that the *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ found as one of the products of aquation of *trans*-$[Cr(en)_2Cl_2]^+$ is not formed directly but is merely the result of a *trans*-to-*cis* isomerization. Neither *cis*-$[Cr(en)_2Cl_2]^+$ arising from isomerization of *trans*-$[Cr(en)_2Cl_2]^+$ nor *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ arising from isomerization of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ could be detected, but in both cases the rate of

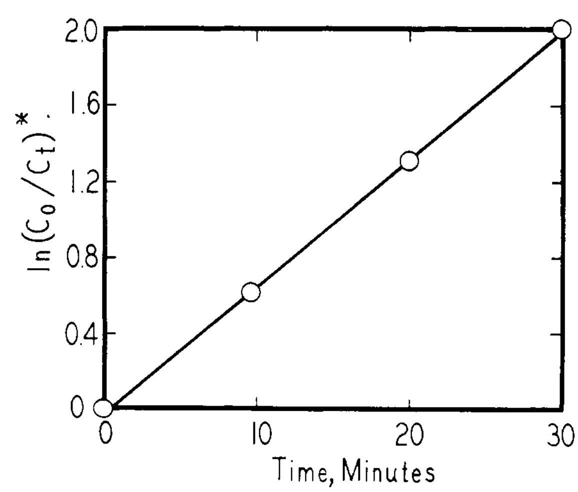


Fig. 4.—Rate of aquation of *cis*-$[Cr(en)_2Cl_2]Cl$ in 0.10 f HCl at 35.0°: *C_0 and C_t are concentrations of *cis*-$[Cr(en)_2Cl_2]^+$ at zero time and time t, respectively.

aquation of the *cis* isomer is so much greater than that of the *trans* isomer that *trans*-to-*cis* isomerization could provide an important reaction path

(6) R. G. Pearson, C. R. Boston and F. Basolo, *J. Am. Chem. Soc.*, **75**, 3089 (1953).

(7) R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

(8) J. P. Mathieu, *Bull. soc. chim.*, **3**, 2121, 2152 (1936).

(9) D. T. Haworth, E. F. Neuzil and S. L. Kittsley, *J. Am. Chem. Soc.*, **77**, 6198 (1955); *Experientia*, **12**, 335 (1956). See also discussion between A. G. Sharpe and D. B. Wakefield, *ibid.*, **13**, 460 (1957), and Kittsley, *ibid.*, **13**, 460 (1957).

(10) P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4803 (1960).

(11) J. P. Mathieu, *Bull. soc. chim.*, **4**, 683 (1937).

(12) R. G. Pearson, R. E. Meeker and F. Basolo, *J. Am. Chem. Soc.*, **78**, 2673 (1956).

even though the concentration of the *cis* isomer would never reach a detectable level. Preliminary experiments[13] on aquation of *trans*-$[Co(en)_2Cl_2]^+$ have indicated considerable change of configuration occurs, and it appears likely that in the chromium case too at least some of the *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ found is a first-formed product.

As for *cis*-to-*trans* isomerization, neither *trans*-$[Cr(en)_2Cl_2]^+$ nor *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ could be detected in the reaction mixture produced by aquation of *cis*-$[Cr(en)_2Cl_2]^+$. The very conservative upper limits for isomerization rate constants given in Table II were derived from estimates of the minimum concentrations of isomerization products which could have been detected spectrophotometrically if they were present, except for k_{12} which is known from the chromatographic separation data not to exceed $(1.12 \pm 0.40) \times 10^{-5}$ sec.$^{-1}$, since $k_{12} + k_{14}$ has this value.

It is clear that neither of the *cis*-to-*trans* isomerizations above can play a significant role in the aquation of *cis*-$[Cr(en)_2Cl_2]^+$. The essentially sole formation of *cis* product is further indicated by the agreement, within the experimental errors, of the aquation rate-constant values obtained chromatographically, spectrophotometrically and titrimetrically (see Table II). Accordingly, the stereochemical result of aquation of *cis*-$[Cr(en)_2Cl_2]^+$ must be ~100% *cis* product. This is in harmony with the fact that in aquation of all cobalt(III) octahedral *cis* complexes studied earlier there is apparently total retention of configuration (including that of optical configuration where investigated), as recently pointed out by Ingold, Nyholm and Tobe.[14] Whether this stereokinetic rule is generally applicable to chromium(III) octahedral complexes and to cases where chloride is not the outgoing ligand remains to be seen.

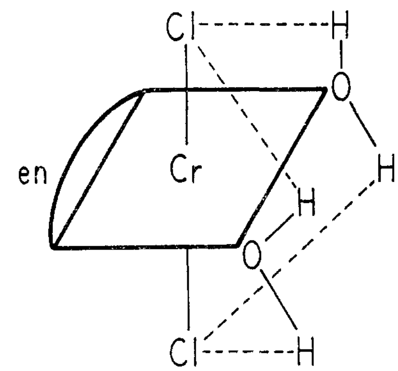
For comparison of our rate constant for aquation of *cis*-$[Cr(en)_2Cl_2]^+$ in 0.1 *f* HCl at 35.0° with that reported by Selbin and Bailar[3] in 0.1 *f* HNO_3 or 0.1 *f* $HClO_4$ at 25.0°, we may make use of the experimental activation energy they found, namely 21.1 kcal. mole^{-1}, to convert our rate constant to one at 25.0°. The result is 34.9×10^{-5} sec.$^{-1}$, which agrees within 6% with the probably more accurate Selbin–Bailar value of 33.0×10^{-5} sec.$^{-1}$. Table II includes the available rate data on the analogous cobalt(III) complexes for comparative purposes. A full comparison is not possible at this time since these cobalt(III) complexes have not yet been subjected to detailed investigations of the kind reported here for the chromium(III) complexes. For both *cis* and *trans* isomers of $[Co(en)_2Cl_2]^+$ and $[Cr(en)_2Cl_2]^+$ aquation probably occurs by an SN1 mechanism. Table III compares the kinetic parameters for chloride release by aquation of these four species. Activation energies for the d^6 cobalt(III) complexes are greater than for the corresponding d^3 chromium(III) complexes, as expected from crystal-field considerations ignoring the influence of solvent water. For the *trans* complexes resolution of these over-all parameters into ones for individual characterized reactions is required for a more meaningful comparison.

TABLE III

AQUATION OF $[M(en)_2Cl_2]^+$ IN 0.1 *f* HNO_3 AT 25° IN THE DARK

M(III)	Config.	$10^5\,k$, sec.$^{-1}$	E_a, kcal.	ΔS^{0*}, cal./deg.
Cr	*cis*	33.0[3]	21.1[3]	− 5.72[3]
Co	*cis*	25[7]	22.3[8]	−11
Cr	*trans*	2.25 ± 0.03[2]	23.23 ± 0.17[2]	− 3.86 ± 0.57
Co	*trans*	3.2[6]	24.2;[3] 28[6]	0; +10

In aquation of *trans*-$[Cr(en)_2Cl_2]^+$ the directly-formed product produced in low yield and tentatively characterized as *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$ was noted to undergo further aquation negligibly even in 12 hr. at 35°. At first thought, one might expect the postulated complex to undergo substitution of water for its chloride ligands at a rate comparable to that for aquation of *trans*-$[Cr(en)_2Cl_2]^+$. However, the relative inertness of the postulated complex may possibly arise as a result of hydrogen-bonding between a chloride ligand and the hydrogen atoms of the water ligands,[15] as



Although a chlorine atom normally does not have an appreciable hydrogen-bonding tendency, the chloride ligands of the complex may become strongly negative relative to the hydrogen atoms of the water ligands inasmuch as the central chromium atom has a stronger electron-withdrawing action on the oxygen atoms of the water ligands than on the chloride ligands.

Comparison of the previously unknown visible absorption spectra of *cis*- and *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ (curves D and C, Fig. 1) with those of

TABLE IV

VISIBLE ABSORPTION SPECTRA OF $[M(en)_2(OH_2)Cl]^{+2}$ AT ~25°

	M = Cr[a]		M = Co[b]	
Isomer	λ, mμ	a_M[c]	λ, mμ	a_M[c]
cis	385[d]	56	373[d]	67
	437[e]	20	435[e]	15
	508[d]	72	515[d]	84
trans	380[d]	46	?	?
	427[e]	24	440[e]	34
	445[d]	25	442[d]	35
	495[e]	16	510[e]	14
	545[d]	21	590[d]	35

[a] In 2 *f* HCl for *cis*, 0.2 *f* HNO_3 or 1.2 *f* HCl for *trans* (this research). [b] In 0.012 *f* $HClO_4$ (ref. 16). [c] Molar absorbancy index, in M^{-1} cm.$^{-1}$. [d] Abs. max. [e] Abs. min.

(13) M. E. Baldwin and M. L. Tobe, *J. Chem. Soc.*, 4275 (1960).

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

(15) We are indebted to Mr. Robert Murashige for this suggestion.

the Co(III) analogs is now possible, since Sargeson[16] recently has isolated these Co complexes as the sulfates and obtained their visible absorption spectra. As shown in Table IV, the two *cis* spectra are very similar, as are the two *trans* spectra.

For complexes of type [MA_2B_2] the total area under the bands (a measure of absorption intensity) of the *cis* isomer, which has no center of symmetry, is substantially greater than for the *trans* isomer, which has a center of symmetry; for [MA_4BC]-type complexes, in which neither geometrical isomer has a center of symmetry, crystal-field theory predicts that the *cis* and *trans* isomers will have approximately the same area under the absorption bands.[17] Examination of Fig. 1[18] shows that this is the case for *trans*- and *cis*-[$Cr(en)_2Cl_2$]$^+$ (curves A and B) but only approximately so for *trans*- and *cis*-[$Cr(en)_2(OH_2)Cl$]$^{+2}$ (curves C and D), the *cis/trans* area-ratios being ~2.1 and ~1.5, respectively. The ratios for these respective cobalt(III) analogs are ~2.0 and ~1.1, respectively.

(16) Private communication from Dr. A. M. Sargeson, The John Curtin School of Medical Research, Australian National University, Canberra.

(17) F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

(18) The plots of a_M *vs.* λ can be used in place of the proper plot of a_M *vs.* wave number since the extrapolated spectra being compared cover essentially the same wave lengths.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

Magnetic Studies of High-spin Cobaltous Compounds. VII. Some Thiocyanate Complexes

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The compound [$Co\{(C_6H_5)_3P\}_2(SCN)_2$] has been carefully studied magnetically and spectroscopically. The data lead to these conclusions: (1) the compound is tetrahedral, (2) the SCN groups are bound to Co *via* the sulfur atoms, (3) the position of S-bonded thiocyanate ions in the spectrochemical series is between Cl^- and Br^- as previously shown by Schäffer. Several salts of the [$Co(NCS)_4$]$^{2-}$ anion have been studied magnetically and spectroscopically. A number of important parameters pertaining to the electronic structure and ligand field have been evaluated and the effect of bonding the S atom to Hg(II) in moving the $-NCS^-$ ion to a stronger position in the spectrochemical series, as observed by Schäffer, has been confirmed. The compound [$Co(Ph_3PO)_2(NCS)_2$] has been prepared. Comparison of spectral and magnetic data for this compound with similar data for its chloride and bromide analogs shows that in this case the thiocyanate ions are coördinated through the nitrogen atoms.

Introduction

Ligands which occur in tetrahedral cobalt(II) complexes may be placed in the spectrochemical series using the spectral data, in a manner analogous to the use of spectral data for Cr(III) and Co(III) complexes,[3] and also using magnetic data as indicated in earlier papers in this series.[4-6] In this paper we report the results of studies by both spectral and magnetic methods of the position of S- and N-coördinated thiocyanate ions in the spectrochemical series, as well as a fairly complete analysis of the spectral and magnetic data for the [$Co(NCS)_4$]$^{2-}$ ion to furnish numerical estimates of certain parameters of the electron configuration of the Co(II) ion in this complex.

Experimental

Preparations. Dithiocyanatobis-triphenylphosphine-cobalt(II).—A solution of triphenylphosphine (12.0 g., 0.046 mole) in acetone (25 ml.) was added to a solution of cobaltous thiocyanate (3.0 g., 0.018 mole) also in acetone (25 ml.). From the blue solution so obtained, a green crystalline compound began to precipitate. The precipitation was completed by careful addition of petroleum ether (~20 ml.) and the compound filtered off. It was recrystallized by solution in methylene chloride and addition of petroleum ether. The yield was practically quantitative, m.p. 140°.

Anal. Calcd. for $C_{38}H_{30}CoN_2P_2S_2$: C, 65.22; H, 4.32; N, 4.00; P, 8.86. Found: C, 65.10; H, 4.33; N, 4.06; P, 8.61.

The compound was soluble in acetone, giving a blue solution, while green solutions were readily obtained with methylene chloride, chloroform or nitrobenzene. The complex was decomposed by methanol and ethanol.

Tetramethylammonium Tetrathiocyanatocobaltate(II).—A blue solid was immediately precipitated on addition of a solution of cobaltous thiocyanate (1.54 g., 0.0093 mole) in hot absolute ethanol (42 ml.) to one of tetramethylammonium thiocyanate (2.46 g., 0.0185 mole) also in hot absolute ethanol (58 ml.). The blue compound was filtered off while the mixture was still hot, washed with absolute ethanol and dried *in vacuo* over sulfuric acid. The yield was 3.50 g. (86%), m.p. 197°.

Anal. Calcd. for $C_{12}H_{24}CoN_6S_4$: C, 32.79; H, 5.50; N, 19.12. Found: C, 32.62; H, 5.52; N, 19.05.

The compound readily forms blue solutions in acetone, nitrobenzene or nitromethane.

Dithiocyanatobistriphenylphosphine oxide-cobalt(II).—A solution of 5.60 g. of triphenylphosphine oxide in 25 ml. of anhydrous ethanol was added to 1.80 g. of $Co(NCS)_2$ dissolved in 25 ml. of the same solvent. After a few minutes, a blue, crystalline compound began to precipitate. After several hours, the precipitate was filtered off, washed with ethanol and dried under vacuum; m.p., 230°. It is soluble in chloroform, dichloromethane, slightly soluble in oxygenated organic solvents and insoluble in non-polar solvents.

Anal. Calcd. for $C_{38}H_{30}CoO_2P_2N_2S_2$: C, 62.38; H, 4.13; N, 3.83. Found: C, 62.45; H, 4.27; N, 4.00.

(1) Alfred P. Sloan Fellow.

(2) On leave from the Istituto di Chimica Generale dell' Universitá di Milano.

(3) For a summary of results and references see T. M. Dunn in "Modern Coördination Chemistry," J. Lewis and R. G. Wilkins, Editors, Interscience Publishers, Inc., New York, N. Y., 1960.

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(6) F. A. Cotton, O. D. Faut, D. M. L. Goodgame and R. H. Holm, *ibid.*, **83**, 1780 (1961).