

that the nitrosyl group in $\text{Mn}(\text{CN})_5\text{NO}^{3-}$ is like a neutral NO molecule because its total density is nearly the same is very misleading if not erroneous. The neutral NO group has a fully occupied 5σ orbital and a single unpaired electron in the 2π orbitals. The nitrosyl group in the complex has less than two electrons in the 5σ orbital and the 2π density it possesses consists of paired electrons contributed to it by virtue of participation in the filled molecular orbitals of E

representation. While it is frequently convenient to relate groups of atoms in a complex to their free ligand counterparts, we should not lose sight of the fact that such devices are primarily for conceptual utility.

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Kinetic and Equilibrium Studies of *cis*-Bis(oxalato)isothiocyanatoaquochromate(III)

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The acidity constant of $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ has been determined spectrophotometrically at $1.0 \pm 0.5^\circ$ and $\mu = 2.0 F$ (NaNO_3) to be $(8.7 \pm 3.0) \times 10^{-8} F$. The formation quotient for $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ at $\mu = 1.00 F$ (NaNO_3) has been determined at 25, 35, 45, and 55° to be 4.50 ± 0.06 , 5.25 ± 0.12 , 5.53 ± 0.07 , and $5.60 \pm 0.04 F^{-1}$, respectively. The values of ΔH° and ΔS° were determined to be 1.2 ± 0.4 kcal/mol and 7.3 ± 1.4 cal/deg mol, respectively. The kinetics of aquation of $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ were pH independent from pH 3 to pH 4 and at $\mu = 1.00 F$ (NaNO_3). The overall aquation reaction occurred with retention of configuration. The values of k_1 at 25, 35, 45, and 55° were $(1.61 \pm 0.11) \times 10^{-5}$, $(4.98 \pm 0.11) \times 10^{-5}$, $(1.59 \pm 0.01) \times 10^{-4}$, and $(4.09 \pm 0.01) \times 10^{-4} \text{ sec}^{-1}$, respectively. The values of ΔH^* and ΔS^* were 20.1 ± 0.4 kcal/mol and -13.1 ± 1.2 cal/deg mol. The aquation reaction was concluded tentatively to occur by an I_d mechanism.

Introduction

There have been very few reports of compounds of the type $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{XY}^{n-}$, where X and Y are simple monodentate ligands.¹ There have been even fewer reports of kinetic and equilibrium studies. Recently the synthesis of the ion $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ has been reported.² In order to understand more about the equilibrium and kinetic properties of the $\text{cis-Cr}(\text{C}_2\text{O}_4)_2^{2-}$ moiety, the aquation of $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ was studied. The formation quotient of the ion was determined, and the acidity constant of the $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ was determined. This paper reports the results of these studies.

Experimental Section

All chemicals used were reagent grade and were used without further purification. The sodium *trans*-bis(oxalato)diaquochromate(III) was prepared by the method described by Werner.³ Solutions of sodium *cis*-bis(oxalato)isothiocyanatoaquochromate(III) were prepared and analyzed as previously reported.²

The spectra of solutions of chromatographically separated pure sodium *cis*-bis(oxalato)diaquochromate(III) at pH 3 in 0.10 F sodium nitrate and of sodium *cis*-bis(oxalato)isothiocyanatoaquochromate(III) at pH 3 in 2.0 F sodium nitrate were determined at 2° using a Beckman DU-2 spectrophotometer with a 0.10-mm slit width. The spectrum of *cis*-bis(oxalato)isothiocyanatohydroxochromate(III) was determined at 1° and at pH 9.0 in a solution of sodium hydroxide and 2.0 F sodium nitrate using a Cary Model 15.

The experiment designed to attempt to separate the possible

cis and *trans* isomers of $\text{Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ was essentially identical with the ones previously reported for the partially successful separation of *cis*- and *trans*- $\text{Cr}(\text{C}_2\text{H}_2\text{O}_4)_2(\text{OH}_2)^{2-}$.⁴ However, 2.0 F NaNO_3 at pH 3 was used as eluent and ten fractions containing Cr(III) were collected.

The rate studies were performed using a Beckman DU-2 fitted with a specially constructed constant-temperature block which completely surrounded the 10-cm cell used and a Cary Model 15 fitted with the commercially available constant-temperature block. The temperature was maintained to within $\pm 0.1^\circ$ of that desired. The rate of aquation was followed at 412 and 550 nm, the wavelengths of maximum absorbance change, using an approximately 0.40 mF solution of sodium *cis*-bis(oxalato)diaquochromate(III) as the reference solution. To prepare the solutions for the kinetic runs, the following procedure was used. A solution of about 2.0 mF sodium *cis*-bis(oxalato)isothiocyanatoaquochromate(III) in 2.0 F sodium nitrate at 0° and pH 2.0–3.0 was mixed with the appropriate amount of water at pH 2.0–3.0 and at an elevated temperature so that the final solution had an ionic strength of 1.0 F and had the desired temperature. The solution was poured immediately into a 10-cm cuvette, the cuvette was placed into the constant-temperature block, and the change in absorbance with time was monitored. The change in absorbance in various runs was from 0.20 to 0.50.

The formation quotients of sodium *cis*-bis(oxalato)isothiocyanatoaquochromate(III) were determined by ion-exchange chromatography. Five-milliliter aliquots containing 0.10 F sodium *cis*-bis(oxalato)diaquochromate(III) (previously purified by anion-exchange chromatography), various amounts of sodium thiocyanate from 0.100 to 0.900 F , and enough sodium nitrate to maintain the ionic strength at 1.00 F were sealed in glass ampoules and thermostated at the desired temperature, 25 – 55° . The solutions were allowed to react for various time intervals from seven to nineteen days to ensure that equilibrium had been attained. After the desired time, the ampoules were opened and the solutions run into Dowex 1-X8, 200–400 mesh, nitrate-form anion-exchange columns maintained at 1° . A flow rate of 3.0 ml hr^{-1} was used. The columns were washed with 0.10 F sodium nitrate to ensure elution of sodium *cis*-bis(oxalato)-

(1) Gmelin, "Gmelin's Handbuch der anorganischen Chemie," 8 Auflage, Chrom Teil C, Verlag Chemie, Weinheim, Germany, 1965, reported the synthesis of ions in which X = Y for X = NH_3 (p 234), X = $\text{C}_2\text{H}_7\text{N}$ (p 274), X = $\text{C}_6\text{H}_7\text{N}$ (p 280), X = $\text{C}_6\text{H}_5\text{N}$ (p 289), and X = $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$ (cinchonin) (p 289).

(2) S. Kulprathipanja and K. R. Ashley, *J. Inorg. Nucl. Chem.*, **32**, 3965 (1970).

(3) A. Werner, *Ann.*, **406**, 216 (1914).

(4) K. R. Ashley and K. Lane, *Inorg. Chem.*, **9**, 1795 (1970).

diaquochromate(III). The sodium *cis*-bis(oxalato)isothiocyanatoquochromate(III) was eluted with 2.0 *F* sodium nitrate. The concentrations of sodium *cis*-bis(oxalato)diaquochromate(III) and sodium *cis*-bis(oxalato)isothiocyanatoquochromate(III) were determined by chromium analysis of the respective effluents.⁴ Preliminary experiments established that the first band to be isolated had the same visible absorption spectrum as *cis*-Cr(C₂O₄)₂(OH₂)₂⁻ and that the second band to be isolated had the same visible absorption spectrum as *cis*-Cr(C₂O₄)₂-NCS(OH₂)₂⁻.

The acid dissociation constant of *cis*-bis(oxalato)isothiocyanatoquochromate(III) was determined spectrophotometrically at the wavelengths of maximum absorbance change using a Cary Model 15. The temperature of the solutions was maintained at 1.0 ± 0.5°. Dry nitrogen was used to purge the cell compartment of the spectrophotometer in order to prevent condensation of moisture. Since the hydroxo species aquated rather quickly, even at 1°, the absorbance was measured as a function of time after mixing and then the absorbance was extrapolated to time zero. This extrapolated value was taken as the absorbance of the solution. The actual procedure was as follows. Twenty ml of a 1.0 *mF* solution of sodium *cis*-bis(oxalato)isothiocyanatoquochromate(III) at pH 3, at a temperature of 1.0 ± 0.5°, and in 2.0 *F* sodium nitrate was pipetted into a 25-ml volumetric flask which was immersed in ice water. The pH of the solution was increased by adding the desired amount of 1.0 *F* NaOH and then the solution was diluted to the mark with 2.0 *F* sodium nitrate at 0°. The solution was poured immediately into a 10-cm cell and the absorbance was measured as a function of time. The pH of the solution was measured with a Beckman Research Model pH meter using a general-purpose glass electrode after recording the absorbance. Independent experiments confirmed that there was no change in pH during these measurements.

Results and Discussion

The values of the molar absorptivities of the pertinent ions are reported in Table I. Notice that the

TABLE I
MOLAR ABSORPTIVITIES OF SOME
CHROMATE(III) COMPLEXES^a

Complex	λ_{\max} , nm	λ_{\min} , nm	λ_{\max} , nm
<i>cis</i> -Cr(C ₂ O ₄) ₂ (OH ₂) ₂ ^{-b}	559 (51.5)	480 (15.0)	414 (66.3)
<i>trans</i> -Cr(C ₂ O ₄) ₂ (OH ₂) ₂ ^{-c}	533 (16.7)	...	398 (17.0)
<i>cis</i> -Cr(C ₂ O ₄) ₂ NCS(OH ₂) ₂ ^{-d}	558 (75.8)	480 (18.0)	412 (89.0)
<i>cis</i> -Cr(C ₂ O ₄) ₂ NCS(OH) ₂ ^{-e}	585 (61.5)	515 (30.6)	415 (74.1)

^a Values in parentheses are molar absorptivities. Units are M⁻¹cm⁻¹. ^b $\mu = 0.10$ *F* (NaNO₃), 2°, and pH 3.0. ^c D. H. Huchital, *Inorg. Chem.*, **9**, 486 (1970). ^d $\mu = 2.0$ *F* (NaNO₃), 2°, and pH 3.0. ^e $\mu = 2.0$ *F* (NaNO₃), 1°, and pH 9.0.

molar absorptivities at the maxima of the *trans*-Cr(C₂O₄)₂(OH₂)₂⁻ are much lower than those of the *cis*-Cr(C₂O₄)₂(OH₂)₂⁻. Also the two maxima of the *trans* isomer are broader than those of the *cis* isomers.⁵ The isomers *trans*- and *cis*-Cr(C₂H₂O₄)₂(OH₂)₂⁻ also show these characteristics.⁴ Garner has reported these same observations for a variety of Cr(C₂H₃N₂)₂XYⁿ⁺, where X and Y are simple monodentate ligands.⁶ Based on these analogies, the shape of the visible absorption spectrum of Cr(C₂O₄)₂NCS(OH₂)₂⁻ indicates that the *cis* isomer has been isolated.

There is the distinct possibility that the solution containing the *cis*-Cr(C₂O₄)₂NCS(OH₂)₂⁻ is contaminated with the *trans* isomer. In actual fact, the isolated isomer is pure. This has been demonstrated by anion-exchange techniques. Garner has successfully isolated *cis* and *trans* isomers of a variety of bis(ethylenediamine)acidoquochromium(III) species by cation-exchange chromatography techniques.⁶ Ashley and

Lane have been able to separate partially *cis*- and *trans*-bis(malonato)diaquochromate(III) by anion-exchange chromatography techniques.⁴ Essentially the same method was used to attempt to separate the *trans* and *cis* isomers in this case. The molar absorptivities and the positions of the maxima of each one of the fractions collected corresponded, within experimental error, to those of the initial solution used. This indicated that the solution contained only one isomer, *i.e.*, the *cis* isomer.

The assignment of the mode of bonding of thiocyanate is based entirely upon spectral considerations. Haim and Sutin have reported the preparation of two isomers of a compound containing chromium and thiocyanate in a ratio of 1.0:1.0.⁷ The linkage isomers were the nitrogen-bonded thiocyanate (isothiocyanate) and the sulfur-bonded thiocyanate (thiocyanate) of Cr(OH₂)₅(SCN)²⁺. The absorption maxima of Cr(OH₂)₆³⁺ are at 577 and at 407 nm, of Cr(OH₂)₅NCS²⁺ are at 570 and at 410 nm, and of Cr(OH₂)₅SCN²⁺ are at 620 and 435 nm.⁸ It is apparent that in Cr(OH₂)₅³⁺ the ordering in the spectrochemical series for the visible absorption maximum at the longer wavelength is -NCS⁻ > OH₂ > -SCN⁻ and for the visible absorption maximum at the shorter wavelength is OH₂ > -NCS⁻ > -SCN⁻. For the thiocyanate-containing compound reported here, the positions of the absorption maxima have changed very little when water was replaced by thiocyanate. Based upon these observations and assuming that the spectrochemical series for the considered ligands is the same both in Cr(OH₂)₅³⁺ and in Cr(C₂O₄)₂OH₂⁻, the nitrogen-bonded isomer is the reported complex.

The four isosbestic points in Figure 1 indicate that as

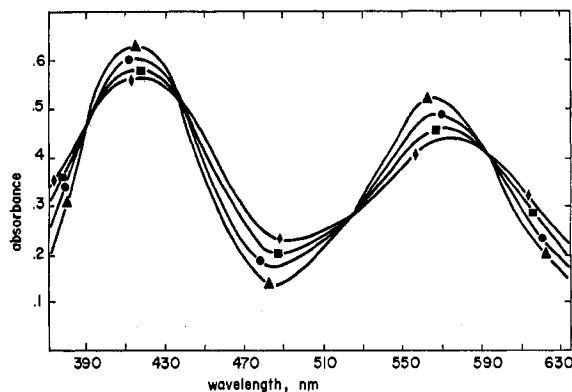
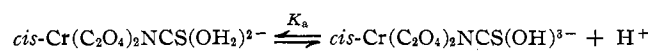


Figure 1.—The visible absorption spectrum of *cis*-Cr(C₂O₄)₂NCS(OH₂)₂⁻ at 1.0 ± 0.5° as a function of pH: ▲, pH 4; ●, pH 6.0; ■, pH 7.5; ◆, pH 9.0. Spectra were obtained on a Cary Model 15. $\mu = 2.00$ *F* (NaNO₃) and [Cr]_{total} = 0.8 *mF*.

the pH of a solution of *cis*-Cr(C₂O₄)₂NCS(OH₂)₂⁻ is increased, there are only two absorbing species present. The logical choice for this second species is the conjugate base, *cis*-Cr(C₂O₄)₂NCS(OH)₂⁻, of *cis*-Cr(C₂O₄)₂NCS(OH₂)₂⁻. The *cis* configuration is assigned because of the similar visible spectra of the two ions.⁴⁻⁶ The equilibrium can be represented by the reaction



(5) K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **5**, 1645 (1966).

(6) J. M. Veigel and C. S. Garner, *ibid.*, **4**, 1569 (1965).

(7) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 434 (1966).

(8) M. Orhavovic and N. Sutin, *ibid.*, **90**, 4286 (1968).

Assuming that Beer's law is valid, that there are only two absorbing species in the solution, and that changes in activity coefficients are negligible, eq 1 and 2 can be

$$K_a \frac{A_b - A}{A - A_a} = [\text{H}^+] \quad (1)$$

$$\text{pH} = \text{p}K_a + \log \frac{A - A_a}{A_b - A} \quad (2)$$

readily derived, where A is the absorbance at a particular $[\text{H}^+]$, A_a is the absorbance at pH 3 (the absorbance of a solution of $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$, and A_b is the absorbance at pH 9 (the absorbance of a solution of $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH})^{3-}$). The absorbances are all extrapolated to zero times. The $[\text{H}^+]$ was derived directly from the measured pH.⁹ Table II

TABLE II
THE ACID DISSOCIATION CONSTANT FOR
 $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ ^a

Run	λ , nm	$\text{p}K_a$	Run	λ , nm	$\text{p}K_a$
1	560	7.18 ± 0.08	4	470	7.20 ± 0.12
2	550	6.99 ± 0.05	5	470	6.78 ± 0.08
3	470	7.13 ± 0.07			$\text{Av } 7.06 \pm 0.18$

^a Unbuffered solutions at $\mu = 2.00$ F (NaNO_3) and $1 \pm 0.5^\circ$. Uncertainties are standard deviations.

gives the results for the $\text{p}K_a$ by fitting the data to eq 1 using a nonlinear least-squares computer program. The data were weighted as $1/[\text{H}^+]^2$. The relatively small standard deviations (12% in the poorest case and 5% in the rest of the cases) indicate that the least-squares fit is reasonably good. The average value of $\text{p}K_a$ at $1.0 \pm 0.5^\circ$ is 7.06 ± 0.18 . Figure 2 is a plot

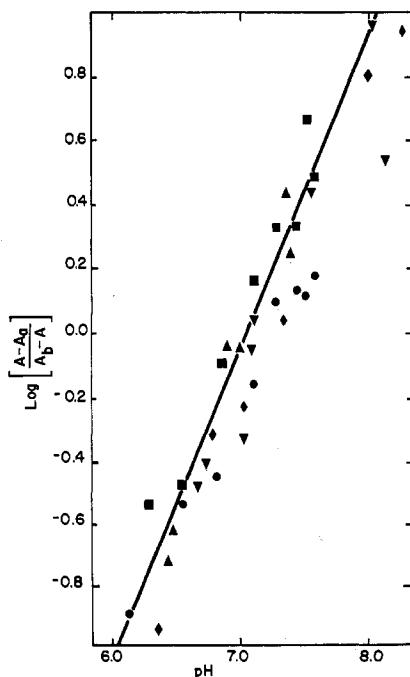
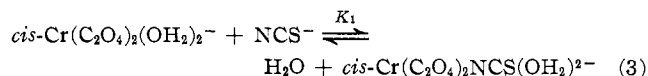


Figure 2.—The plot of eq 2 for the acid dissociation constant of $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ at $1.0 \pm 0.5^\circ$. The line has a slope of 1.00. $\mu = 2.00$ F (NaNO_3) and $[\text{Cr}]_{\text{total}} = 0.8$ mF . Data points: ●, run 1, λ 560 nm; ▲, run 2, λ 550 nm; ■, run 3, λ 470 nm; ◆, run 4, λ 470 nm; ▼, run 5, λ 470 nm.

(9) The $[\text{H}^+]$ was taken as $-\text{antilog pH}$. Since pH is a measurement of the hydrogen ion activity and not concentration, both activity and concentrations were used in the determination of K_a . Thus, K_a is a "mixed" constant in that it is neither a concentration quotient nor an activity quotient.

of pH vs. $\log [(A - A_a)/(A_b - A)]$ using all of the data. The slope of the line is 1.00.

The formation quotient for reaction 3 was determined



at an ionic strength of 1.00 F (NaNO_3) and at pH 3.0. The equilibrium expression for eq 3 is

$$K_1[\text{NCS}^-] = \frac{[\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}]}{[\text{cis-Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2^-]} \quad (4)$$

A plot of $[\text{NCS}^-]$ vs. the right-hand side of eq 4 should be a straight line with zero intercept and a slope of K_1 . Figure 3 is the plot for eq 4 at 25, 35, and 55°. The

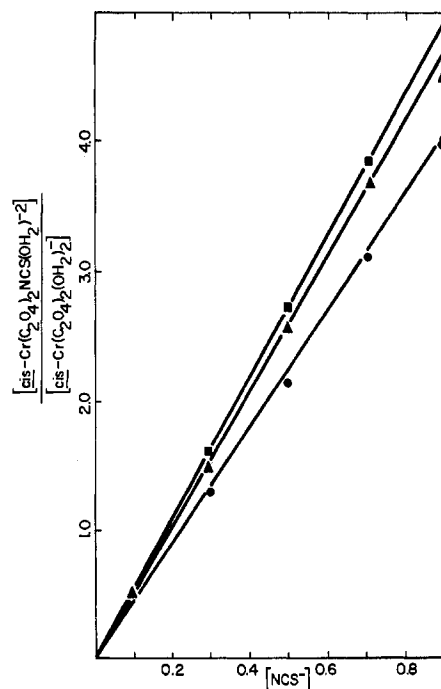


Figure 3.—Plots of eq 4 for the formation quotients for $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ at various temperatures. $\mu = 1.00$ F (NaNO_3), pH is 3, and $[\text{Cr}]_{\text{total}} = 0.10$ F . Data points: ●, 25°; ▲, 35°; ■, 55°.

drawn lines are the least-squares fit of the data. At 25°, the data points represent reaction times of 7, 8, and 15 days. At 35° the reaction times represented are 7 and 19 days. The samples were allowed to react for 8 and 7 days at 45 and 55°, respectively. At 25 and 35° there was no significant variation in K_1 as a function of time. Figure 3 shows that eq 4 adequately describes the data. In Table III are reported the

TABLE III FORMATION QUOTIENTS FOR $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$ ^a			
Temp, °C	K_1, M^{-1}	Temp, °C	K_1, M^{-1}
25	4.50 ± 0.06	45	5.53 ± 0.07
35	5.25 ± 0.12	55	5.60 ± 0.04

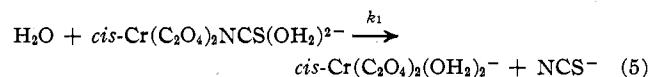
$$\Delta H_1^\circ = 1.2 \pm 0.4 \text{ kcal/mol}, \Delta S_1^\circ = 7.3 \pm 1.4 \text{ cal/deg mol}$$

^a Unbuffered solutions at pH 3.0 and $\mu = 1.00$ F (NaNO_3). Associated uncertainties are standard deviations.

formation quotients for $\text{cis-Cr}(\text{C}_2\text{O}_4)_2\text{NCS}(\text{OH}_2)^{2-}$. These data were derived from a least-squares fit of the data to eq 4. Unit weights were used and the reported uncertainties are standard deviations. The ΔH_1°

and ΔS_1° for the formation of *cis*-Cr(C₂O₄)₂NCS(OH₂)₂²⁻ are also reported. The thermodynamic parameters were calculated from the equation $K_1 = \exp(-\Delta H_1^\circ/RT) \exp(\Delta S_1^\circ/R)$ by a least-squares fit of the data using unit weights.

The rate of aquation of *cis*-Cr(C₂O₄)₂NCS(OH₂)₂²⁻ was determined between 25 and 55° and between pH 2 and pH 3. The ionic strength was maintained at 1.00 *F* (NaNO₃). The overall reaction was shown to be



by observing that the final visible absorption spectrum corresponded to that of *cis*-Cr(C₂O₄)₂(OH₂)₂⁻.

The decrease in absorbance was measured at 412 and 550 nm as a function of time. The pseudo-first-order rate constant was derived by using a generalized least-squares program to fit the absorbance-time measurements to the equation $A = A_\infty + (A_0 - A_\infty)e^{-k_1 t}$ where A is the absorbance at time t , A_∞ is the absorbance after 10 half-lives, A_0 is the initial absorbance at time zero, and k_1 is the pseudo-first-order rate constant. The parameters A_∞ and A_0 were allowed to vary in order to obtain the best fit. Unit weights were used. The final computer-calculated values of A_∞ and A_0 were identical within experimental error with the experimental values. Two or three runs were made at each temperature and the values of k_1 obtained in the different runs and at the two wavelengths were averaged. The results are tabulated in Table IV.

TABLE IV

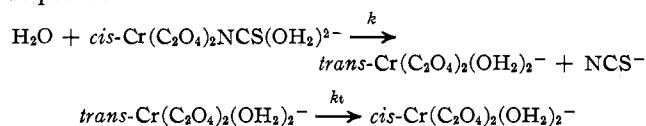
FIRST-ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE AQUATION OF *cis*-Cr(C₂O₄)₂NCS(OH₂)₂²⁻ ^a

Temp, °C	10 ³ k ₁ , sec ⁻¹	Temp, °C	10 ³ k ₁ , sec ⁻¹
25	1.61 ± 0.11	45	15.94 ± 0.04
30	3.16 ± 0.20	50	23.09 ± 0.05
35	4.98 ± 0.11	55	40.86 ± 0.11
40	8.90 ± 0.55		

$\Delta H^* = 20.1 \pm 0.4$ kcal/mol, $\Delta S^* = -13.1 \pm 1.2$ cal/deg mol

^a Unbuffered solutions at pH 2 to pH 3 and $\mu = 1.00$ *F* (NaNO₃). Associated uncertainties are standard deviations.

Even though the overall reaction occurs with retention of configuration, it is possible that the reaction sequence



is the actual one. This is possible because k_2 is

37 times k_1 at 25° and 20 times k_1 at 55°. ¹⁰ This would mean that eq 5 would be the only reaction observed and that k_1 is actually k . In principle, it might be possible to determine if the trans isomer is produced by examining the aquation kinetics of an optically active isomer of *cis*-Cr(C₂O₄)₂NCS(OH₂)₂²⁻. However, this is not possible since the rate constant for racemization of *cis*-Cr(C₂O₄)₂(OH₂)₂⁻ at 25° is about 14 times the observed rate constant for aquation. ¹¹ Therefore, the loss of optical activity could occur by production of *trans*-Cr(C₂O₄)₂(OH₂)₂⁻ or by racemization of *cis*-Cr(C₂O₄)₂(OH₂)₂⁻, and there would be no way to discern between these two reactions.

The activation parameters reported in Table IV were derived from the least-squares fit of the pseudo-first-order rate constant-temperature data to the absolute reaction rate equation, $k_1 = \kappa(kT/h) \exp(\Delta H^*_1/RT) \exp(\Delta S^*_1/R)$, where all symbols have their usual significance and the transmission coefficient, κ , is assumed to be unity. ¹² The ΔH^* and ΔS^* values for the aquation of *cis*-Cr(C₂O₄)₂[(CH₃)₂SO]OH₂⁻ are 17.0 ± 0.8 kcal/mol and -17.6 ± 2.6 cal/deg mol, respectively. ⁵ At present, there are no data for other similar systems.

As with all aquation reactions, the order with respect to water is unknown. Hence, in trying to postulate a mechanism, the true rate law is not known. However, from the similarities of the activation parameters in these two compounds it is very tempting to suggest that the mechanisms might be similar. From the fact that the ΔH^* values are somewhat intermediate and independent of the leaving ligand, an I_d mechanism is proposed tentatively. ¹³ Although it is incorrect to argue positively that the similarity in the ΔH^* values for aquation implies similar mechanisms, it is still very tempting to suggest that they might be.

Acknowledgment.—This research was supported by the East Texas State University Faculty Research Fund and the Robert A. Welch Foundation. The funds to purchase the Cary Model 15 were provided in part by a Frederick Gardner Cottrell Grant administered by Research Corp.

(10) K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **4**, 1120 (1965).

(11) G. L. Welch and R. E. Hamm, *ibid.*, **2**, 295 (1963). In this paper the rate constant for racemization at 25° is reported to be 4.30×10^{-4} sec⁻¹. However, this is the rate constant for the *d* → *dl* conversion, which is the same as that for the *l* → *dl* conversion, and the reported rate constants in this paper are twice what they should be: G. L. Welch, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1963.

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2 ed, Wiley, New York, N. Y., 1961, p 77.

(13) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, Chapter 1.