The values of k, calculated with respect to a value of $d = 7.08$ Å, as the function of the temperature (Table I and Figure 2), and determined in the present work at 11.5, 15.0, 20.0 and 25.0°, fit satisfactoily the Arrhenius plot of Stranks' data[4] obtained by isotopic-exchange measurements. The enthalpy and entropy of activation are 13.4 ± 0.6 kcal/mol and 35 ± 2 eu, respectively. These data are much more accurate than those of Stranks because of the broad temperature range involved.

TABLE I

Range of evaluation	Temp, °C	cm²/sec $10^6D'$	10^6D	$10^6(D' - D)$	$10^{-10}k$, M^{-1} sec^{-1}
$x < 0$	11.5	1.0	0.8	0.2	0.5
	15.0	4.7	3.6	1.1	1.0
	20.0	9.9	7.9	2.0	2.9
	25.0	16.0	8.9	7.1	6.6
$x > 0$	11.5	3.4	2.2	1.2	1.9
	15.0	9.1	5.6	3.5	5.4
	20.0	25.9	13.9	12.0	17.9
	25.0	32.1	9.9	22.2	22.6

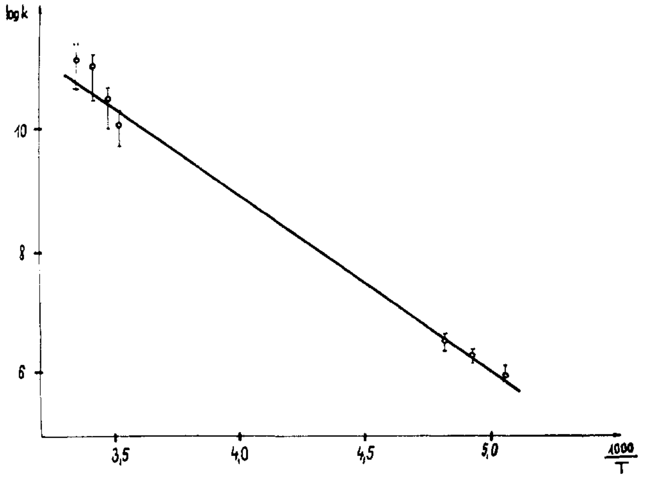

Figure 2.—The Arrhenius plot of the rate constants calculated with $d = 7.08$ Å. The three points on the right-hand side have been determined by isotopic exchange.[3]

It should be mentioned, however, that there is a large uncertainty in calculating with the former value of d. Though this involves the reasonable assumption that the reactants are as close as possible, there are some theoretical models supposing significantly higher distances.[5,6] This possibility is not excluded, and, if true, k would be considerably lower and the activation parameters altered.

A modification of the diffusion constant measurement which does not necessitate the fractioning of the liquid column will probably yield a higher accuracy. This work is in progress in our laboratory.

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Single Crystal Polarized Electronic Spectrum of *trans*-Difluorobis(ethylenediamine)chromium(III) Perchlorate

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The single crystal polarized spectra of a number of tetragonal Co(III) complexes have been measured[1,2] but except for *trans*-$[Cr(en)_2Cl_2]Cl \cdot HCl$[3] no corresponding measurements on tetragonal Cr(III) complexes have been reported. The compound *trans*-$[Cr(en)_2F_2]ClO_4$ is of particular interest because the large splitting of the $^4T_{1g}(a)$ band requires κ $(=Ds/Dt)$ to be large. In an attempt to rationalize the sign and magnitude of κ by applying the empirical molecular orbital theory of Yamatera[4] and McClure[5] it has been predicted that κ is negative and that $\sigma_{F^-} > \sigma_{en}$ for this complex.[6] σ_X is the σ component of the antibonding energy experienced by a d orbital in the field of a ligand X.

We have measured the spectra of single crystals of *trans*-$[Cr(en)_2F_2]ClO_4$ using polarized light over a temperature range down to 4°K. It is now established that a vibronic mechanism[7] provides most of the intensity of the "d–d" transitions in a complex of this type, and it has been shown that the electronic spectra of the related *trans*-bis(ethylenediamine)cobalt complexes can be adequately explained using the effective point group D_{4h}.[2] Assuming a vibronic mechanism, the only spin-allowed "d–d" transitions in Cr(III) forbidden in D_{4h} symmetry are $^4B_{1g} \rightarrow {}^4B_{2g}$ and $^4B_{1g} \rightarrow {}^4A_{2g}$, both in z polarization (*cf.* Table I). Thus, if the orientation of the molecules is favorable, considerable information can be derived from the crystal spectrum of *trans*-$[Cr(en)_2F_2]ClO_4$ even though the crystal structure is not known.

TABLE I

VIBRONIC SELECTION RULES FOR Cr(III) COMPLEXES IN D_{4h} SYMMETRY

Transition	Polarization xy	z
$^4B_{1g} \rightarrow {}^4E_g$	α_{2u}, β_{2u}	ϵ_u
$^4B_{2g}$	ϵ_u	. . .
$^4A_{2g}$	ϵ_u	. . .

The complex *trans*-$[Cr(en_2)F_2]ClO_4$ crystallizes as large needles with each crystal face having extinction directions at 42 and 132° to the needle axis. The spectra of several crystals were measured at room temperature with the vector of polarized light along each extinction direction, and the spectrum of one crystal

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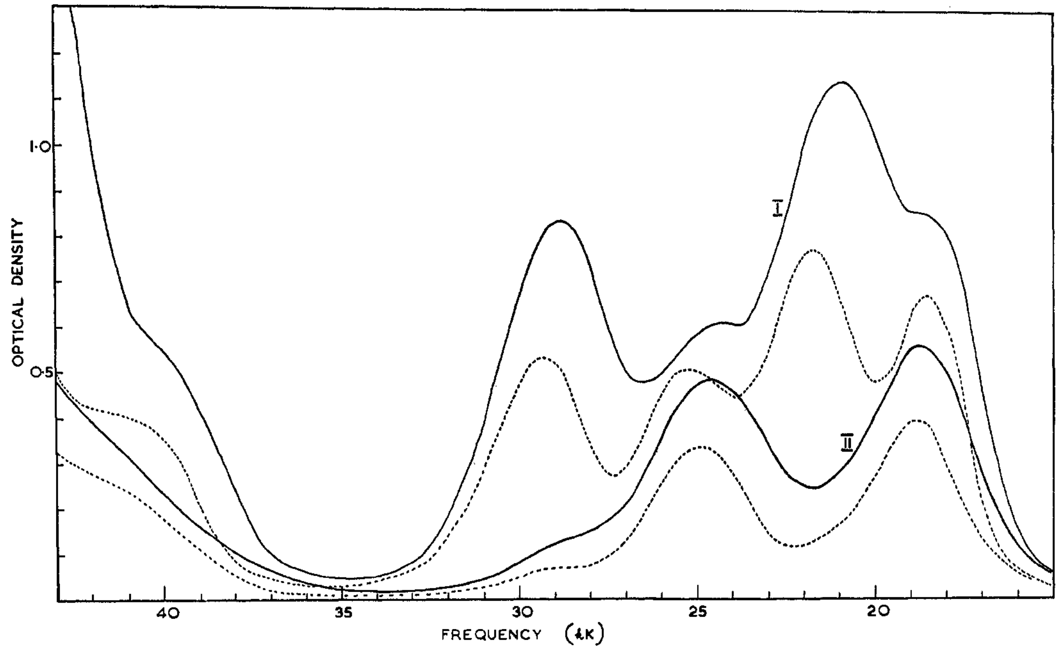

Figure 1.—Spectra I and II with the electric vector being approximately along the molecular *xy* and *z* axes, respectively. The solid line shows the room-temperature spectrum, while the broken line shows that at 4°K.

was measured over a temperature range down to 4°K (*cf.* Figure 1). In every case, bands were observed at 18.5, 21.7, 25.3, and 29.3 kK in one polarization (spectrum I), but the bands at 21.7 and 29.3 kK were almost totally absent in the other polarization (spectrum II). The molecular orientation in these crystals must therefore be very favorable for the measurement of polarized crystal spectra and the vibronic selection rules suggest that the bands at 21.7 and 29.3 kK are due to the transitions $^4B_{1g} \rightarrow {}^4B_{2g}$ and $^4A_{2g}$, with the electric vector being approximately along the molecular *z* axis for spectrum II and in the *xy* plane for spectrum I. The assignment of the components of the $^4T_{2g}$ and $^4T_{1g}$ (a) bands is then unambiguous (*cf.* Table II) and agrees with the previous assignment of Dubicki and Martin.[6] The assignments are further supported by the observed polarization of the shoulder occurring at ~41kK, which is likely to be the[4] A_{2g} component of the $^4T_{1g}$(b) band. The *xy* spectra obtained at six different temperatures from 295 to 4°K were analyzed into gaussian curves using a computer program written by Mr. B.D. Bird of this department. The bands at 18.5 and 25.3 kK showed no temperature dependence in *xy* polarization within experimental error, but those at 21.7 and 29.3 kK decreased markedly in intensity as the temperature was lowered (*cf.* Figure 1) and approximately obeyed the relationship $f = f_0 \coth (h\nu/2kT)$[8] for values of $h\nu \approx 220$ and 275 ± 50 cm^{-1}, respectively. In *z* polarization, however, the intensity of the bands at 18.8 and 25.0 kK followed the coth rule with $h\nu \approx 310 \pm 70$ cm^{-1} for each band. This suggests (*cf.* Table I) that some relatively low-frequency vibrations of ϵ_u symmetry are active in producing intensity but that the vibrational frequencies of α_{2u} and β_{2u} symmetry are of too high an energy for the excited vibrational states of the electronic ground state to be populated at room temperature.

TABLE II

SPECTRAL DATA OF *trans*-[Cr(en)$_2$F$_2$]ClO$_4$[a]

Obsd freq, cm^{-1}		Calcd freq, cm^{-1}[b]	Assignment	
Polarization I	Polarization II			
18,500	18,800	18,822	^4E_g	($^4T_{2g}$)
21,700		21,700	$^4B_{2g}$	($^4T_{2g}$)
25,300	25,000	24,898	^4E_g	($^4T_{1g}$(a))
29,300		29,327	$^4A_{2g}$	($^4T_{1g}$(a))
41,000 sh		40,348	$^4A_{2g}$	($^4T_{1g}$(b))
		43,655	^4E_g	($^4T_{1g}$(b))

[a] Taken at 4°K. [b] Calculated using the matrices of Perumareddi[9] for $Dq = 2170$ cm^{-1}, $Dt = -320$ cm^{-1}, $B = 625$ cm^{-1}, $C/B = 5.5$, and $\kappa = -2.5$.

The observed ordering of the components of the $^4T_{1g}$ (a) band requires κ to be negative in order to fit the experimental energies using the ligand field matrices of Perumareddi.[9] Treating κ and Dt as symmetry parameters and expressing them in terms of the empirical molecular orbital parameters $\delta\sigma$ and $\delta\pi$,[6] we calculate for *trans*-[Cr(en)$_2$F$_2$]ClO$_4$

$$\delta\sigma = \frac{3Dt}{2}(\kappa + {}^5/_4) \approx +600 \text{ cm}^{-1}$$

and

$$\delta\pi = \frac{3Dt}{2}(\kappa - {}^5/_3) \approx +2000 \text{ cm}^{-1}$$

where $\delta\sigma = \sigma_{F^-} - \sigma_{en}$ and $\delta\pi = \pi_{F^-} - \pi_{en}$. These values indicate that the fluoride ion enters into both strong σ and π bonding with the Cr(III) ion and the sign of $\delta\sigma$ suggests that $\sigma_{F^-} > \sigma_{en}$ in this complex.[6]

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In contrast, Yamada's analysis[8] of the single crystal polarized spectrum of *trans*-$[Cr(en)_2Cl_2]Cl \cdot HCl$ requires a small positive value of κ. His spectral data at room temperature can be fitted reasonably well with $\kappa = +^1/_3$ and $Dt = -500\ cm^{-1}$. We then obtain $\delta\sigma \approx -1200\ cm^{-1}$ and $\delta\pi \approx +1000\ cm^{-1}$ which imply that the σ and π bondings of the chloride are considerably weaker than those of the fluoride ion. The spectra of the *trans*-dibromo and *trans*-dichloro complexes are similar[6,10] and the corresponding $\delta\sigma$ and $\delta\pi$ parameters for the bromide ion are not expected to differ very much from the values for the chloride ion. On the other hand the large splitting of the $^4T_{1g}(a)$ band in the *trans*-difluoro complex is also found in the *trans*-dihydroxy complex.[10] Thus in the nature of its bonding to a Cr(III) ion the fluoride has little in common with the other halide ions and instead resembles more closely the hydroxide ion. These results are in accord with the recent work of Glerup and Schäffer,[11] who reached the same conclusions from a systematic study of the solution spectra of *trans*-$[Cr(NH_3)_4X_2]$ ($X = Br^-, Cl^-, F^-, H_2O, OH^-$)

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Oxygen Exchange between Nitric Oxide and Water

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Salts of the anion $N_2O_3^{2-}$ have long been well characterized,[2] and while free $H_2N_2O_3$, or "α-oxyhyponitrous acid,"[3] has never been isolated, this species and its related anions have been postulated as reaction intermediates in some of the older literature of aqueous solution inorganic nitrogen chemistry. Since NO may be taken to be the stoichiometric anhydride of $H_2N_2O_3$, aqueous NO solutions have in the past been assumed to contain this species, an assumption which in turn has been employed in mechanistic interpretations.[4] This view of the status of dissolved NO was bolstered by a report that aqueous NO solutions exhibit conductivities substantially greater than water,[5] and its persistence in more recent literature is illustrated by references to the "natural" (acidic) pH of NO solution.[6] In this study, the nature of aqueous NO has been explored by isotopic exchange, as has been done previously in the case of the apparent anhydride relationship N_2O–$H_2N_2O_2$.[7]

Experimental Section

NO–H_2O exchange experiments were carried out by vacuum-line techniques, employing a cell designed to give high efficiency of mixing of aqueous and gas phases, adapted from a similar cell employed in H_2–NH_3 exchange studies.[8] A charge of H_2O^{18} was outgassed in a vessel other than the reaction cell by a series of repeated freeze–pump–thaw cycles and then distilled into the reaction cell. After temperature equilibration, ^{15}NO was then admitted to the cell at measured pressure, and high speed stirring was begun with a motor-driven horseshoe magnet held externally and in line with an internal magnet, the latter sealed in glass and mounted on and at right angles to a vertical mixing shaft in the cell. The gas phase was sampled at intervals by momentarily interrupting the stirring and turning the main (three-way) stopcock to a position providing communication between the cell and a small dead-end sample volume. In a typical cell design the reaction vessel volume was about 100 ml and sample volume was about 2.0 ml; in a typical experiment the partial pressure of NO was between 100 and 200 Torr, and the charge of H_2O was 10.0 ml.

Gas samples were drawn through an extended helical trap held at Dry Ice temperature and then distilled into sample tubes for subsequent mass spectrometric analysis. The possibility of isotope effect in this sampling method was checked by experiment and found to be absent under the conditions employed. The sample volume and purification line were pumped between sampling operations.

For experiments employing a nonvolatile solute (see below), the cell described in ref 8 could not be used. A simpler cell was therefore employed, in which stirring was carried out by a Teflon-enclosed stirring magnet, sealed inside the cell and turned by a motor-driven magnet located below the cell and its associated constant-temperature bath. Adequate outgassing of the Teflon for these experiments required pumping periods up to 12 hr; the Teflon stirring bar was held out of the aqueous phase by an external magnet during this procedure and during outgassing of the solutions employed. While less efficient than the other cell, it was found to provide adequate mixing of phases for kinetic runs of relatively long half-life.

The oxygen-18-enriched H_2O employed in these experiments (Weizmann Institute) was normalized with respect to deuterium and contained 1.667 atom % ^{18}O (determined by CO_2 equilibration). Nitrogen-15-labeled NO was used in all experiments, and ^{15}NO at about 34% enrichment was synthesized by vacuum-line techniques, employing the quantitative reaction between NO_2^- and I^- in acid medium, starting with $Na^{15}NO_2$ obtained from the Organization National Industriel de l'Azote, Toulouse. The product NO gas was purified by repeated distillations between liquid *n*-pentane and liquid N_2 and by passage over a molecular sieve material.

Nitrogen-15 enrichment permitted direct mass spectrometry on NO without dependence on mass 32, since exchange of oxygen was detected by measurement of the ratio 33/31 in ^{15}NO. A single-collector mass spectrometer was employed (Metropolitan-Vickers), and reported ratios are based in each case on average values obtained from ten or more repeated scans. The ratio

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[1] Department of Chemistry, State University of New York at Stony Brook, Stony Brook, N. Y. 11790; NSF Senior Postdoctoral Fellow, 1964–1965.

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