the Rh–Rh distance is about the same (Table VI). Whether the observed transition energy differences are due mainly to the nature of the distortions at each Rh atom or are attributable to interunit (CNR···CNR) interactions, or some combination of effects, cannot be determined without further study.

Additional evidence that the rotameric conformation influences the relative energy of the $^1A_{2u}$ excited state of these binuclear rhodium(I) isocyanide complexes comes from studies of their emission spectra in fluid solution (Table VII). The relatively high emission quantum yields and short lifetimes (<2 ns) suggest that the emission originates from the same excited state reached in absorption; i.e., the transition is $^1A_{2u} \rightarrow {}^1A_{1g}$. It is interesting that the largest Stokes shifts are observed for the complexes with staggered ground-state conformations, the order being $CNPhCH_3$ (staggered)[20] > 4-bridge ~ TM4-bridge (partially staggered) > bridge (eclipsed). The half-widths of the emission bands also follow the same order.

The intense bands at 318 nm for $Rh_2(bridge)_4{}^{2+}$ and at 313 nm for $Rh_2(TM4\text{-}bridge)_4{}^{2+}$ and $Rh_2(4\text{-}bridge)_4{}^{2+}$ are assigned to the fully allowed $^1A_{1g} \rightarrow {}^1E_u$ ($d_{xz},d_{yz} \rightarrow \pi^*$ CNR) transition. The fact that the position of this band in the various binuclear Rh(I) complexes is close to that in a related monomer (310 nm in $Rh(CN\text{-}t\text{-}Bu)_4{}^+$) suggests that the d_{xz},d_{yz} orbitals on one Rh atom do not interact significantly with those on the other Rh atom. The corresponding singlet–triplet transition, $^1A_{1g} \rightarrow {}^3E_u$, occurs at about 340 nm in the spectrum of each complex. Assignment of this band also follows from the interpretation of the spectrum of $Rh(CNEt)_4{}^+$ given previously by Isci and Mason.[21]

Acknowledgment. We thank Richard Marsh, Wayne Gladfelter, and Andrew Maverick for many helpful discussions. This research was supported by National Science Foundation Grant No. CHE78-10530. The X-ray instrumentation was obtained with the aid of NSF Instrument Grant No. CHE76-05471.

Registry No. $Rh_2(bridge)_4(BPh_4)_2 \cdot CH_3CN$, 73367-40-5; $Rh_2(TM4\text{-}bridge)_4(PF_6)_2 \cdot 2CH_3CN$, 73367-43-8; $[Rh(COD)Cl]_2$, 12092-47-6; $Rh_2(CO)_4Cl_2$, 14523-22-9; $Rh(CN\text{-}t\text{-}Bu)_4{}^+$, 34195-61-4; $Rh(CNPh)_4{}^+$, 56192-48-4; $Rh_2(CN\text{-}t\text{-}Bu)_8{}^{2+}$, 73367-44-9; $Rh_2(4\text{-}bridge)_4{}^{2+}$, 67783-56-6; $Rh_2(CNPhMe)_8{}^{2+}$, 65918-76-5.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes and best fit planes (30 pages). Ordering information is given on any current masthead page.

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(20) It is reasonable to assume that the ground-state structure of $Rh_2(CNPhCH_3)_8{}^{2+}$ does not differ significantly from that of $Rh_2(CNPh)_8{}^{2+}$, the latter possessing a staggered CNPh–CNPh rotameric conformation.[2]

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Notes

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Stereochemistry of the Photolysis of *trans*-$Cr(en)_2F_2{}^+$

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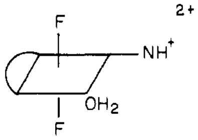
The stereochemical consequences upon photoaquation of Cr(III) complexes have been a central theme of such studies,[1,2] perhaps only slightly less important than the issue of models to identify the leaving group.[3–7] Especially important in this area are the careful experiments of Kirk and co-workers[8,9] on a variety of Cr(III) complexes in which "stereomobility"—a net change in stereochemistry upon photoaquation—is generally observed. However, a number of reactions have been reported in which the net stereochemistry of the reaction is retentive.[6,10–12] (The difference between the apparent and mechanistic stereochemical inversion is discussed by Walters and Linck.[12]) This conclusion was first demonstrated by Pyke and Linck,[10] who claimed the major photoproduct of *trans*-$Cr(en)_2F_2{}^+$ was the isomer of $Cr(en)(enH)(H_2O)F_2{}^{2+}$ produced from thermal aquation[13] of *trans*-$Cr(en)_2F_2{}^+$, presumably **1**. With two recent developments the subject of lack of apparent stereomobility, especially in *trans*-$Cr(en)_2F_2{}^+$, has taken on added importance. These are (1) a theoretical treatment of the stereomobility in Cr(III) complexes,[14] even a specific discussion of the role of fluoride[15] in affecting stereochemistry, and (2) a report indicating that the products of photoaquation on *trans*-$Cr(en)_2F_2{}^+$ are substantially[16] different from **1**. In this note we reexamine the products of photoaquation of *trans*-$Cr(en)_2F_2{}^+$ to establish the stereochemical consequences.



1

Experimental Section

[*trans*-$Cr(en)_2F_2$]ClO_4 was prepared and purified as described previously.[13] Photolysis was carried out either under broad-band (λ >400 nm) irradiation or through a 520-nm interference filter (the latter for quantum yield experiments). The apparatus used has been described.[10] Actinometry was based on Wegner and Adamson's

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Table I. Ion-Exchange Results

		yield of products[a]			H^+-uptake data[a]			abs data[c]	
expt	$10^{-3}[H^+]$, M	1[b]	2	3	obsd	calcd(1)	calcd(2)	$\Delta\bar{A}_{calcd}$	$\Delta\bar{A}_{obsd}$
1	4.0	62	12	5.0	74	75	80	0.0895	0.089
2	2.0	51	10	7.5	68	62	69	0.075	0.079
3	4.0	52	11	6.7	73	62	69	0.082	0.075
4	4.0	50	11	6.6	66	60	68	0.079	0.075

[a] In micromoles. [b] Corrected for thermal product. [c] Calculated from quantity of products isolated after correction for thermal aquation during separation, their respective ε's, and the corresponding quantity of *trans*-$Cr(en)_2F_2^+$ destroyed. Value at 520 nm in a 2-cm cell.

procedure using *trans*-$Cr(NH_3)_2(NCS)_4^-$.[17]

Ion exchange was performed on SP-Sephadex-C-25 resin by using Na^+ as an elutant in dilute (pH 2.5) acid. All separations were performed in a cold room; T = 2–3 °C. A Radiometer Model 51 pH meter was used to monitor hydrogen ion concentration. All spectra were recorded on a Cary Model 14 recording spectrophotometer.

Results and Discussion

Absorbance and pH Studies. The first step in the elucidation of the nature of the photoproducts was to determine the value of the extinction coefficient of products at 520 nm. To do this, we carried out experiments that measured absorbance change and hydrogen ion consumption concurrently. This procedure requires calibration of the pH meter; instead of doing this by addition of base,[16] we used the meter simply as an indicator: a photolyzed solution of *trans*-$Cr(en)_2F_2^+$ was titrated with H^+ until the pH of the photolyzed solution was equal to that of a thermal blank. During pH measurements (done in an ice bath) the solution, which is very poorly buffered, was vigorously stirred with a magnetic stirring bar to prevent buildup of a stagnant layer of solution at the glass–solution interface.[18] In the absence of vigorous stirring slow and irreproducible changes in pH were observed.

The change in absorbance, $\Delta\bar{A}$, at 520 nm, and the $[H^+]$ consumed in photolysis of *trans*-$Cr(en)_2F_2^+$ were measured under various conditions. Experiments with the initial $[H^+]$ varying between 2×10^{-3} and 4×10^{-3} M, with F^- absent or present at 10^{-4} M, under normal or an N_2 atmosphere, and with both broad-band (λ >400 nm) and 520-nm irradiation, showed no effect of these variables. Because any F^- liberated by photolysis of *trans*-$Cr(en)_2F_2^+$ may be titrated by H^+, depending on the pH to which titration occurs and the activity effects pertinent to the equilibrium constant of HF in the solution at hand, a simple titration does not reveal the concentration of products after titration. But two extreme models cover all possibilities: case 1, F^- is titrated. In this case the moles of H^+ titrated into the solution are equal to the moles of products; the change in extinction coefficients, $\Delta\epsilon$, between products and *trans*-$Cr(en)_2F_2^+$ is evaluated from $\Delta\bar{A}$ and the $[H^+]$ consumed to be 27.7 ± 2.3 M^{-1} cm^{-1}. (The error is the standard deviation based on 11 experiments.) Case 2 is that F^- is not titrated, but the ratio of products that have lost F^- to those that have consumed H^+ is approximately 1:10 (see below). With this assumption, $\Delta\epsilon = 25.2 \pm 2.3$ M^{-1} cm^{-1}. Since the value of ϵ_{520} of *trans*-$Cr(en)_2F_2^+$ is 15.6 ± 0.3 M^{-1} cm^{-1} (at 15 °C), these values indicate the extinction coefficient of products is between 40.8 ± 2.6 and 43.3 ± 2.6 M^{-1} cm^{-1}. Because the extinction coefficient of **1** is 42.2 ± 0.3 M^{-1} cm^{-1} at 519.0 nm, the absorbance/hydrogen ion uptake data suggest that **1** is the dominant product.

Ion-Exchange Experiments. In the determination of products of photoaquation, ion-exchange chromatography is a useful method because it removes starting material, and starting material usually contributes greater than 90% of the total chromium and hence strongly influences the spectrum. In our previous report[10] results from ion-exchange experiments were used to examine the photoproducts; some of these experiments have been repeated with an improvement on the older techniques. Instead of using H^+ as an elutant, we have used Na^+ (containing $[H^+] = 2 \times 10^{-3}$ M). This change generated a clean separation of the components *and* reduced H^+-induced aquation of the Cr–F bond.

We observed three, and only three, product bands in the four ion-exchange experiments performed. This differs from our earlier report, on which H^+-induced aquations led to a greater number of apparent photoproducts. Since that earlier report, one of the products reported there has been identified as $Cr(en)(enH)(H_2O)F^{3+}$, which most likely arises from H^+-induced aquation of **1**.

The three bands obtained from Na^+ elutions are **1**, a second substance, **2** (see below), and *cis*-$Cr(en)_2F(H_2O)^{2+}$, **3**. The material **1** obtained from photolysis of *trans*-$Cr(en)_2F_2^+$ is identical with that obtained from thermal aquation. The spectral properties are λ (ϵ, M^{-1} cm^{-1}): for **1** from photolysis, 519 nm (42.4 ± 0.3), 410 (10.2 ± 0.6), 364 (19.0 ± 0.4); for **1** from thermal aquation, 519 nm (42.2 ± 0.3), 410 (9.8 ± 0.4), 364 (18.8 ± 0.3). The second band, **2**, has ion-exchange behavior that demands a dipositive charge; the spectral features of **2** are inconsistent with either *cis*- or *trans*-$Cr(en)_2F(H_2O)^{2+}$. We therefore assign this material to one of the other isomers of **1**. We note it has $\epsilon = 45$ M^{-1} cm^{-1} at 520 nm. The final band is identified as *cis*-$Cr(en)_2F(H_2O)^{2+}$ on the basis of spectral properties.[11,19] The yields of these three materials found in four experiments with broad-band (λ >400 nm) irradiation are given in Table I. The values for the yield of **1** have been corrected for thermal aquation during photolysis and separation.

Note in Table I that the ion-exchange recovered materials duplicate, within experimental error, the measured properties of the photolyzed solution. First, the micromoles of H^+ consumed by photolysis, as determined by the titration procedure given above agrees closely with either the calculated value on the basis of titration of only en [calcd(1) in Table I] or on complete titration of both en and F^- [calcd(2)]. Second, the observed absorbancies of the three ion-exchange separated products, corrected for thermal production of **1**, $\Delta\bar{A}_{calcd}$, accounts for the absorbance difference between sample and blank prior to the separation. Third, the recovered yields of products with their spectra can be used to determine weighted extinction coefficients at the isosbestic points observed during photoaquation. We find λ (ϵ, M^{-1} cm^{-1}): 467.5 nm (20.0), 410 (13.0), 348 (14.3). These values are in satisfactory agreement with the extinction coefficients of *trans*-$Cr(en)_2F_2^+$ at these wavelengths and account for the isosbestic behavior during photolysis. All three of these experiments establish that what occurs during photolysis is correctly determined by the ion-exchange separation: complex **1** accounts for more than 80% of the photoproducts with composition $Cr(en)(enH)H_2OF_2^{2+}$.

Quantum Yields. The H^+ titration technique has been used to redetermine the quantum yield for photolysis of *trans*-$Cr(en)_2F_2^+$ in 4.0×10^{-3} M $HClO_4$ when irradiated with 520-nm

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light. The results of six experiments, when the apparent Φ is plotted vs. fraction of complex photolyzed and extrapolated to zero fraction, yield Φ of 0.35 ± 0.03. As this value is for H^+ uptake, the real quantum yield for disappearance of *trans*-$Cr(en)_2F_2^+$ is equal to or slightly greater than this value depending on how much of the F^- is titrated at a pH of 2.4. This value is lower than reported previously,[10] presumably because of incorrect correction for thermal aquation and H^+-induced processes.

Conclusions. The photoaquation of *trans*-$Cr(en)_2F_2^+$ leads to three products, with **1** the dominant material formed. This material retains the net stereochemistry of the starting material but is still subject to mechanistic stereochemical inversion.[12]

Our results appear to disagree[20] with those of Manfrin et al.;[16] we have only one explanation of this disagreement. In the course of our studies on this system we noted that a solution of *trans*-$Cr(en)_2F_2^+$ has a relatively strong temperature dependence to its absorbance at 520 nm. This amounts to about a 2% change in absorbance between 10 and 20 °C; thus the small spectral differences between photolyzed and unphotolyzed solutions must be made on solutions at the same temperature (as we have done in what is reported herein).

We have examined this phenomenon in sufficient detail to understand its origin in general terms if not in detail. The temperature dependence (for constant absorbance) is more pronounced in the concentrated solutions (short path length) than in dilute ones (long path length). This is, we believe, because ion pairs are the source of the temperature-sensitive absorbancies, and the more concentrated solution causes the greatest number of ion pairs. Photolysis on solutions as concentrated as those used by Manfrin et al. will be subjected to this temperature-dependent absorbancy. However, whatever the cause of difficulty in the absorbance–pH experiments, it is clear that their values of $\Delta\bar{A}$/mol of H^+ consumed are greater than what we find; we are confident of our results because they are verified by ion-exchange separations.

Acknowledgment. We thank Don Dubois for his work on the temperature-sensitive absorbance changes.

Registry No. **1**, 34398-37-3; **2**, 73650-10-9; **3**, 34431-44-2; *trans*-$Cr(en)_2F_2^+$, 24407-74-7.

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[20] From the reported values of Φ_{H^+} and Φ_F of Manfrin et al.[16] and their statement that ϵ of "$Cr(en)_2H_2OH^{2+}$" would have to be 200 M^{-1} cm^{-1} at 520 nm, we calculate that they believe the apparent extinction coefficient of the H^+-consuming products of photolysis of *trans*-$Cr(en)_2F_2^+$ is 53 M^{-1} cm^{-1}.

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Superexchange in Copper(II) Dimers. 1. Synthesis, Characterization, and Magnetic Behavior of the Novel Di-μ-bromo-bis[bromo(dimethylglyoxime)copper(II)], $[CuBr_2(dmgH)]_2$

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The study of magnetic superexchange[2-4] interactions in dimeric copper(II) complexes has recently received increased scientific attention from inorganic chemists.[5-9] This rapidly growing interest has been motivated mainly by the urgent search for a sufficiently sound theory on which to base the explanation of the two types of expected intradimer spin orderings, notably the *ferromagnetic* or triplet ground state with the spins oriented parallel and the *antiferromagnetic* or singlet ground state with the spins oriented antiparallel to each other. So far, correlations of experimental results aimed at assessing sign and magnitude of the superexchange effect in such dimers have been based, unfortunately, essentially on the oversimplified theory of molecular field approximation or Heisenberg–Dirac–Van Vleck (HDVV) model.[10] The tenuous character of this theory, therefore, calls for at least a supplementation by systematic correlations of empirical observations.

Table I. Crystal Data of $[CuBr_2(dmgH)]_2$ and $[CuCl_2(dmgH)]_2$ (Triclinic $P\bar{1}$)

	$[CuBr_2(dmgH)]_2$, $[(C_4H_8O_2N_2)\text{-}CuBr_2]_2$	$[CuCl_2(dmgH)]_2$, $[(C_4H_8O_2N_2)\text{-}CuCl_2]_2$
mol wt	678.96	501.14
a, Å	7.786	7.702 (7.697)[a]
b, Å	8.577	8.161 (8.194)
c, Å	8.262	8.111 (8.120)
α, deg	108.26	108.06 (108.14)
β, deg	68.98	69.14 (69.16)
γ, deg	78.86	78.60 (78.69)
V, Å^3	458.63	424.92 (425.84)
Z, dimers/unit cell	1	1 (1)
d_{calcd}, g/cm^3	2.46	(1.96)
d_{obsd}, g/cm^3	2.45[b]	(1.95)

[a] Values in parentheses are from ref 12. [b] Density determined by flotation methods in $CBr_4/CBrCl_3$.

In the special category of dimeric halo-bridged adducts of copper(II) halides with α,β-dione dioxime ligands, some $CuCl_2$ adducts with a number of glyoxime derivatives have been prepared earlier,[11] but only one member of this category, di-μ-chloro-bis[chloro(dimethylglyoxime)copper(II)] or di-μ-chloro-bis[chloro(2,3-butanedione dioxime)copper(II)], $[CuCl_2(dmgH)]_2$, has been structurally well characterized[12] so far and its magnetic behavior briefly examined.[7,13] Analogous adducts of $CuBr_2$, however, have not been reported hitherto.

In this work, we have synthesized the first member of a $CuBr_2$ addition complex with an α,β-dione dioxime ligand,

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