Synthesis and Magnetic Properties of Copper(II) Complexes Derived from Acetylacetone and Various Alcoholamines

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Some new tetrameric copper(II) Schiff base complexes derived from acetylacetone and various alcoholamines are reported. The magnetic susceptibility data suggest a quintet ground state for all of the complexes. The experimental data were fitted to theoretical models for the various symmetries of the Cu_4O_4 core, viz. C_2, C_s, T_d, and D_{2d}.

Introduction

There is considerable interest in the tetrameric copper(II) Schiff base complex [Cu(acac–ethanolamine)]$_4$ derived from acetylacetone and 2-aminoethanolamine. The complex has a magnetic moment of 1.84 μ_B at room temperature.[3] Bertrand and Kelly have provided the structural basis for understanding the unusual properties of this complex.[4] The structure is of the cubane type and contains pentacoordinated copper(II) and triply bridged alkoxide groups arranged in approximately D_{2d} symmetry with copper–copper distances of 3.006 and 3.259 Å. The complex has been reported to have both antiferromagnetic and ferromagnetic interactions with a singlet ground state.[5] The bridging angle associated with the antiferromagnetic interactions is 97.8°. This angle is close to the crossover angle from antiferromagnetic coupling to ferromagnetic coupling in other copper complexes.[6] The arrangement of the Cu_4O_4 cubane is sensitive to ligand structural changes as evidenced by the magnetic behavior of [Cu(sal–ethanolamine)]$_4$ and [Cu(pyrr–ethanolamine)]$_4$.[7,8] These complexes differ markedly in that they have magnetic properties which suggest a quintet ground state. Recently, evidence has been presented that [Cu(acac–ethanolamine)]$_4$ can exist in two forms depending on preparative conditions.[9] The α form has a singlet ground state whereas the β form has a quintet ground state. The sensitivity of the magnetic properties to ligand structural changes has prompted us to study the effect of substitutents on the ethanolamine part of the molecule.

Experimental Section

Chemicals. Acetylacetone was obtained from Eastman Organic Chemical Co., 2-amino-1-phenylethanol was from Aldrich Chemical Co., and ethanolamine and 2-amino-1-butanol were obtained from Matheson Coleman and Bell. Copper(II) acetate monohydrate and potassium hydroxide were obtained from J. T. Baker.

[Cu(acac–2-amino-1-butanol)]$_4$. Acetylacetone (0.035 mol) was dissolved in 100 mL of anhydrous methanol. 2-Amino-1-butanol (0.035 mol) was added to the solution which was stirred at reflux for 1 h. The resulting yellow solution was slowly added to copper(II) acetate monohydrate (0.0315 mol) in 150 mL of anhydrous methanol. The mixture was stirred at reflux for 1 h and potassium hydroxide (0.063 mol) was added. After refluxing for 18 h the mixture was filtered, yielding a blue powder which was recrystallized from acetone giving blue microcrystals; yield 75%; mp 216–217 °C. Anal. Calcd for Cu(C$_9$H$_{15}$NO$_2$): C, 46.44; H, 6.50; N, 6.02; Cu, 27.30. Found: C, 46.38; H, 6.75; N, 5.89; Cu, 26.72.

[Cu(acac–2-amino-1-phenylethanol)]$_4$. The complex was prepared as above except that a precipitate formed without the addition of base and the blue powder gave blue microcrystals on recrystallization from chloroform; yield 80%; mp 219–219.5 °C. Anal. Calcd for Cu(C$_{13}$H$_{15}$NO$_2$): C, 55.60; H, 5.30; N, 4.98; Cu, 22.63. Found: C, 54.79; H, 5.43; N, 4.75 Cu, 22.34.

[Cu(acac–ethanolamine)]$_4$. The Schiff base derived from acetylacetone and ethanolamine when reacted with copper(II) acetate monohydrate gave two distinct products. A blue product was obtained when a 1:1 mixture of Schiff base and copper(II) acetate monohydrate was refluxed in methanol, and a green product was obtained when

excess ligand was used. Anal. Calcd for Cu(C$_7$H$_{11}$NO$_2$): C, 41.06; H, 5.43; N, 6.84. Found (blue product): C, 41.07; H, 5.38; N, 6.74.

4[Cu(acac–ethanolamine)]·toluene. This complex resulted from the recrystallization of blue [Cu(acac–ethanolamine)]$_4$ from toluene. Anal. Calcd: C, 46.14; H, 5.71; N, 6.15; Cu, 27.92. Found: C, 45.15; H, 5.71; N, 6.09; Cu, 27.49.

Physical Measurements. Magnetic susceptibilities were determined by the Faraday method.[10] All measurements were calibrated with Hg[Co(NCS)$_4$] as the standard. The diamagnetic corrections for the ligand and copper atoms were computed using a standard source.[11] Molecular weight measurements were obtained at 37 °C with a Mechrolab Model 301A vapor pressure osmometer calibrated with benzil. All the complexes are tetrameric in benzene.

Analyses. Copper analyses were obtained on a Sargent-Welch analyzer by plating copper onto a platinum electrode. Carbon, hydrogen, and nitrogen analyses were obtained from PCR, Gainesville, Fla., and Galbraith Laboratories, Knoxville, Tenn. The data were computed on a IBM 360/65 using the D. W. Marquart's maximum-neighborhood method. The experimental susceptibility data were fitted to the theoretical susceptibility equations derived from the HDVV model (for appropriate symmetry) employing a nonlinear least-squares curve-fitting program utilizing $\sum_i (\chi_M(\text{exptl})_i - \chi_M(\text{calcd})_i)_i^2 T_i^2$ as the fitting criterion.[14]

Results and Discussion

Magnetic susceptibilities for the complexes (Table I) show an increase in magnetic moments with a decrease in temperature. This is in contrast to the behavior[9] of α-[Cu(acac–ethanolamine)]$_4$ which shows a decrease in moments with a decrease in temperature. α-[Cu(acac–ethanolamine)]$_4$ has been reported[5,9] to exhibit both antiferromagnetic and ferromagnetic coupling with a singlet ground state. The copper–copper interactions can be determined from the temperature dependence of the magnetic susceptibilities using the Heisenberg–Dirac–Van Vleck model in which the effective Hamiltonian describing the various energy levels with different total spin S' has the form

$$H = -2 \sum_{i>j} J_{ij} S_i S_j$$

The appropriate susceptibility equation for the four-center–spin $^1/_2$ system of symmetry D_{2d} per mole of copper(II) is

$$\chi_m = \frac{N_g{}^2\beta^2}{2kT} \frac{5e^{2x} + e^{-2x} + 2e^{-2y}}{5e^{2x} + 3e^{-2x} + e^{-4x} + 6e^{-2y} + e^{-4y}} + N\alpha \quad (1)$$

where $x = J_L/kT$ and $y = J_S/kT$. The exchange coupling constants J_S (interaction between Cu–Cu shorter distances) and J_L (interactions between the longer distances) were reported[5] by Ginsberg et al. to be −15 and +4 cm^{-1}, respectively. A best-fit procedure for the determination of the various exchange parameters in the theoretical model (eq 1) by Merz and Haase[9] with their data support the results of Ginsberg et al. They obtained $J_S = -17$ cm^{-1} and $J_L = +3.5$ cm^{-1} with a g value of 2.13 and $N\alpha = 60 \times 10^{-6}$ cgs emu. An independent study in our laboratory also corroborated these results. The best-fit procedure using susceptibility data

Table I. Magnetic Susceptibility Data

Complex	Temp, K	$10^6 \chi_M$, cgs emu (per mol of Cu)	μ_{eff}, μ_B
[Cu(acac–ethanolamine)]$_4$· toluene	298.0	1539	1.92
	270.0	1704	1.92
	245.1	1915	1.94
	227.4	2082	1.95
	216.1	2195	1.95
	202.4	2372	1.96
	194.6	2471	1.96
	178.1	2746	1.98
	174.8	2792	1.98
	161.8	3047	1.99
	142.2	3571	2.02
	120.3	4325	2.04
	99.6	5446	2.08
	90.9	6088	2.10
	82.4	6930	2.14
	76.7	7485	2.14
	68.2	8710	2.18
	58.4	10712	2.24
	47.2	14223	2.32
	44.6	15292	2.34
	39.4	17953	2.38
	34.6	21184	2.42
	29.3	26347	2.48
	27.1	29108	2.51
	25.7	30783	2.52
	22.4	36915	2.57
[Cu(acac-2-amino-1-butanol)]$_4$	295.3	1530	1.91
	265.1	1732	1.93
	242.6	1903	1.93
	236.0	1987	1.95
	204.4	2362	1.97
	174.7	2841	2.00
	145.5	3615	2.06
	127.4	4167	2.07
	103.2	5381	2.12
	79.1	7692	2.22
	67.7	9361	2.26
	38.6	19486	2.46
	33.1	25591	2.61
[Cu(acac-1-phenyl-2-aminoethanol)]$_4$	297.1	1369	1.81
	254.8	1593	1.81
	212.4	1910	1.81
	170.3	2387	1.81
	129.9	3113	1.81
	109.7	3705	1.81
	78.0	5307	1.83
	60.7	6925	1.84
	47.4	9195	1.88
	32.0	14410	1.93

Figure 1. Magnetic susceptibility data for [Cu(acac–ethanolamine)]$_4$·2C$_6$H$_6$. In all figures circles represent the experimental susceptibility values, solid lines calculated curves, and crosses the inverse susceptibility values.

Figure 2. Magnetic susceptibility data for [Cu(acac–ethanolamine)]$_4$·C$_6$H$_5$CH$_3$.

collected in our laboratory have the exchange parameters in eq 1 as $J_S = -15.6$ cm^{-1}, $J_L = +3.8$ cm^{-1}, $g = 2.12$, and $N\alpha = 60 \times 10^{-6}$ cgs emu. All of these results agree with a singlet ground state for the green α-[Cu(acac–ethanolamine)]$_4$ with coppers in a Cu$_4$O$_4$ cubane core arranged approximately in D_{2d} symmetry. Recrystallization of [Cu(acac–ethanolamine)]$_4$ from toluene resulted in a blue material analyzed as [Cu-(acac–ethanolamine)]$_4$·C$_6$H$_5$CH$_3$ and has magnetic properties similar to those of the β-[Cu(acac–ethanolamine)]$_4$·2C$_6$H$_6$ complex[9] which has ferromagnetic interactions. However the magnitudes of the coupling constants were not ascertained since Merz and Haase expressed their inability to suggest an appropriate theoretical model which could give a good fit with the experimental data. On the other hand we obtained reasonably good fits (Figures 1 and 2) for β-[Cu(acac–ethanolamine)]$_4$·2C$_6$H$_6$ and [Cu(acac–ethanolamine)]$_4$·C$_6$H$_5$CH$_3$. The susceptibility data for the former were taken from ref 9 and the data for the latter were obtained in our
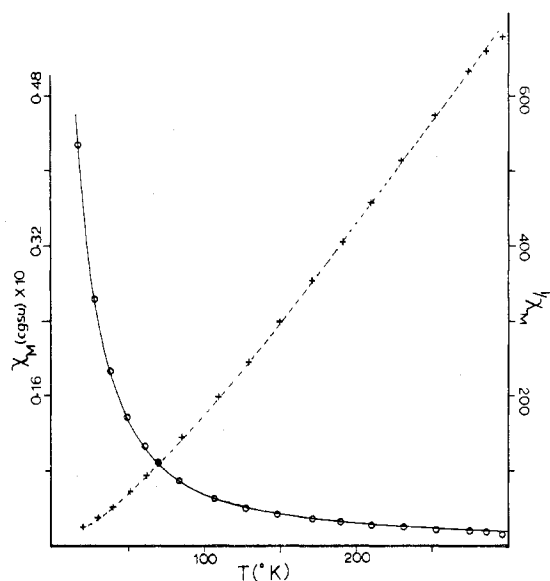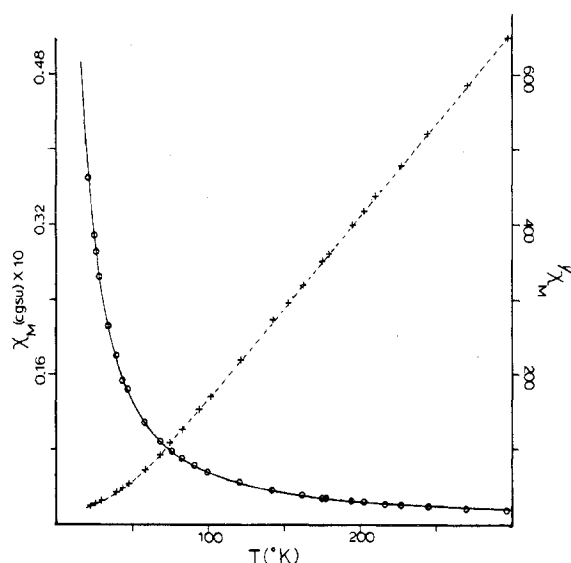
laboratories. The fits could be obtained by using eq 1 but with J_S and J_L both being positive. The results indicate that a net ferromagnetic interaction results on each face of the cube (approximate) in spite of the fact that some of the Cu–O–Cu angles are greater than the crossover angle. Justification of these results lies in the fact that in β-[Cu(acac–ethanolamine)]$_4$·2C$_6$H$_6$ a Cu–O–Cu bridging angle[12] of 105°, which gives rise to an antiparallel exchange pathway, has a Cu–O–Cu bridge with an angle of 90° opposite to it which is expected to favor a parallel pathway. The two opposing pathways on a face of the cube can contribute to a net ferromagnetic effect. The success of the use of positive coupling constants reflects the dominance of the contribution of the parallel pathway over the antiparallel pathway of exchange in this case. The other theoretical models appropriate for T_d, C_S, and C_2 symmetries of the Cu$_4$O$_4$ core were also considered for both of these complexes. The fitting procedure gave satisfactory results only below 150 K (Table II).

In order to study the effects of substitution on the five-membered part of the chelate ring in tetranuclear systems we

Table II

Compd	Sym of Cu_4O_4 core	J (cm^{-1}) and g values	10^2R^a
α-[Cu(acac–ethanolamine)]$_4$	D_{2d}	$J_+ = 2.8, J_- = 17.0, g = 2.13$	0.2
β-[Cu(acac–ethanolamine)]$_4$·$2C_6H_6$	D_{2d}	$J_+ = 15.2, 9.8, g = 2.13$	0.4
	C_s	$J_1 = 16.3, J_2 = 15.3, J_3 = 12.9, J_4 = 9.9, g = 2.13$	0.46^b
	C_2	$J_1 = 19.2, J_2 = 19.1, J_3 = 10.1, J_4 = 9.8, g = 2.13$	0.67^b
[Cu(acac–ethanolamine)]$_4$·toluene	D_{2d}	$J_+ = 12.0, 11.9, g = 2.14$	0.7
	C_s	$J_1 = 12.5, J_2 = 12.5, J_3 = 13.8, J_4 = 11.0, g = 2.12$	1.3^b
	C_2	$J_1 = 12.5, J_2 = 12.5, J_3 = 12.2, J_4 = 12.0, g = 2.13$	1.2^b
[Cu(acac–2-amino-1-phenylethanol)]$_4$	D_{2d}	$J_+ = 4.83, J_- = 0.1, g = 2.01$	0.21
	T_d	$J_+ = 5.99/2, g = 2.01$	0.25
[Cu(acac–2-amino-1-butanol]$_4$	T_d	$J_+ = 36.5/2, g = 2.06$	0.6
	D_{2d}		c

^{a} $R = [\Sigma(\chi_{obsd} - \chi_{calcd})^2/\Sigma\chi_{obsd}^2]^{1/2}$. ^{b} All J's are positive and the fitting is unsatisfactory above 150 K. ^{c} Does not give a satisfactory fit.
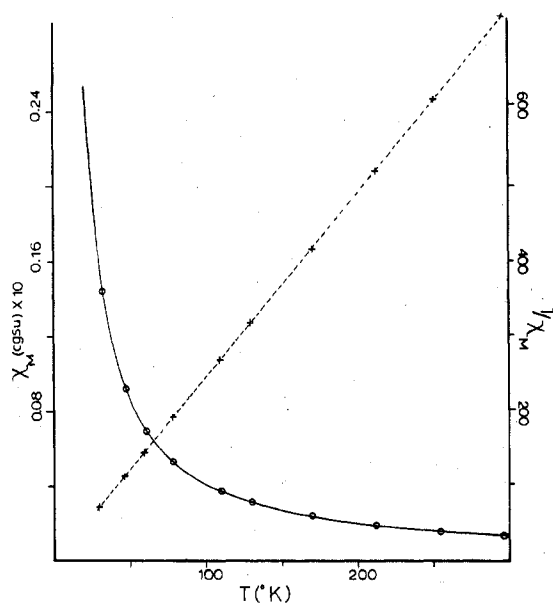

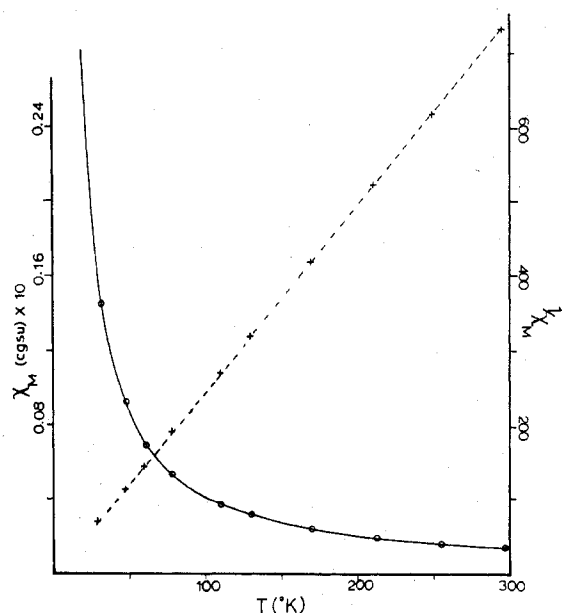**Figure 3.** Magnetic susceptibility data for [Cu(acac–1-phenyl-2-aminoethanol)]$_4$.

Figure 4. Magnetic susceptibility data for [Cu(acac–1-phenyl-2-aminoethanol)]$_4$.

synthesized [Cu(acac–2-amino-1-phenylethanol)]$_4$ and [Cu(acac–2-amino-1-butanol)]$_4$. The susceptibility data for [Cu(acac–2-amino-1-phenylethanol)]$_4$ (Table I) are suggestive of a quintet ground state. Fitting procedures using a D_{2d} model (eq 1) yield an excellent fit (Figure 3) with $J_S \approx -0.003$ cm^{-1} and $J_L = +4.83$ cm^{-1}. However a T_d model[13] (eq 2) also

$$\chi_M = \frac{N\beta^2g^2}{2kT}\frac{J + 3x^2}{5 + 9x^2 + 2x^3} + N\alpha \quad \text{(per mol of Cu(II))} \quad (2)$$

$$x = e^{-2J/kT}$$

provides a close agreement between experimental and calculated susceptibility values (Figure 4) with $2J = +5.99$ cm^{-1}. These results suggest that structurally (Cu_4O_4 core only) this complex is intermediate between the α and β forms of [Cu(acac–ethanolamine)]$_4$. The in-plane Cu–O bonds are shorter than the out-of-plane Cu–O bonds in the α form whereas in the β form the previously defined out-of-plane bonds are shorter than the in-plane bonds. Thus the axis of the square pyramid of copper ion is changed in going from the α form (out of plane) to β form (in plane). The complex [Cu(acac–2-amino-1-butanol)]$_4$ exhibits a sharp increase in magnetic moments with decrease in temperature (Table I) indicating larger ferromagnetic interactions. A good agreement (Figure 5) between the experimental and calculated values could be obtained only for the T_d model (eq 2; Table II). These results can be rationalized in view of the foregoing
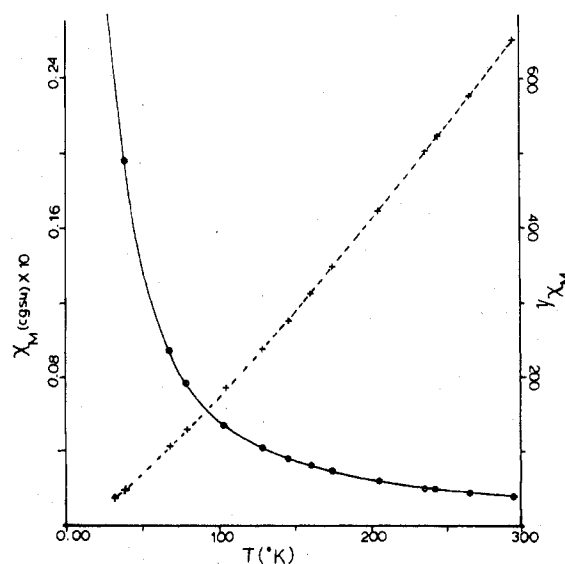

Figure 5. Magnetic susceptibility data for [Cu(acac–2-amino-butanol)]$_4$.

discussion.

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Photochemistry of *trans*-Difluorobis(ethylenediamine)chromium(III)

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The photochemical behavior of *trans*-Cr(en)$_2$F$_2$$^+$ in aqueous solutions (pH ~3) has been investigated. Regardless of the excitation wavelength (254, 365, 530 nm), the irradiation of the complex causes two photoreactions, i.e., the release of F$^-$ ions and the consumption of H$^+$ ions. The latter photoreaction is due to the detachment of one ethylenediamine end from the metal, followed by the protonation of the free amine group. For this photoreaction, which is predominant at each one of the irradiation wavelengths, spectrophotometric analyses have shown that at least a noticeable fraction of the product must have the two F$^-$ ions cis to one another. The quantum yields at 254, 365, and 530 nm are 0.15, 0.22, and 0.20 for ethylenediamine detachment and 0.030, 0.030, and 0.020 for F$^-$ release. The photochemical behavior of the complex is compared to that of analogous complexes and the role played by the various excited states in determining the photochemical behavior is discussed.

Introduction

The photochemistry of Cr(III) complexes continues to be a very important area of research since it offers unusual opportunities to investigate both the role played by the various excited states and the chemical mechanism of the observed photoreactions. The earlier work in this field has been summarized and discussed by several authors.[1-3] Most of the recent investigations have dealt with mixed-ligand Cr(III) complexes[4-17] with the aim of elucidating the directional nature of the ligand labilization, the wavelength dependence of the observed photoreactions, and the stereochemical course of the photoreactions. In the meantime numerous theoretical models have appeared[18-23] in an attempt to account for the experimental results and predict the photochemical behavior.

trans-Cr(en)$_2$F$_2$$^+$ is an important member within the family of the mixed-ligand Cr(III) complexes because of its spectroscopic properties.[24-26] Experiments carried out by Pyke and Linck[4] using 520-nm excitation have in fact indicated that the photochemical behavior of this complex is different from that of the other *trans*-Cr(en)$_2$X$_2$$^+$ complexes.[5,11,17] This paper reports a quantitative investigation of the photochemical behavior of *trans*-Cr(en)$_2$F$_2$$^+$ at three different excitation wavelengths.

Experimental Section

Materials. *trans*-Difluorobis(ethylenediamine)chromium(III) perchlorate, *trans*-[Cr(en)$_2$F$_2$]ClO$_4$, was prepared by the method of Vaughn et al.[27] and recrystallized three times from acidic water. Anal. Calcd for Cr(C$_2$H$_8$N$_2$)$_2$F$_2$ClO$_4$: C, 15.52; H, 5.21; Cl, 11.45; Cr, 16.79; F, 12.27; N, 18.09. Found:[28] C, 15.40; H, 5.18; Cl, 11.38; Cr, 17.03; F, 12.26; N, 17.99. The absorption spectrum of the complex was in excellent agreement with that reported in the literature.[29] All of the other chemicals used were of reagent grade.

Apparatus. Radiations of 254, 365, and 530 nm were obtained as previously described.[30] The intensity of the incident light, which was measured by means of ferric oxalate[31a] or reineckate[31b] actinometers,

was of the order of 10^{-7} N$h\nu$/min at each one of the nominal wavelengths used. The fraction of absorbed light was calculated from the optical density of the irradiated solutions. The reaction cells were standard spectrophotometric cells (thickness, 1 cm; capacity, 3 mL) housed in a thermostated cell holder. The absorbance measurements and the recording of the spectra were performed with a Shimadzu QV-50 and a Perkin-Elmer 323 spectrophotometer. pH measurements were made by a Knick KpH 34 pH meter equipped with an Ingold Lot-type combined microelectrode. The same pH meter was used as a potentiometer for determining the concentration of F$^-$ ions by means of an Orion Model 96-09 combined fluoride electrode.

Procedure. A weighted amount of the complex was dissolved in a water solution containing 2×10^{-3} M HClO$_4$ and 1×10^{-4} M F$^-$ ions. The complex concentration was 5×10^{-2} M in all cases. The reaction cell was filled with a freshly prepared solution and then placed in the thermostated cell holder of the irradiation equipment. All the experiments were carried out at 10 °C unless otherwise noted. A sample of the same solution was maintained in the dark at the same temperature in order to provide control for the thermal reactions. No more than 10% of the reactant was decomposed, in order to avoid secondary photochemical reactions. A stream of purified nitrogen was used for stirring the irradiated solution. pH measurements were directly performed during irradiation. Potentiometric (F$^-$) and spectrophotometric measurements were performed after suitable irradiation periods.

Analytical Methods. The detachment of amine groups from the complex was followed by means of pH measurements. For each experiment, the pH changes resulting from irradiation were converted into changes in H$^+$ concentration by means of a ΔpH vs. Δ[H$^+$] calibration plot, obtained by adding known amounts of base to a portion of the same solution maintained in the dark. The concentration of F$^-$ ions present in the irradiated solutions was measured potentiometrically with the F$^-$ selective electrode. The potentiometric signals were converted into changes of the F$^-$ concentration using a Δmv vs. Δ[F$^-$] calibration plot obtained at the actual pH of the solution.

Results

Thermal Behavior. Before studying the photochemical behavior, the thermal reactivity of the complex was briefly