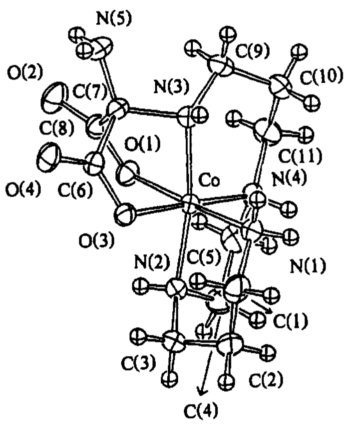

Figure 2. ORTEP representation of a Δ-isomer of $\mathbf{2}^+$. Thermal ellipsoids are drawn at the 50% probability level.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[Co(p\text{-}3,2,3\text{-tet-AM})]NO_3{\cdot}H_2O$ (**2b**)

(a) Bond Lengths			
Co–O(1)	1.928 (1)	Co–O(3)	1.929 (1)
Co–N(1)	1.965 (1)	Co–N(2)	1.965 (1)
Co–N(3)	1.962 (1)	Co–N(4)	1.959 (1)
O(1)–C(8)	1.289 (2)	O(2)–C(8)	1.226 (2)
O(3)–C(6)	1.291 (2)	O(4)–C(6)	1.225 (2)
N(3)–C(7)	1.507 (2)	N(5)–C(7)	1.424 (2)
C(6)–C(7)	1.543 (2)	C(7)–C(8)	1.548 (2)
(b) Bond Angles			
O(1)–Co–O(3)	89.63 (5)	O(1)–Co–N(1)	177.28 (6)
O(1)–Co–N(2)	88.68 (6)	O(1)–Co–N(3)	83.15 (5)
O(3)–Co–N(1)	89.26 (1)	O(3)–Co–N(2)	91.64 (5)
O(3)–Co–N(3)	82.97 (5)	O(3)–Co–N(4)	177.08 (5)
N(1)–Co–N(2)	93.84 (6)	N(2)–Co–N(3)	170.22 (6)
N(2)–Co–N(4)	85.77 (6)	N(3)–Co–N(4)	99.40 (6)
N(3)–C(7)–N(5)	113.4 (1)	N(3)–C(7)–C(6)	104.2 (1)
N(3)–C(7)–C(8)	103.9 (1)	N(5)–C(7)–C(6)	114.9 (1)
N(5)–C(7)–C(8)	115.1 (1)	C(6)–C(7)–C(8)	104.1 (1)

aminoethyl)-*N*-(6-amino-4-azahexyl)-α,α-diaminomalonato)]$^+$ (95.2 ppm),[7] which contains the new C–N bond between the α-carbon and a secondary amino group of the 2,3,2-tet ligand. The configuration of the 3,2,3-tet moiety of the hexadentate ligand in $\mathbf{3}^+$ is expected to be cis-β since in a cis-α configuration the AM^{2-} moiety in the condensed ligand should be inevitably located in the opposite position of the secondary amino groups in the 3,2,3-tet, as shown in Figure 1, thus making the formation of the new C–N bond impossible.

A single-crystal X-ray analysis confirmed the molecular structure of **2b**. A perspective view of a Δ-isomer of complex cation $\mathbf{2}^+$ is shown in Figure 2. Selected bond lengths and angles are cited in Table III. The 3,2,3-tet moiety in the condensed ligand of **2b** was found to be a cis-β configuration, as observed in the 2,3,2-tet system: the conformation of both of the two six-membered chelate rings is the chair form; that of the five-membered ring is δ in the Δ-isomer. The geometry around the α-carbon of the AM moiety is approximately tetrahedral and the bond length of the newly formed C–N bond (N(3)–C(7)) is 1.507 (2) Å, which lies in the normal range for those of C(sp^3)–N bonds.[11] Conversely, the bond length between the α-carbon (C(7)) and a nitrogen (N(5)) of an uncoordinated amino group is shortened to 1.427 (2) Å, similar to those of C–N bonds for aniline derivatives. This feature is common for α-diamine complexes derived from AM^{2-} and Co(III)–polyamine complexes.[7b] The newly formed α-diamine linkage imposes severe distortion on the octahedral geometry around the cobalt center (N(2)–Co–N(3), 170.22 (6)°). In addition, unlike $\mathbf{4}^+$ and $\mathbf{5}^+$, no hydrogen bonding around the nitrogen atom N(5) of the uncoordinated amino group was found in the unit cell of **2b**.[6,7b]

The regioselective C–N bond formation has been reported in the reaction of aminoacetaldehyde with Co(III)–tetraamine complexes such as $[CoCl_2(tren)]^+$.[5,12] In those cases, the regioselectivity was attributed to the trans effect of the chloride ligand in a starting complex. Although, the reason for the regioselectivity regulated by the counteranion of $\mathbf{1}^+$ and dioxygen in our system is still under investigation, the reactions under air and an inert atmosphere appear to proceed via different pathways regarding the reaction of **1b**. Apparently, under an inert atmosphere, an electron transfer from AM^{2-} to the Co(III) ion should occur to form a putative cobalt–iminomalonato intermediate.[7,9,13,14] In contrast, under air a photochemical dioxygen activation probably occurs for the oxidation of AM^{2-}.

Thus the present observations suggest to us the importance of selection of counterions, ligands, and reaction conditions when we use metal complexes as catalyst or mediators to regulate reactions.

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Supplementary Material Available: Tables listing experimental details for X-ray crystallography, anisotropic thermal parameters, positional parameters of hydrogen atoms, and complete bond lengths and angles of $[Co(p\text{-}3,2,3\text{-tet-AM})]NO_3{\cdot}H_2O$ (**2b**) and a figure showing a PLUTO drawing with the complete atom-labeling scheme (9 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Laser Flash Photolysis and Pulse Radiolysis of Aqueous Solutions of the Fluoroxysulfate Ion, SO_4F^-

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The fluoroxysulfate ion, SO_4F^-, is the only known ionic hypofluorite.[1] It is a very strong oxidant capable of oxidizing water, but the rate of its reaction with water is sufficiently low to allow studies of its chemistry in aqueous solution.[2] Aqueous fluoroxysulfate appears to react primarily as a 1-electron oxidant, and an F atom transfer mechanism has been proposed to account for many of its reactions.[2] The present work is a study of the laser flash photolysis and pulse radiolysis of aqueous solutions of SO_4F^-.

Results and Discussion

Solutions containing SO_4F^- in concentrations between 6×10^{-4} and 3.6×10^{-3} M and $HClO_4$ in concentrations up to 1 M were laser-flash-irradiated with light of wavelength 193 nm. Upon irradiation, an instantaneous increase of transient absorbance was observed in the wavelength region 290–550 nm. Figure 1 shows a plot of the optical absorbance 30 ns after the laser pulse as a

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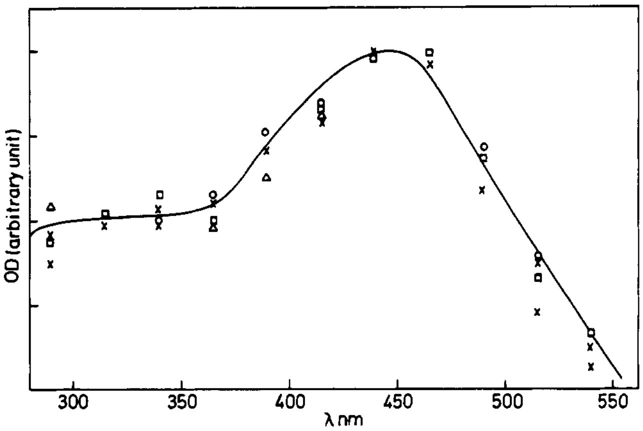

Figure 1. Full curve: spectrum of SO_4^- from ref 3. Points showing the absorbance measured at the end of the laser pulse, normalized to the value at 450 nm: (△) $[HClO_4] = 0$; (□) $[HClO_4] = 10^{-3}$ M; (×) $[HClO_4] = 10^{-2}$ M; (○) $[HClO_4] = 1$ M.

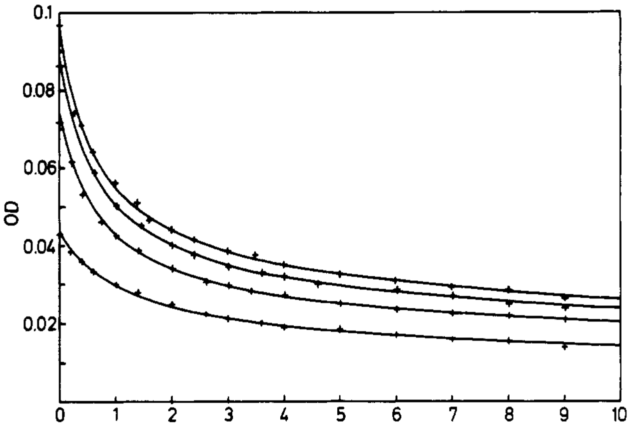

Figure 2. Absorbance of SO_4F^- solutions containing 0.01 M $HClO_4$ at 465 nm as a function of time after laser flash irradiation with light of wavelength 193 nm. From below, $[SO_4F^-] = 6.0 \times 10^{-4}$, 1.2×10^{-3}, 2.4×10^{-3}, and 3.6×10^{-3} M; + = experimental points; full curves were computed for $\epsilon_{465}(SO_4^-) = 1500$ M^{-1} cm^{-1},[4] $k_3 = 4.5 \times 10^8$ M^{-1} s^{-1}, $k_4 = 6 \times 10^9$ M^{-1} s^{-1}, and from below, $k_5 = 1.0 \times 10^{10}$, 1.05×10^{10}, 0.95×10^{10}, and 0.90×10^{10} M^{-1} s^{-1} (see text).

function of wavelength and concentration of $HClO_4$. No change of the spectrum with $HClO_4$ concentration was observed. In the figure, the measured spectrum is compared with that of the sulfate radical ion, SO_4^-, reported in the literature.[3] The agreement is satisfactory, and we assign the transient absorbance to SO_4^- formed in reaction 1

$$SO_4F^- \xrightarrow{h\nu} SO_4^- + F \qquad (1)$$

The decay of the transient absorbance at 465 nm is shown in Figure 2 for SO_4F^- concentrations of 6×10^{-4}, 1.2×10^{-3}, 2.4×10^{-3} and 3.6×10^{-3} M in 0.01 M $HClO_4$. Taking the extinction coefficient of SO_4^- at 465 nm equal 1500 M^{-1} cm^{-1},[4] the kinetics of the decay were found to agree with the mechanism

$$F + H_2O \rightarrow HF + OH \qquad k_2 > 10^8\ s^{-1} \qquad (2)$$

$$2SO_4^- \rightarrow S_2O_8^{2-} \qquad k_3 = 4.4 \times 10^8\ M^{-1}\ s^{-1}\,{}^{3} \qquad (3)$$

$$2OH \rightarrow H_2O_2 \qquad k_4 = 6 \times 10^9\ M^{-1}\ s^{-1}\,{}^{5} \qquad (4)$$

$$SO_4^- + OH \rightarrow HSO_5^- \qquad (5)$$

if k_5 is taken to be $(0.95 \pm 0.08) \times 10^{10}$ M^{-1} s^{-1}.

Calculation of the wavelength of the absorbance maximum, λ_{max}, for F atoms in water, made by a method analogous to that used for Cl, Br, and I atoms,[6] gives $\lambda_{max} \sim 370$ nm. The fact that the present laser flash photolysis data can be accounted for by assuming that only equal amounts of SO_4^- and OH are present in the solution after irradiation suggests $k_2 > 10^8$ s^{-1}. In contrast, Cl and Br atoms are readily observed after laser flash photolysis of aqueous ClO^- and BrO^-.[7] This is in accordance with the fact that the change in standard Gibbs energy, $\Delta G°$, for the reactions

$$Cl + H_2O \rightarrow H^+ + Cl^- + OH \qquad (6)$$

$$Br + H_2O \rightarrow H^+ + Br^- + OH \qquad (7)$$

are positive, 31 and 78 kJ mol^{-1}, respectively,[8-10] whereas $\Delta G°$ for

$$F + H_2O \rightarrow HF + OH \qquad (8)$$

is negative, −100 kJ mol^{-1}.[10,11]

In pulse radiolysis of neutral initially O_2-free solutions containing SO_4F^- in concentrations varying from 2.5×10^{-4} to 6×10^{-3} M, only the SO_4^- radical was seen. The same yield and decay kinetics were observed by irradiating O_2-free $S_2O_8^{2-}$ solutions. Subsequent to the primary radiolytic process

$$H_2O \rightarrow e_{aq}^-,\ OH,\ H,\ H_2O_2,\ H_2 \qquad (9)$$

SO_4^- radicals are formed from $S_2O_8^{2-}$ by the reaction

$$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^- + SO_4^{2-} \qquad (10)$$

while the OH radical does not react with $S_2O_8^{2-}$. Consequently we suggest that the formation of SO_4^- radicals upon electron irradiation of SO_4F^- solutions takes place via an analogous reaction

$$SO_4F^- + e_{aq}^- \rightarrow SO_4^- + F^- \qquad (11)$$

and that the decay of the SO_4^- radicals takes place by reactions 3–5 in both SO_4F^- and $S_2O_8^{2-}$ solutions. The experiments imply that the OH radicals, formed in reaction 9, react very slowly with SO_4F^- ($k < 10^6$ M^{-1} s^{-1}). Calculations of k_5 from the pulse radiolysis experiments were made for 20–50 Gy, using an extinction coefficient of 1600 M^{-1} cm^{-1} for SO_4^- at 450 nm.[4] The average value, $k_5 = (1.0 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}, is in agreement with the laser flash photolysis experiments.

SO_4^- radicals were also observed in solutions containing perchloric acid. The rate constant for reaction of H atoms with SO_4F^-

$$SO_4F^- + H \rightarrow SO_4^- + HF$$
$$k_{12} = (6 \pm 2) \times 10^8\ M^{-1}\ s^{-1} \qquad (12)$$

was estimated in the following way. Air-free solutions containing 1.2×10^{-3}, 3.8×10^{-3} and 6.0×10^{-3} M SO_4F^- in 0.1 M $HClO_4$ were irradiated with a dose of 67 Gy approximately 3 min (3.07, 3.20 and 2.45 min) after preparation. The concentration of molecular oxygen formed by the thermal decomposition of SO_4F^- was calculated by taking the rate constant for the decomposition to be 7×10^{-4} s^{-1} and the yield of O_2 to be 36% of the amount of SO_4F^- decomposed.[2]

Assuming $k_{11} = 2 \times 10^{10}$ M^{-1} s^{-1} and using $k_5 = 1 \times 10^{10}$ M^{-1} s^{-1}, the literature value[3] for k_3, and $k_{13} = 1 \times 10^{10}$ M^{-1} s^{-1} [17]

$$H + SO_4^- \rightarrow HSO_4^- \qquad (13)$$

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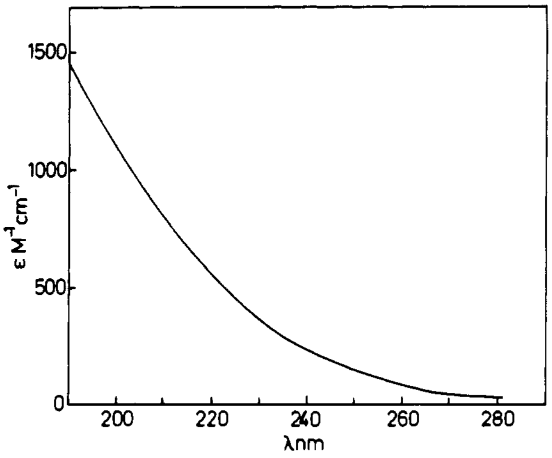

Figure 3. Spectrum of SO_4F^- in neutral aqueous solution.

we find by computer simulations[18,19] of the SO_4^- concentration as a function of time $k_{12} = (6 \pm 2) \times 10^8$ M^{-1} s^{-1}.

In conclusion, our measurements indicate that the primary photochemical process is a homolytic breakage of the fluorine–oxygen bond (reaction 1), followed by hydrolysis of the fluorine atom produced (reaction 2). The pulse radiolytic measurements of SO_4F^- solutions indicate that reaction of SO_4F^- with the hydrated electron also entails rupture of the fluorine–oxygen bond (reaction 11). The primary process 1 and reaction 11 are thus analogous to the corresponding processes undergone by hypochlorite and hypobromite.[5,7,12] And finally, it was found in pulse radiolysis of acidic solutions that O–F bond rupture could also result from reaction of SO_4F^- with the hydrogen atom (reaction 12).

Experimental Section

The apparatus for pulse radiolysis and laser flash photolysis was essentially the same as described previously.[13-15] The pulse width was 0.5 μs. Dosimetry for pulse radiolysis was made with the hexacyanoferrate(II) dosimeter ($\epsilon_{420}(Fe(CN)_6^{3-}) = 1000$ M^{-1} cm^{-1}, $G(Fe(CN)_6^{3-}) = 5.9$). Other G values (yields per 100 eV absorbed) were taken to be $G(e_{aq}^-) = G_{OH} = 2.8$ and $G_H = 0.55$. All aqueous solutions were prepared from triply distilled water. The gases were ultrahigh-purity grade. Perchloric acid used in the laser flash photolysis experiments was double-vacuum-distilled from Vycor (G. Frederick Smith). Cesium fluoroxysulfate (97–98%, assayed iodometrically) was prepared as described elsewhere by fluorination of aqueous cesium sulfate.[16] Other materials were commercial products of reagent grade. Fluoroxysulfate concentrations in aqueous solution were determined by addition of ClO_2^-, followed by spectrophotometric determination of the ClO_2 formed.[2] The rate constant for the decomposition of fluoroxysulfate in water was found to be 7×10^{-4} s^{-1}, in agreement with previous determinations.[2] The spectrum of the fluoroxysulfate ion is shown in Figure 3. During the first 15 min after preparation of the solution, no absorbance of decomposition products was observed. Most laser flash photolytic and pulse radiolytic experiments were completed within less than 3 min after preparation of the solution. The temperature in all of the experiments was 21 ± 1 °C. Simulations of formation and decay kinetics were performed on a VAX computer using the CHEMSIMUL program.[18,19]

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