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Contribution from the Department of Chemistry,
Columbia University, New York, New York 10027

Crystal and Molecular Structure of $(MeCp)_2MoO$ (MeCp = η^5-$CH_3C_5H_4$)

Ned D. Silavwe, Michael Y. Chiang, and David R. Tyler*

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We are interested in the photochemistry of organometallic oxide complexes and for that reason we have been studying the Cp_2MoO complex (Cp = η^5-C_5H_5). This complex was first prepared by Green and co-workers[1] whose mass spectroscopic data suggested that the molecule was monomeric.[1] Interestingly, when Cp_2MoO is irradiated in inert solvents with a near-UV source, dioxygen is a product of the reaction,[2] a result we thought might be more easily explainable if the complex were dimeric with bridging oxo ligands.[3] To properly interpret our photochemical results, it was clearly necessary to know the structure of the molecule but, unfortunately, attempts to prepare crystals of the Cp_2MoO complex suitable for an X-ray diffraction study were unsuccessful. However, suitable single crystals of the methyl-substituted cyclopentadienyl complex, $(MeCp)_2MoO$ (MeCp = η^5-$CH_3C_5H_4$) (which also gives O_2 on irradiation), were obtained, and this paper reports the results of an X-ray study of this derivative.

Experimental Section

All manipulations were carried out in an inert atmosphere on a Schlenk line or in a Vacuum Atmospheres glovebox. Solvents are distilled and purged of oxygen according to standard procedures.[4] ^{1}H NMR spectra were obtained (in acetone-d_6) on a Varian XL-200 instrument. $(MeCp)_2MoCl_2$ was prepared according to the method of Green and co-workers.[5] Elemental analyses were done by Galbraith Laboratories.

Preparation of $(MeC_5H_4)_2MoO$. About 5 g (0.015 mol) of $(MeCp)_2MoCl_2$ and 20 g (0.5 mol) of NaOH were mixed together in a 500-mL flask, 200 mL of water was added, and the resulting mixture was stirred at room temperature for 12 h. The mixture changed color from dull light green to bright olive green. The crude product was filtered through a medium-porosity sintered-glass frit, and the residue was dried under vacuum for 18 h, yielding a green solid. The solid was then transferred into the drybox and extracted with about 75 mL of dry benzene. Addition of 100 mL of dry heptane to the filtered extract, followed by concentration under vacuum, resulted in the formation of shiny olive green platelets. The product was dried under vacuum to give 1.5 g (36%) of the bright olive green crystals of $(MeCp)_2MoO$. The infrared spectrum is similar to that reported by Green and co-workers for Cp_2MoO.[1] Also, the ^{1}H NMR spectrum is consistent with the formulation $(MeCp)_2MoO$ (in acetone-d_6): δ 6.10 (t, J = 2.1 Hz), and 4.81 (t, J = 2.3 Hz), cyclopentadienyl protons, 8 H; 1.60 (s) methyl protons, 6 H. Anal. Calcd for $C_{12}H_{14}MoO$: C, 53.38; H, 5.28. Found: C, 50.60; H, 5.23. Crystals suitable for X-ray diffraction were obtained by the vapor diffusion method with benzene used to dissolve the complex and pentane in the bath.

Collection and Reduction of X-ray Data. A dark green platelike crystal was put in a capillary for X-ray data collection. The sample was bounded by {110}, {1$\bar{1}$0}, and {001} faces. The largest pair of faces were identified to be (001) and (00$\bar{1}$). Unit cell and orientation parameters were determined on the basis of the setting angles (2θ, ω, ϕ, and χ) of 25 carefully centered reflections (2θ = 32–34°). Intensities were measured by the ω-scan technique. Three check reflections, (1,2,1), (2,2,3), and (2,3,11), were measured every 50 reflections to monitor crystal and instrumental stabilities, and no significant variation in intensities was found. Due to the strong diffracting power of the sample, the three strongest reflections (020), (110), and (021) and their Friedel pairs were measured separately at lower operating power. Intensities of these six reflections were scaled up so that the average intensities of the check reflections remain the same at all times during data collection. Lorentz and polarization corrections were applied. An empirical absorption correction was applied to adjust the uneven absorption effect by the plate crystal. All data processing and calculations were carried out on a Data General NOVA computer using the SHELXTL program system.

Table I. Crystal Data and Structural Analysis Results for $(MeCp)_2MoO$

A. Crystal Data	
formula	$MoC_{12}H_{14}O$
fw	270.18
cryst system	orthorhombic
space group	$P2_12_12_1$
Z	4
cell params	
a, Å	6.694 (1)
b, Å	9.487 (1)
c, Å	16.541 (3)
V, Å^3	1050.5 (3)
d_{calcd}, g cm^{-3}	1.71
cryst size, mm	0.45 × 0.45 × 0.20
μ_{calcd}, cm^{-1}	11.9
F(000)	543.78
B. Data Measurement Parameters and Analysis Results at (298 °K)	
diffractometer type	Nicolet R3m
radiation	Mo Kα ($\bar{\lambda}$ = 0.71073 Å)
scan type	ω
scan speed, deg min^{-1}	3.91–29.3
scan width, deg	1.5
$(\sin\theta)/\lambda$ limit, Å^{-1}	0.65 ($2\theta_{max}$ = 55°)
range of hkl	$(+h,+k,+l)$, $(-h,-k,-l)$
no. of reflcns measd	2865
no. of unique reflcns	2369
N_o, no. of reflcns used in analysis ($F > 2.5\sigma(F)$)	2324
N_v, no. of variable params	183
final agreement factors[6]	R = 0.0239; R_w = 0.0296
GOF	1.236
largest shift/esd, final cycle	0.097
largest remaining peak (e/Å^3)	0.79

The systematic absences ($h00$, $h = 2n$) indicated space group $P222_1$, which led to no solution. After considering reflection (010) and some (00l) reflections to be spurious (possibly caused by radiation with longer wavelength), a more common space group $P2_12_12_1$ was assigned and confirmed by the successful solution and refinement of the structure. Crystallographic data for the structure are summarized in Table I.

Structural Determination. The structure was solved by the direct-method program of SHELXTL, which revealed the molybdenum position in the first calculation. All non-hydrogen atoms were located via a difference Fourier map. Subsequent difference Fourier maps, phased with refined non-hydrogen atoms, gave all hydrogen positions at once. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. Refinement was carried out by use of a blocked-cascade least-squares procedure. The final residual factors[6] and other data measurement parameters are incorporated in Table I. The largest peak in the final difference electron density map (0.79 e/Å^3) is near the molybdenum atom.

Final positional and thermal parameters of non-hydrogen atoms appear in Table II. Interatomic distances and angles are given in Tables III and IV, respectively. All atomic parameters of hydrogen atoms are listed in Table V. A list of final observed and calculated structure factor amplitudes is available as supplementary material.

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*To whom correspondence should be addressed at the Department of Chemistry, University of Oregon, Eugene, OR 97403.

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Table II. Atom Coordinates (×10⁴) and Temperature Factors (Å × 10³) for Non-Hydrogen Atoms of $(MeCp)_2MoO$

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	1823 (1)	565 (1)	1909 (1)	25 (1)	33 (1)	22 (1)	1 (1)	−2 (1)	0 (1)
O	−732 (3)	369 (4)	1885 (2)	29 (1)	127 (3)	38 (1)	−1 (2)	−4 (1)	−6 (1)
C(1)	1366 (4)	536 (4)	3315 (2)	35 (1)	50 (2)	23 (1)	1 (1)	−2 (1)	−4 (1)
C(2)	2537 (5)	−634 (3)	3114 (2)	42 (1)	38 (1)	36 (1)	9 (2)	−7 (1)	−1 (1)
C(3)	4415 (5)	−138 (4)	2838 (2)	31 (2)	45 (2)	34 (1)	4 (1)	−7 (1)	5 (1)
C(4)	4375 (5)	1321 (4)	2849 (2)	33 (2)	41 (2)	30 (1)	0 (1)	−6 (1)	−4 (1)
C(5)	2474 (5)	1775 (3)	3106 (2)	42 (1)	35 (1)	33 (1)	−7 (2)	−4 (1)	−1 (1)
C(6)	1631 (6)	76 (4)	487 (2)	43 (2)	54 (2)	23 (1)	−4 (1)	1 (1)	−8 (2)
C(7)	1754 (7)	1531 (4)	577 (2)	59 (2)	52 (2)	28 (1)	8 (1)	−3 (2)	−1 (2)
C(8)	3600 (6)	1875 (4)	935 (2)	63 (2)	59 (2)	34 (2)	6 (2)	−2 (2)	−26 (2)
C(9)	4643 (5)	639 (6)	1046 (2)	34 (1)	90 (3)	33 (1)	−2 (2)	5 (1)	−7 (2)
C(10)	3404 (5)	−512 (5)	819 (2)	52 (2)	60 (2)	33 (2)	−9 (2)	7 (1)	18 (2)
C(11)	−671 (5)	511 (6)	3665 (2)	39 (2)	97 (3)	38 (2)	−1 (2)	9 (1)	−4 (2)
C(12)	−107 (7)	−697 (6)	135 (2)	70 (3)	93 (4)	34 (2)	−10 (2)	−6 (2)	−31 (3)

Table III. Selected Bond Lengths (Å) in $(MeCp)_2MoO$

Mo–O	1.721 (2)	Mo–C(1)	2.347 (3)
Mo–C(2)	2.345 (3)	Mo–C(3)	2.413 (3)
Mo–C(4)	2.419 (3)	Mo–C(5)	2.331 (4)
Mo–C(6)	2.401 (3)	Mo–C(7)	2.386 (3)
Mo–C(8)	2.357 (4)	Mo–C(9)	2.367 (3)
Mo–C(10)	2.326 (4)	C(1)–C(2)	1.399 (5)
C(1)–C(5)	1.432 (5)	C(1)–C(11)	1.481 (5)
C(2)–C(3)	1.418 (5)	C(3)–C(4)	1.385 (5)
C(4)–C(5)	1.409 (5)	C(6)–C(7)	1.391 (5)
C(6)–C(10)	1.422 (5)	C(6)–C(12)	1.493 (6)
C(7)–C(8)	1.408 (6)	C(8)–C(9)	1.377 (6)
C(9)–C(10)	1.422 (6)	Mo–Ω_1[a]	2.047
		Mo–Ω_6	2.044

[a] Ω_1 is the centroid of the C(1)–C(5) ring and Ω_6 is the centroid of the C(6)–C(10) ring.

Table IV. Selected Bond Angles (deg) in $(MeCp)_2MoO$

O–Mo–C(1)	83.8 (1)	O–Mo–C(2)	99.8 (1)
C(1)–Mo–C(2)	34.7 (1)	O–Mo–C(3)	134.4 (1)
C(1)–Mo–C(3)	57.2 (1)	C(2)–Mo–C(3)	34.6 (1)
O–Mo–C(4)	138.5 (1)	C(1)–Mo–C(4)	57.2 (1)
C(2)–Mo–C(4)	56.8 (1)	C(3)–Mo–C(4)	33.3 (1)
O–Mo–C(5)	105.0 (1)	C(1)–Mo–C(5)	35.7 (1)
C(2)–Mo–C(5)	58.5 (1)	C(3)–Mo–C(5)	57.3 (1)
C(4)–Mo–C(5)	34.5 (1)	O–Mo–C(6)	84.5 (1)
C(1)–Mo–C(6)	164.1 (1)	C(2)–Mo–C(6)	138.6 (1)
C(3)–Mo–C(6)	127.6 (1)	C(4)–Mo–C(6)	136.5 (1)
C(5)–Mo–C(6)	159.7 (1)	O–Mo–C(7)	90.1 (1)
C(1)–Mo–C(7)	156.5 (1)	C(2)–Mo–C(7)	167.2 (1)
C(3)–Mo–C(7)	135.1 (1)	C(4)–Mo–C(7)	119.6 (1)
C(5)–Mo–C(7)	126.8 (1)	C(6)–Mo–C(7)	33.8 (1)
O–Mo–C(8)	122.9 (1)	C(1)–Mo–C(8)	138.6 (1)
C(2)–Mo–C(8)	137.2 (1)	C(3)–Mo–C(8)	102.6 (1)
C(4)–Mo–C(8)	85.8 (1)	C(5)–Mo–C(8)	103.1 (1)
C(6)–Mo–C(8)	57.3 (1)	C(7)–Mo–C(8)	34.5 (1)
O–Mo–C(9)	141.4 (1)	C(1)–Mo–C(9)	134.6 (1)
C(2)–Mo–C(9)	111.4 (1)	C(3)–Mo–C(9)	79.6 (1)
C(4)–Mo–C(9)	79.4 (1)	C(5)–Mo–C(9)	110.4 (1)
C(6)–Mo–C(9)	57.2 (1)	C(7)–Mo–C(9)	56.5 (1)
C(8)–Mo–C(9)	33.9 (2)	O–Mo–C(10)	112.8 (1)
C(1)–Mo–C(10)	145.3 (1)	C(2)–Mo–C(10)	110.7 (1)
C(3)–Mo–C(10)	92.6 (1)	C(4)–Mo–C(10)	107.9 (1)
C(5)–Mo–C(10)	142.2 (1)	C(6)–Mo–C(10)	35.0 (1)
C(7)–Mo–C(10)	57.5 (1)	C(8)–Mo–C(10)	58.2 (1)
C(9)–Mo–C(10)	35.2 (2)	Mo–C(1)–C(2)	72.6 (2)
Mo–C(1)–C(5)	71.6 (2)	C(2)–C(1)–C(5)	107.7 (3)
Mo–C(1)–C(11)	120.5 (2)	C(2)–C(1)–C(11)	126.6 (4)
C(5)–C(1)–C(11)	125.7 (4)	Mo–C(2)–C(1)	72.7 (2)
Mo–C(2)–C(3)	75.3 (2)	C(1)–C(2)–C(3)	108.1 (3)
Mo–C(3)–C(2)	70.1 (2)	Mo–C(3)–C(4)	73.6 (2)
C(2)–C(3)–C(4)	108.1 (3)	Mo–C(4)–C(3)	73.1 (2)
Mo–C(4)–C(5)	69.3 (2)	C(3)–C(4)–C(5)	109.1 (3)
Mo–C(5)–C(1)	72.8 (2)	Mo–C(5)–C(4)	76.2 (2)
C(1)–C(5)–C(4)	106.8 (3)	Mo–C(6)–C(7)	72.6 (2)
Mo–C(6)–C(10)	69.6 (2)	C(7)–C(6)–C(10)	107.3 (3)
Mo–C(6)–C(12)	121.2 (2)	C(7)–C(6)–C(12)	125.1 (4)
C(10)–C(6)–C(12)	127.5 (4)	Mo–C(7)–C(6)	73.7 (2)
Mo–C(7)–C(8)	71.6 (2)	C(6)–C(7)–C(8)	109.1 (4)
Mo–C(8)–C(7)	73.9 (2)	Mo–C(8)–C(9)	73.5 (2)
C(7)–C(8)–C(9)	107.7 (4)	Mo–C(9)–C(8)	72.6 (2)
Mo–C(9)–C(10)	70.8 (2)	C(8)–C(9)–C(10	108.8 (3)
Mo–C(10)–C(6)	75.4 (2)	Mo–C(10)–C(9)	74.0 (2)
C(6)–C(10)–C(9)	106.7 (4)		

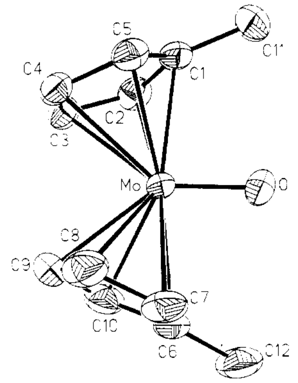

Figure 1. Geometry of the $(MeCp)_2MoO$ complex showing the atom-labeling scheme. The thermal ellipsoids are depicted at the 50% probability level.

Results and Discussion

The structure of the title compound consists of monomeric molecules of $(MeCp)_2MoO$ wherein each formally Mo(IV) atom is coordinated to two methylcyclopentadienyl rings and an oxo ligand (Figure 1). The Mo–O bond length of 1.721 (2) Å is characteristic of a terminal oxo ligand, although it is slightly longer than the Mo–O bonds in those complexes that formally may have Mo–O triple bonds (Table VI). The two MeCp rings are staggered, probably for steric reasons. The dihedral angle between the methyl groups is equal to 29°, where the dihedral angle was taken as the angle between the planes defined by Mo, C(1), and C(11) and Mo, C(6), and C(12). The geometry around the Mo atom may be considered trigonal planar if one considers only the vectors from the Mo atom to the Cp ring centroids and the Mo–O bond. The sum of the angles centroid(1)-Mo–centroid(2) (133.7°), centroid(2)–Mo–O (111.8°), and O–Mo–centroid(1) (114.5°) is 360°.

All of the C_{ring}–C_{ring} (average 1.41 (2) Å) and Mo–C (Mo–C_{av} 2.37 (3) Å) bond distances are within the normal range for a Mo–Cp complex, and there is no indication that the cyclopentadienyl groups are unsymmetrically bonded to the Mo atom, i.e., there is no tendency for the MeCp rings to be coordinated in a "nondelocalized" fashion (e.g. in a bis(η^2-ene) + η^1) or an η^3–η^2 fashion.[13] In addition, the MeCp rings are essentially flat. For example, the C(2), C(3), C(4), C(5) plane is displaced from the C(1), C(2), C(5), C(11) plane by 4.1°, and the C(7), C(8), C(9), C(10) plane is displaced from the C(6), C(7), C(10), C(12) plane by 2.3°.

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Table V. Hydrogen Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) of $(MeCp)_2MoO$

atom	*x*	*y*	*z*	*U*
H(2)	2000 (63)	−1634 (45)	3194 (23)	56 (11)
H(3)	5486 (54)	−711 (36)	2655 (21)	39 (9)
H(4)	5472 (68)	1891 (42)	2623 (24)	59 (12)
H(5)	2109 (55)	2751 (39)	3214 (20)	42 (9)
H(7)	784 (78)	2114 (54)	464 (28)	86 (16)
H(8)	4101 (65)	2841 (46)	1100 (26)	57 (12)
H(9)	6030 (73)	523 (54)	1271 (29)	82 (15)
H(10)	3595 (71)	−1540 (52)	878 (28)	73 (14)
H(11a)	−1622 (75)	−389 (52)	3339 (31)	78 (14)
H(11b)	−706 (64)	455 (46)	4226 (25)	72 (13)
H(11c)	−1503 (75)	1358 (50)	3453 (28)	66 (14)
H(12a)	−34 (94)	−714 (63)	−568 (34)	119 (19)
H(12b)	−1519 (109)	−365 (71)	567 (43)	157 (24)
H(12c)	−412 (89)	−1513 (59)	274 (33)	100 (19)

Table VI. Terminal Mo–O Distances (Å) in Molybdenum Oxo Complexes

compd	bond dist	ref
$(\eta^5\text{-}MeC_5H_4)_2Mo^{IV}O$	1.721 (2)	this work
$Mo^{IV}O(S_2CNPr_2)_2$	1.664 (8)	7
$Mo^{IV}O(S_2CNPr_2)_2(TCNE)$	1.682 (4)	7
mer-$Mo^{IV}OCl_2(PEt_2Ph)_3$ (green isomer)	1.803 (7)	8
mer-$Mo^{IV}OCl_2(PMe_2Ph)_3$ (blue isomer)	1.676 (7)	8
trans-$K_3Na[Mo^{IV}O_2(CN)_4]\cdot 6H_2O$	1.834 (9)	9
$[Cr(en)_3]$[*eq*-$MoO(OH)(CN)_4]\cdot 2H_2O$	1.698 (7)	10
$[Pt(en)_2]$[*eq*-$MoO(H_2O)(CN)_4]\cdot 2H_2O$	1.668 (5)	10
$Mo^{VI}O_3(dien)$	1.737 (8)	11
$(\eta^5\text{-}C_5H_5)_2Mo_2O_2S_2$	1.679 (6)	12

The shortest intermolecular distances are as follows: Mo···O, 4.987 Å; Mo···Mo, 5.682 Å; O···O, 5.254 Å; and O···H, 2.348 Å. This latter distance precludes any O–H hydrogen bonding.[11,14] The shortest Mo–H distance, 2.881 Å, is intramolecular and involves H(9).

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Registry No. $(MeC_5H_4)_2MoO$, 98525-67-8; $(MeC_5H_4)_2MoCl_2$, 63374-10-7.

Supplementary Material Available: Tables of observed and calculated structure factors for $(MeCp)_2MoO$ (14 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry,
Northern Illinois University, De Kalb, Illinois 60115,
and University of Colorado, Boulder, Colorado 80309

Rate of Aquation of the Fluoropentaaquochromium(III) Ion in Concentrated Perchloric Acid

Joe W. Vaughn*[1] and Edward L. King*[2]

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The rates of aquation of complexes of chromium(III) with relatively basic ligands are governed by rate laws involving terms with positive dependences upon the concentration of hydrogen ion as well as terms that are acid-independent and inversely dependent upon the hydrogen ion concentration.[3-8] Extending the range of acidity in which such studies are made reveals measurable basicity for (acetato)chromium(III) ion,[5] azidochromium(III) ion,[6] and (trichloroacetato)chromium(III) ion.[8] This paper deals with a study in concentrated perchloric acid (1.0–10.0 mol L^{-1}) at 30 °C of aquation of fluorochromium(III) ion:

Table I. First-Order Rate Constant, k_{obsd},[a] for Aquation of the Fluoropentaaquochromium(III) Ion in Perchloric Acid Solution at 30 °C[b]

C_{HClO_4}/mol L^{-1}	$10^7 k_{obsd}/s^{-1}$	C_{HClO_4}/mol L^{-1}	$10^7 k_{obsd}/s^{-1}$
1.00	0.264[c,d]	6.00	7.3[c]
2.00	0.820	7.00	10.9[c]
3.00	1.75[c]	8.00	15.4[c]
4.00	3.16[c]	9.00	17.8[c]
5.00	5.2[c]	10.00	22.3[c]

[a] $k_{obsd} = -d \ln [CrF^{2+}]/dt$; reactions were nicely first order. In most runs, reaction was followed >70% to completion. [b] The total concentration of chromium(III) was in the range 0.04–0.13 mol L^{-1}. [c] The average of values obtained in two experiments. The average difference between the values so averaged is 7.3%. [d] Extrapolation from studies at higher temperatures[4] yields a value of $0.282 \times 10^{-7}\ s^{-1}$ for the first-order rate constant at $C_{HClO_4} = 1.0$ mol L^{-1}.

$$Cr(OH_2)_5F^{2+} + H_3O^+ = Cr(OH_2)_6^{3+} + HF$$

The objective of the study is comparison of the aquation kinetics for fluorochromium(III) ion and azidochromium(III) ion in relatively concentrated perchloric acid solution. Although the acid strengths of hydrofluoric acid and hydrazoic acid differ by only a factor of 24 (at 25 °C, $K_a(HF) = 6.8 \times 10^{-4}$ mol L^{-1} and $K_a(HN_3) = 2.8 \times 10^{-5}$ mol L^{-1}), the charge densities in the anionic conjugate bases, the ligands, differ greatly, as do the hydration energies of the acids, which are reaction products. This may have an effect on the dependence of the rates of aquation upon the activity of water, which is lowered appreciably at the high acid concentration extreme of this study.

Experimental Section

Synthesis of the Fluorochromium(III) Ion. This complex ion was prepared and analyzed both for chromium and for fluoride as described previously.[4] The Cr/F ratio was 0.98, within experimental error of 1.00. The spectrum (visible and ultraviolet) was in good agreement with that reported.[4]

Kinetic Studies. Solutions for the aquation studies were prepared by diluting stock solutions of the fluoro complex of known concentration with the appropriate amounts of standardized concentrated perchloric acid. To prevent an increased temperature during dilution, ice-cold solutions were used. The solutions being studied were contained in sealed polyethylene bottles in a constant-temperature bath at 30 °C. At various times, portions of the reaction mixtures were withdrawn and diluted with doubly distilled water to lower the hydrogen ion concentration to ~0.2 mol L^{-1}. A refrigerated column of Dowex 50W-X4 (H^+ form, 50–100 mesh, column 1 × 12 cm) then was used to separate from one another the chromium(III) species of different charges. The columns were rinsed with ca. 100 mL of doubly distilled water, followed by elution with 100 mL of 1.0 M perchloric acid to remove all of the unreacted fluorochromium(III) ion of charge 2+. To remove the aquation product, $Cr(OH_2)_6^{3+}$, from the column, the perchloric acid concentration was raised to 4–6 mol L^{-1}.

In experiments at 7–10 M perchloric acid, an excess of potassium fluoride was added to freshly prepared solutions of fluorochromium(III) ion in perchloric acid, and the rates of aquation were compared to those observed in solutions of the same acid concentration that did not contain added fluoride ion. The added fluoride had no appreciable effect upon the rate.

Results and Discussion

Results of the kinetic studies are presented in Table I. A small correction for the acid-independent pathway ($k_0 = 1.4 \times 10^{-9}\ s^{-1}$,

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