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).

Acknowledgment is made to the Procter and Gamble Co. for a University Exploratory Research Grant. Ned Silavwe is grateful to the University of Zambia for a fellowship. Prof. M. L. H. Green is thanked for useful advice on the preparation of the complex.

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

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Received May 14, 1985

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:

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

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}	$10^7k_{obsd}/s^{-1}$	C_{HClO_4}/mol L^{-1}	$10^7k_{obsd}/s^{-1}$
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 0.282×10^{-7} s^{-1} for the first-order rate constant at C_{HClO_4} = 1.0 mol L^{-1}.

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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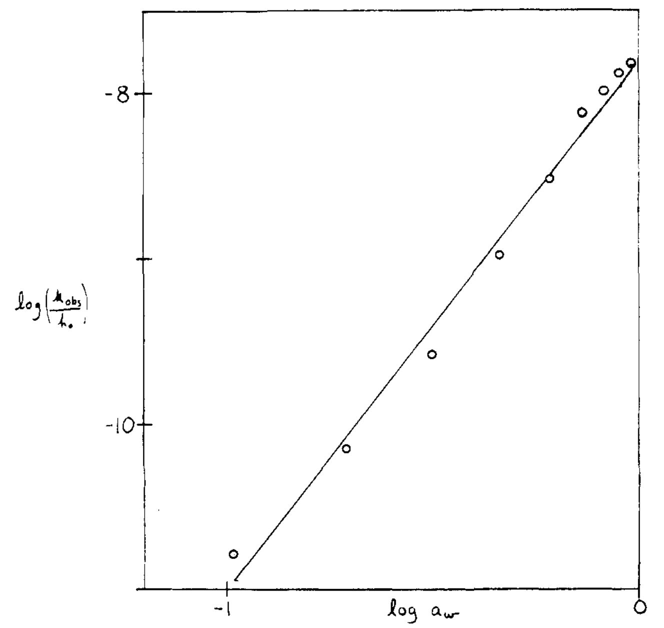

Figure 1. log (k_{obsd}/h_0) vs. log a_w (data for C_{HClO_4} = 1-9 mol L^{-1}). The line is given by the equation log (k_{obsd}/h_0) = $-7.800 + 3.21$ log a_w. (Values of a_w for 25 °C for perchloric acid solution containing no other electrolytes were used.)

evaluated by extrapolating from the studies carried out at higher temperatures[4]) is less than the experimental uncertainty at all acidities. The increase in reaction rate with increasing acidity is attributable to the rate law term $k_1[CrF^{2+}][H^+]$ detected by Swaddle and King in studies at lower acidity, constant ionic strength, and higher temperature.[4] In this study the problem of medium effects has not been suppressed by maintainance of constant ionic strength, and as in the study of azidochromium(III) ion, an appropriate handling of medium effects is a crucial aspect of correlating the data.

There are marked differences between aquation reactions of fluorochromium(III) ion and azidochromium(III) ion. Between 1 and 6 M perchloric acid, the value of k_1 increases by a factor of ~28 for the fluorochromium(III) ion but by a factor of ~185 for the azidochromium(III) ion. Over this same range of acidity, the corrected value of k_{obsd} divided by the product of the Hammett function h_0 and the activity of water decreases gradually by a factor of 6.8 for the fluorochromium(III) ion but is essentially constant for the azidochromium(III) ion. At still higher acidities, the first-order rate constant for aquation of azidochromium(III) displays a transition from $k \propto (h_0 a_w)^1$ to $k \propto (h_0 a_w)^0$ that allows estimation of the acid dissociation constant for the (hydrogen)-azidochromium(III) ion. The data for the present system are not amenable to a quantitative interpretation that yields the acid dissociation constant for (hydrogen)fluorochromium(III) ion. Rather, the gradual increase of k with increasing acidity suggests a dependence of k/h_0 upon a power of the activity of water greater than first, as shown in Figure 1. The data in Table I, excluding the value of k at C_{HClO_4} = 10 mol L^{-1}, are correlated with the equation

$$k_{obsd} = (1.59 \times 10^{-8}\ s^{-1}) h_0 a_w^{3.2}$$

The average difference between calculated and observed values of k_{obsd} is 19%. No other two-parameter equation correlates the data as well as this. The value of k_{obsd} at 10 M HClO$_4$ is ~3.7-fold larger than predicted by this equation; this deviation is in the opposite direction from that expected if the deviation were due to an appreciable fraction of fluorochromium(III) ion being converted to its protonated form. Thus in the context of this correlation, one concludes that $K_a((H_2O)_5CrFH^{3+}) > {\sim}10^6$. (This statement is based upon the assumed appropriateness of using h_0 as a measure of proton-donating ability of the solution toward the fluorochromium(III) ion and of correlating the data with the activity of water raised to a single power, rather than with more complex functions of this variable.) This sensitivity to the activity of water is reasonable for formation of an activated complex from which hydrofluoric acid is being produced and into which water is being incorporated.

Registry No. $Cr(OH_2)_5F^{2+}$, 19559-07-0.

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The (Dimethylamido)tris(1-pyrazolyl)borate(1-) Ion, a New Hybrid Poly(1-pyrazolyl)borate Ligand

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Received March 8, 1985

Among the various poly(1-pyrazolyl)borate ligands only one example is known where, apart from the pz groups (Hpz = pyrazole), an additional coordination site is attached to boron. That ligand, $[HB(pz\text{-}3,5\text{-}Me_2)_2(SAr)]^-$ (Me = CH$_3$, Ar = C$_6$H$_4$-4-CH$_3$), was synthesized from $K[H_2B(pz\text{-}3,5\text{-}Me_2)_2]$ and ArSH.[1]

When tris(dimethylamino)borane, $B(NMe_2)_3$, was reacted with Hpz at room temperature, the dimethylamine adduct of tris(1-pyrazolyl)borane was obtained in essentially quantitative yield. On the basis of low-temperature ^{1}H NMR data, the species may be presented by the formula $Me_2HN{\cdot}B(pz)_3$. However, at room temperature the N-bonded proton undergoes site exchange, and $H[Me_2NB(pz)_3]$ may be a better illustration of the compound.[2]

In this context it was of interest to establish whether or not an ion $[Me_2NB(pz)_3]^-$ (=L*) exists and can act as chelating poly(1-pyrazolyl)borate ligand and what type of denticity it would exhibit.

The lithium salt of L* was easily prepared from HL* by treatment with MeLi. The salt is soluble in Me$_2$SO and exhibits the expected ^{1}H and ^{11}B NMR spectra. However, even the acid HL* was found to react readily with $(MeCN)_2Mo(CO)_2X(\eta^3\text{-}CH_2CRCH_2)$ (X = Cl, Br; R = H, CH$_3$) to form the complexes $L^*Mo(CO)_2(\eta^3\text{-}CH_2CRCH_2)$ in good yield as yellow solids that are quite soluble in organic solvents.

An 18-electron configuration of Mo demands tridentate coordination of L* in these complexes, which can be either of the type $Me_2NB(\mu\text{-}pz)_3Mo$ or $(pz)B(\mu\text{-}pz)_2(\mu\text{-}NMe_2)Mo$. ^{1}H NMR data of the species indicate stereochemical nonrigidity, due to rotation of the $Mo(CO)_2(CH_2CRCH_2)$ moiety around the B-Mo axis. The barrier to rotation is high for the case of R = H (which is in consonance with earlier findings on related $RB(pz)_3Mo(\eta^3\text{-}CH_2CRCH_2)$ compounds[3,4]), and a variable-temperature study is depicted in Figure 1.

As can be seen from Figure 1, the high-temperature spectrum still shows two different types of pz groups in 2:1 ratio, consistent with a $(pz)B(\mu\text{-}pz)_2(\mu\text{-}NMe_2)Mo(CO)_2(\eta^3\text{-}CH_2CHCH_2)$ structure, since analogous $RB(pz)_3$ complexes show all pz groups to be identical at high temperatures. Furthermore, for $RB(pz)_3$ complexes the η^3-allyl part of the spectrum remains unchanged throughout the temperature range, while in the L* complex the η^3-allyl protons end up in a variety of environments at low temperature. In addition, one has to account for three types of Me groups and four different types of pz groups (evidenced best via the 4-H signals near 6.4 ppm) at low temperature.

The $(pz)B(\mu\text{-}pz)_2(\mu\text{-}NMe_2)Mo(CO)_2(\eta^3\text{-}CH_2CHCH_2)$ formulation accounts for all these features as follows: Looking down the Mo-B axis and disregarding the uncoordinated pz group, one

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