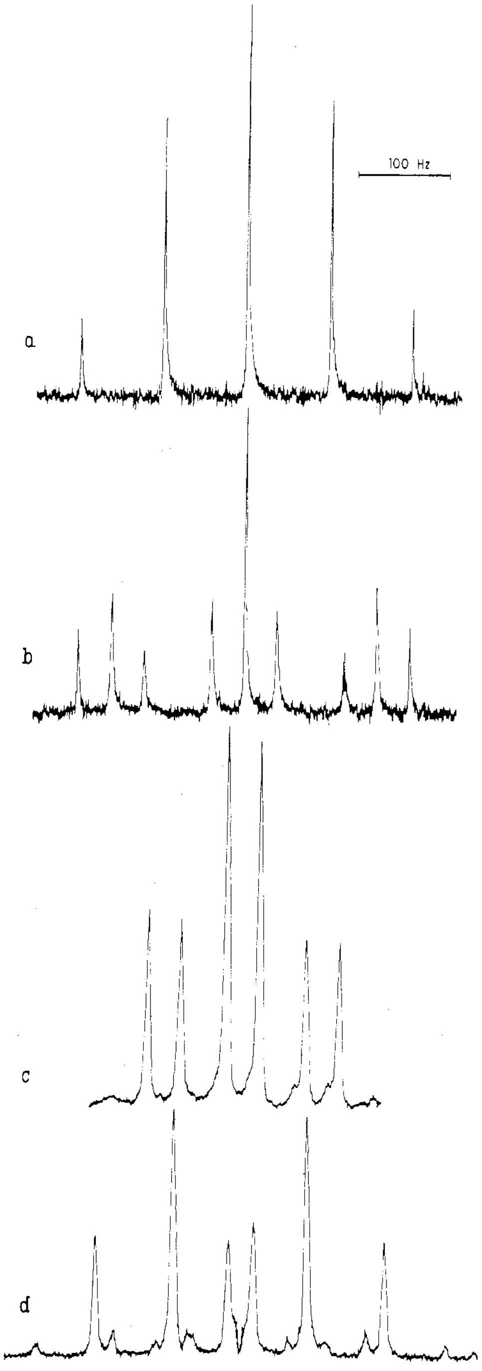

Figure 1. Nmr spectra of a 2.0 *M* solution of HPF_4 in $HCClF_2$: (a) downfield component of the 100-MHz ^1H spectrum at −80°; (b) downfield component of the 100-MHz ^1H spectrum at −140°; (c) downfield component of the 94.1-MHz ^{19}F(equatorial) resonance at −140°; (d) downfield component of the 94.1-MHz ^{19}F(axial) resonance at −140°.

spectroscopic equivalence of the fluorine atoms (see, *e.g.*, Figure 1a) could be due to structure **2**, it is more reasonably ascribed to the fluxional behavior of the trigonal-bipyramidal species, **1**. Accordingly it seemed appropriate to secure more extensive low-temperature nmr data in order to shed more light on this question.

When HPF_4 is dissolved in Freon-22 ($HCClF_2$) and cooled below −120°, two fluorine environments of equal abundance become detectable in both the ^1H and the ^{19}F spectra. This observation of the limiting spectrum establishes the trigonal-bipyramidal ground-state geometry (**1**) for HPF_4 and rules out structure **2**. The assignment of the +65.9- and +27.4-ppm ^{19}F resonances (relative to external CCl_3F) to the equatorial and axial fluorine sites, respectively, is based on the fact that the equatorial resonances appear at higher field.[7] Thus the large doublet splitting in Figure 1d is due to the H-P-F_a coupling and the small doublet splitting in Figure 1c is due to the H-P-F_e coupling; in both Figures 1c and 1d the triplet splitting is due to $J_{F_aPF_e}$. The low-temperature ^1H spectrum (Figure 1b) is likewise assignable on this basis. The following new coupling constant data are available from the limiting spectra: $J_{PF_a} = 941.0$ Hz; $J_{PF_e} = 1025$ Hz; $J_{HPF_a} = 147.5$ Hz; $J_{HPF_e} = 36.47$ Hz; $J_{F_aPF_e} = 87.89$ Hz.

Registry No. Tetrafluorophosphorane, 36994-84-0.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP 28634) and the Robert A. Welch Foundation for generous financial support.

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Contribution from the Institute "Ruder Boskovic,"
Bijenicka 54, Zagreb, Croatia, Yugoslavia

Preparation and Kinetics of the Aquation of Pentaaquo(3-picoline)chromium(III) Ion

M. Orhanovic* and M. Avdagic

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Comparisons of kinetic and thermodynamic parameters for the aquation and anation reactions of the $Cr(H_2O)_5X^{2+}$ series of complex ions (X = uninegative ions) have given important information about the mechanisms of these reactions.[1] The chemistry of analogous chromium complexes[2] with a net charge other than 2+ was of interest to us and is reported here.

The reaction of diperoxychromium(IV) amines with acids has proved useful as a route to produce chromium(III) diamines and triamines.[3] Similar adducts of nitrogen bases with diperoxychromium(VI) species, $BCr(O)(O_2)_2$, are reported to decompose in acidic aqueous solution to hexaaquochromium(III) ion and chromate ion, the relative amounts of which vary with pH.[4] We find that the reaction of acidic ferrous perchlorate with some base adducts of diperoxychromium(VI) species produces monosubstituted chromium(III) ions, $(H_2O)_5CrB^{n+}$. This paper deals with the preparation of pentaaquo(3-picoline)chromium(III) ion and with the kinetics of its aquation. The aquation kinetics of

$$(H_2O)_5Cr(3\text{-pic})^{3+} + H^+ \rightarrow Cr(H_2O)_6{}^{3+} + H(3\text{-pic})^+ \qquad (1)$$

was studied as a function of acidity and temperature.[5]

Experimental Section

Preparation of Pentaaquo(3-picoline)chromium(III). To a cooled

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(5) 3-pic = 3-picoline.

(0°) equimolar 1 *M* aqueous mixture of 3-picoline (1-5 mmol) and chromium(VI) oxide (1-5 mmol) 2 equiv of cooled 30% hydrogen peroxide was added. A blue paste formed which, by analogy with pyridine,[4] was probably the (3-pic)CrO$(O_2)_2$ species. The blue paste was immediately treated with a cooled solution containing 7.5 equiv of ferrous perchlorate and 11 equiv of perchloric acid. Shortly, a bluish red color appeared—the color typical for chromium(III) monoamines. The solution was absorbed onto a Dowex 50W-X8 column, ferric ion and lower charged ions were washed off the column with 1 *M* $HClO_4$ containing 0.1 *M* NaSCN, and chromium(III) species were then eluted with 3 *M* $HClO_4$. Blue-gray $Cr(H_2O)_6{}^{3+}$, which is formed in a small relative amount, elutes first and separates from the bluish red band, a middle portion of which was collected.

The concentration of pentaaquo(3-picoline)chromium(III) perchlorate[6] obtained in this way was (5-8) × 10^{-3} *M*. Solutions of the complex stored at −5° did not change for an extended period of time.

The acid concentration of some (3-picoline)chromium(III) solutions was reduced to ~0.1 *M* by titration of cooled stock solutions with cooled (0°) 3 or 1 *M* potassium hydroxide. However, some aquation of the complex was observed and the solutions were used only for kinetic studies at low acidities. Because of this observation no attempts were made to determine the acid dissociation constant of (3-picoline)chromium(III).

Other Materials and Analytical Methods. Laboratory grade 3-picoline (Fluka) was distilled and a middle fraction with bp 142-144° was used. All other chemicals used (Merck) were analytical grade. Qualitative and quantitative determination of 3-picoline was made by the uv spectrophotometry in aqueous perchloric solutions (ϵ 5.22 × 10^3 M^{-1} cm^{-1} at 263 nm) after aquation of the complex for 10 or more half-lives. The other analyses were performed as previously described.[7]

Kinetic Measurements. The aquation of $(H_2O)_5Cr(3\text{-pic})^{3+}$ was followed spectrophotometrically at 262 nm where there is an adequate absorption difference between the reactants and the products (ϵ value of the complex ion at this wavelength is 3.1 × 10^3 M^{-1} cm^{-1}, of 3-picolinium ion 5.2 × 10^3 M^{-1} cm^{-1}, and of hexaaquochromium(III) ion about 4.3 M^{-1} cm^{-1}). The technique used and the manner of calculation of the rate constants were similar to those previously employed.[7]

Results

Characterization of (3-Picoline)chromium(III) Ion. The chromium to ligand ratio in $(H_2O)_5Cr(3\text{-pic})^{3+}$ was found to be 1:1 within an average deviation of 2%. The monomeric form is confirmed by the behavior of the species on the cation-exchange column. The behavior is similar to that of hexaaquochromium(III) ion and is compatible with a 3+ charge. The visible spectrum of the complex ion in 1 and 3 *M* perchloric acid shows absorption maxima at 558 nm (ϵ 18.6 M^{-1} cm^{-1}) and 400 nm (ϵ 22.0 M^{-1} cm^{-1}). These are very similar to the maxima of pentaaquopyridinechromium(III) ion (λ_{max} 560 nm, ϵ 18.2 M^{-1} cm^{-1}; λ_{max} 402 nm, ϵ 20.8 M^{-1} cm^{-1}) which were found to lie between the corresponding maxima of two other nitrogen-bonded species: those of isothiocyanatochromium(III) ion and of amminechromium(III) ion.[7] The uv spectrum, given in Figure 1, is unaffected by 0.1-3.0 *M* ionic strength and by 10^{-3}-1.0 *M* $HClO_4$ at 1.0 *M* ionic strength. The absorption maximum at 268 nm has a molar absorbance index of 3.52 × 10^3 M^{-1} cm^{-1}.

Aquation of $Cr(H_2O)_5(3\text{-pic})^{3+}$ Ion. The product of the aquation, as implied by eq 1, was identified as 3-picolinium ion by its uv spectrum given in Figure 1. The isosbestic points at 272 and 238 nm shown by the absorption spectra in the figure were also observed during the kinetic runs within ±1 nm.

The initial concentration of (3-picoline)chromium(III) was in the range 1.9 × 10^{-4} to 1.6 × 10^{-5} *M*. At a particular constant hydrogen ion concentration the reaction obeyed the first-order rate law

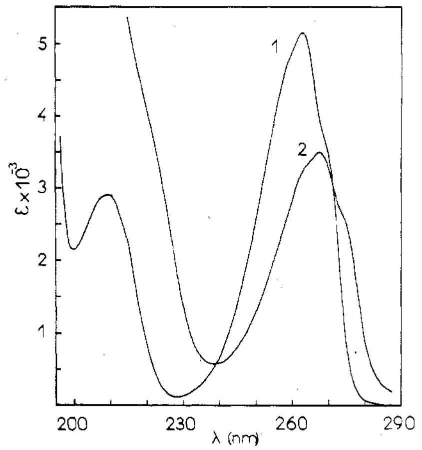

Figure 1. Ultraviolet spectra in 1.0 *M* $HClO_4$: (1) 3-picolinium ion and (2) pentaaquo(3-picoline)chromium(III) ion.

$$-d[Cr(3\text{-pic})^{3+}]/dt = k_{obsd}[Cr(3\text{-pic})^{3+}] \qquad (2)$$

The rate constants obtained at different hydrogen ion concentrations and different temperatures are presented in Table I. The ionic strength was maintained constant at 1.0 *M* with sodium perchlorate. The change of perchloric acid concentration during a run due to the protonation of the liberated 3-picoline was negligible.

A linear dependence is obtained when plotting k_{obsd} *vs.* $1/(H^+)$ as shown in Figure 2. A least-squares treatment of the lines 1-5 according to the equation

$$k_{obsd} = k_0 + k_{-1}/(H^+) \qquad (3)$$

shows that the calculated values of k_{obsd} agree with the experimental values with an average deviation of 1.5-3.5%. Although sodium ion is not the best choice to replace hydrogen ion in order to keep the ionic strength constant,[8] the nature of k_{obsd} *vs.* $1/(H^+)$ dependence strongly suggests that the two terms in expression 3 are associated with two reaction pathways. The rate constants given in Table I were therefore treated simultaneously for all hydrogen ion concentrations and temperatures according to the expression

$$k_{obsd} = (kT/h)\Sigma_i(H^+)^i e^{\Delta S_i^{\ddagger}/R} e^{-\Delta H_i^{\ddagger}/RT} \qquad (4)$$

with $i = 0$ and −1. The best values of the enthalpies and entropies of activation as well as the values of the specific rates at different temperatures were calculated for the two terms in the rate law using a CAE 90-40 computer and a nonlinear least-squares program.[9] Each rate constant was weighted according to the inverse of its square. The calculated values of the rate constants agreed with the experimental values given in Table I with an average deviation of 3.1%.

The activation parameters obtained in this way are $\Delta H_0{}^{\ddagger}$ = 31.3 ± 1.2 kcal mol^{-1}, $\Delta S_0{}^{\ddagger}$ = 6.9 ± 3.4 cal mol^{-1} deg^{-1}, $\Delta H_{-1}{}^{\ddagger}$ = 34.7 ± 0.2 kcal mol^{-1}, and $\Delta S_{-1}{}^{\ddagger}$ = 11.8 ± 0.6 cal mol^{-1} deg^{-1}. The specific rates extrapolated to 25° are k_0 = 2.1 × 10^{-9} sec^{-1} and k_{-1} = 9.0 × 10^{-11} sec^{-1} *M*.

Discussion

Monosubstituted chromium(III) complex ions with basic ligands and with amines in particular are not readily obtain-

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(6) Hereafter (3-picoline)chromium(III).

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Table I. First-Order Rate Constants for the Aquation of $Cr(H_2O)_5(3\text{-pic})^{3+}$ at 1.0 *M* Ionic Strength ($HClO_4$ + $NaClO_4$)[a]

Temp, °C	($HClO_4$), m*M*	10^4k_{obsd}, sec^{-1}	Temp, °C	($HClO_4$), m*M*	10^4k_{obsd}, sec^{-1}
99.0	1000	1.08	85.0	99.6	0.407
99.0	100	2.38	85.0	14.1	1.65
99.0	24.4	6.19	85.0	5.91	3.55
99.0	14.3	9.79	85.0	2.76	7.17
99.0	8.28	15.4	80.0	14.3	0.781
99.0	6.15	20.8	80.0	8.24	1.32
99.0	4.88	25.4	80.0	4.12	2.36
99.0	4.12	32.1	80.0	2.77	3.47
90.0	1000	0.346	80.0	2.06	4.92
90.0	100	0.740	80.0	1.54	6.76
90.0	14.5	3.08	80.0	1.28	7.86
90.0	8.24	5.02	80.0	1.03	9.96
90.0	6.15	6.88	80.0	0.824	12.0
90.0	4.12	10.3	75.0	25.0	0.229
90.0	2.79	13.7	75.0	10.0	0.511
90.0	2.06	19.3	75.0	5.00	0.970
90.0	1.64	24.6	75.0	3.57	1.29
90.0	1.38	28.5	75.0	2.33	2.10
90.0	1.18	33.0	75.0	1.56	2.93
90.0	1.03	38.5	75.0	1.17	3.89

[a] Concentration of $Cr(H_2O)_5(3\text{-pic})^{3+}$ varied in the range 1.6×10^{-5} to 1.9×10^{-4} *M*.

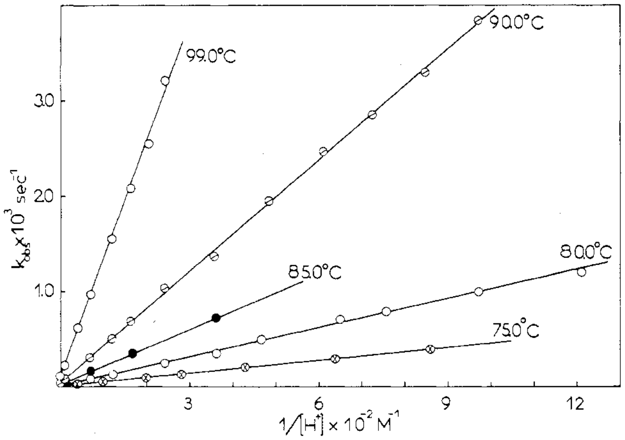

Figure 2. Plot of k_{obsd} *vs.* $1/(H^+)$ for the aquation of $Cr(H_2O)_5(3\text{-pic})^{3+}$ in 1.0 *M* ionic strength ($NaClO_4$) at different temperatures.

able in a simple preparative way. The ready formation of chromium(III) hydroxo- or oxo-bridged polynuclear complexes in weakly acidic and basic aqueous solutions makes the direct reaction between Cr^{3+} and ligand(s) very restrictive. The reaction of ferrous ion with base adducts of diperoxychromium(VI) species used in this work might prove useful as a method for preparation of monosubstituted chromium(III) complex ions with ligands having basic nitrogen or oxygen as the donor atom. Preliminary results show that the chromium(III) species with ligand being 3-chloropyridine, 3-cyanopyridine, pyridine *N*-oxide, and 3-picoline *N*-oxide are formed in the respective reactions.[10]

The rate law of the same form as given by eq 3 has been found for the aquation of monosubstituted chromium(III) complex ions having an acidic ligand[11-15] as well as an amine ligand: ammine,[16] unidentate diethylenetriamine,[17] unidentate tetraethylenepentamine,[18] and pyridine.[7] Analogous rate laws were also observed for the dissociation of the Cr-O bond in the Ru(II)-Cr(III) and Ru(III)-Cr(III) binuclear complexes bridged by substituted pyridines.[19] The failure to observe an inverse-acid term in the rate law for aquation of the complexes with unidentate ethylenediamine ligand[20] and with unidentate triethylenetetramine ligand[21] is most likely due to a narrow acidity range used.

The rate law is consistent with k_0 in eq 3 being the rate constant for the aquation of $Cr(H_2O)_5(3\text{-pic})^{3+}$ and $k'_{-1} = k_{-1}/K_h$ the rate constant for the aquation of the conjugate base $Cr(H_2O)_4(OH)(3\text{-pic})^{2+}$, where K_h is the equilibrium constant for the acid dissociation reaction

$$Cr(H_2O)_5(3\text{-pic})^{3+} \rightarrow Cr(H_2O)_4(OH)(3\text{-pic})^{2+} + H^+$$

The interpretation assumes that $K_h/(H^+) \ll 1$ at the experimental conditions employed. This would not be true, however, if K_h and the corresponding ΔH had values similar or higher than those of hexaaquochromium(III) ion.[22] Unfortunately, a reliable K_h value for the complex ion studied is not available.

The pK_a's for the protonated forms of 3-picoline, pyridine, and 4-amidopyridine at 25° are 5.67, 5.21, and 3.61, respectively.[23,24] The specific rates for aquation of the corresponding monosubstituted chromium(III) complexes *via* the acid-independent path at 70° follow the same sequence ($k_0 \times 10^6$ in sec^{-1}: 2.5, 5.5, and 43, respectively[25]). Qualitatively, the reactivity parallels the basicity of the ligands.

Registry No. $(H_2O)_5Cr(3\text{-pic})^{3+}$, 36994-85-1.

Acknowledgment. We wish to thank Miss V. Butkovic for the help with some experiments.

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Contribution from the Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001

Exchange of Acetonitrile on Complexes of Nickel(II) and Cobalt(II) Formed with 2,2′,2″-Triaminotriethylamine and 2,2′,2″-Tri(*N*,*N*-dimethylamino)triethylamine

R. J. West and S. F. Lincoln*

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Nickel(II) and cobalt(II) are six- and five-coordinated, respectively, in complexes formed with the tetradentate ligand 2,2′,2″-triaminotriethylamine (tren)[1,2] but are both