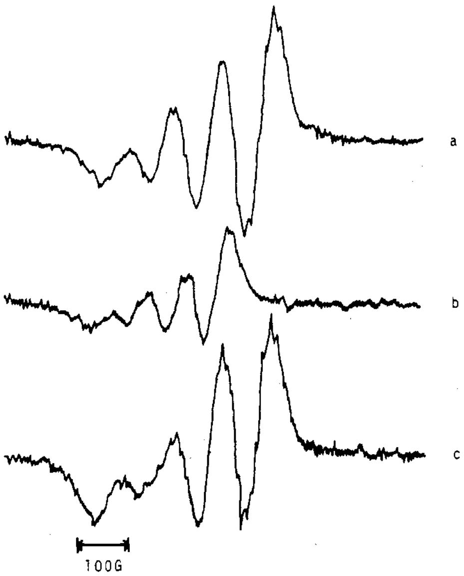

Figure 8. ESR spectra of the binary and ternary Cu(II) systems containing GlyGlyHis and His in neutral pH solutions: curve a, Cu(II)–GlyGlyHis; curve b, Cu(II)–His; curve c, Cu(II)–GlyGly-His–His.

tion site of the copper(II) complex with His was faster at higher pH than at lower pH.[22] This fact strongly suggests that the completely deprotonated species of His becomes more effective for its nucleophilic attack on the complex $CuH_{-2}B$. A direct attack of His on the highly square-planar complex $CuH_{-2}B$ seems to be difficult since His probably in the first step has to approach the complex from an apical direction. On the other hand, the route involving dissociation of GlyGlyHis does not seem important because the reaction rates were not essentially affected even by the presence of a slight excess of GlyGlyHis, which is expected to ensure the complete complex formation. The ligand-exchange rates were approximately first order with respect to the concentration of His in the presence of 100- to 500-fold excess His, strongly indicating that the step to form the ternary complex of the structures shown as **4** and **5** is a rate-determining one. As is suggested from the foregoing argument, the His molecule may not attack the completely deprotonated copper-binding site of albumin in the ligand displacement but may attack a partially protonated one. Once copper is bound with His, another amino acid may quite easily expel albumin from the coordination sphere to form an amino acid complex of low molecular weight. The resulting amino acid complexes can easily migrate to tissues through biological membranes. As for such amino acid complexes, we intend to point out a high probability of the binary His complex and some ternary complexes containing His and a specific amino acid such as threonine, serine, asparagine, or glutamine with polar side-chain groups which are necessary to form potential intramolecular hydrogen bonding.[23] The equilibrium between Cu(II), serum albumin, and amino acids might be sufficiently fast to realize rapid equilibrium of copper between blood and tissues in living systems, where a statistical factor rather than a structural factor may play a vital role in the formation of intermediary copper–albumin–amino acid complexes.

Acknowledgment. We are grateful to Miss Yoshimi Inagaki for technical assistance. The computations of the stability constants were performed at the Osaka University Computer Center. The financial support of the Takeda Science Foundation and the Ministry of Education of Japan is gratefully acknowledged.

Registry No. $CuH_{-2}B$, 53554-01-1; $NiH_{-2}B$, 60165-85-7; His, 71-00-1; Hm, 51-45-6; Gly, 56-40-6.

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(22) The values of 10^2k_{obsd} (s^{-1}) for the reactions of 5×10^{-4} M Cu^{II}trien and 2×10^{-2}, 3×10^{-2}, and 5×10^{-2} M His were 7.67, 17.45, and 52.11 at pH 7.5 and 1074, 2280, and 3301 at pH 10.0, respectively.

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Cyanopentaamminechromium(III). Synthesis, Characterization, and Aquation Kinetics

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The $Cr(NH_3)_5(CN)^{2+}$ cation was synthesized by cyanide anation of $Cr(NH_3)_5(Me_2SO)^{3+}$ in dimethyl sulfoxide (Me_2SO) solution. The complex was isolated as the perchlorate salt and characterized by conductance, an ion-exchange technique, and infrared and electronic spectra. The ligand-field maxima agree with previous theoretical predictions. A vibrational structure on the charge-transfer band is consistent with a metal → ligand transition. The complex phosphoresces in aqueous solution at room temperature. The kinetics of CN^- aquation were studied over a wide range of acidities ((5×10^{-4})–2.0 M $HClO_4$) and ionic strengths (0.5–2.0 M $NaClO_4$). Cyanide release proceeds through two pathways: one is acid independent while the other is acid catalyzed and follows equilibrium protonation of the complex. The latter reaction path ($k_H = 1.5 \times 10^{-2}\ s^{-1}$ at 25 °C and $\mu = 2.0$) predominates largely over the former ($k_0 < 10^{-7}\ s^{-1}$ at 25 °C). The activation enthalpy for k_H (17.2 kcal mol^{-1}) is unusually low. Proton uptake by coordinated CN^- occurs to a considerable degree under the experimental conditions ($K = 0.28\ M^{-1}$ at 25 °C and $\mu = 2.0$). The ionic strength enhances the complex protonation but decreases the rate of acid-assisted aquation.

Introduction

Acidopentaammine complexes of chromium(III) have been extensively studied, especially with regard to their thermal[1,2] and photochemical[3] aquation reactions. Despite the wealth of information available on $Cr(NH_3)_5X^{2+}$ species, with X = halogeno,[1,2] pseudohalogeno,[1,2] carboxylato,[4,5] and oxo-

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aniono,[1,2,6,7] one important member of this series, $Cr(NH_3)_5(CN)^{2+}$, has not been described as yet. Compared with all other known acidopentaammines, the missing term is unique for several reasons: (i) the largest base strength of the acido group, (ii) the presence of a π-acceptor bond, (iii) the higher spectrochemical position of the X^- ligand, relative to NH_3, and, consequently, (iv) a different energy ordering of the ligand-field (LF) excited states arising upon descent from octahedral to quadrate symmetry. While theoretical background for interpreting the LF absorption spectrum is available,[8,9] the above properties make this complex photochemically unusual.

As part of a systematic investigation of the ground-state and excited-state reactivity of cyanoamminechromium(III) species,[10] we present the synthesis, characterization, and spectra of the $Cr(NH_3)_5(CN)^{2+}$ ion. In addition, we report on the aquation kinetics of the new compound for a variety of acidities and ionic strengths. Release of the highly basic cyanide ligand was expected to be favored by protonation. An acid-catalyzed reaction pathway was, in fact, observed, and the extent of proton uptake by bound CN^- was established. To date, only two accounts of mixed cyanoamine species of chromium(III), namely, *trans*-[11] and *cis*-$Cr(en)_2(CN)_2^+$,[11,12] have appeared in the literature.

Experimental Section

Materials. Dimethyl sulfoxide, Me_2SO (Erba RPE), was dried with 4-Å molecular sieves (Merck), distilled under nitrogen atmosphere at reduced pressure, and stored over anhydrous sodium sulfate.[13] All other chemicals and solvents employed were of reagent grade.

Aquopentaamminechromium(III) perchlorate was prepared by precipitation with concentrated $HClO_4$ from an aqueous solution of $[Cr(NH_3)_5(H_2O)](NO_3)_3 \cdot NH_4NO_3$ which, in turn, was obtained by a standard method.[14] The solution absorption spectrum shows maxima at 480 (ϵ 36) and 359 nm (ϵ 31), in agreement with literature values.[1]

(Dimethyl sulfoxide)pentaamminechromium(III) Perchlorate. The preparation followed a recently outlined procedure,[15] which was modified by some improvements. A 17-g portion of $[Cr(NH_3)_5(H_2O)](ClO_4)_3$ was dissolved in 40 mL of Me_2SO and heated at 70 °C for 20 min. The solution was cooled and then treated with 60 mL of 3 M $LiClO_4$ in methanol, which caused precipitation of the product. After additional ice-cooling, the red crystals were collected by filtration, washed with methanol and then with ethanol and ether, and vacuum dried. The yield was 17 g or 88%. The crude salt was recrystallized from aqueous solution (220 mL) by dropwise addition of 70 mL of concentrated $HClO_4$ and then washed and dried as above. Recovery was 83%. Reaction of the $[Cr(NH_3)_5(H_2O)](NO_3)_3 \cdot NH_4NO_3$ double salt with Me_2SO in the same conditions was unsuccessful, since decomposition of the complex prevailed over exchange with Me_2SO. Anal. Calcd for $[Cr(NH_3)_5(C_2H_6SO)](ClO_4)_3$: Cr, 10.13; NH_3, 16.58. Found: Cr, 10.1 ± 0.1; NH_3, 16.6 ± 0.1. The maxima of the ligand-field absorption spectrum in aqueous solution are at 498 (ϵ 41.5) and 367 nm (ϵ 33.4). The minimum in between occurs at 417 nm (ϵ 8.6). In addition, the following features, associated with the transition to the first doublet excited state, are observed: 667 (ϵ 0.4), 661 (ϵ 0.3), and 634 nm (ϵ 0.3).

Cyanopentaamminechromium(III) Perchlorate. A 1.9-g amount of sodium cyanide (ca. 40 mmol) was dissolved on heating in 80 mL of Me_2SO. After addition of 5.0 g of $[Cr(NH_3)_5(Me_2SO)](ClO_4)_3$ (ca. 10 mmol), the mixture was kept at 70 °C for 20 min. The deep-orange solution was cooled and treated with 100 mL of 3 M LiCl in methanol. A yellow salt slowly precipitated and, after additional cooling (3 h), was filtered off, washed with methanol and then with ethanol and ether, and air-dried. The yield of $[Cr(NH_3)_5(CN)]Cl_2$ was 1.5 g or 65%.

Precipitation from the Me_2SO solution as the perchlorate salt by addition of $NaClO_4$ in methanol led to a considerably lower product recovery. When the reaction was carried out in the presence of a larger molar excess of NaCN (fivefold or more), the complex started to separate earlier from the hot solution as the cyanide salt. In this case the crude compound was impure (possibly by products of further CN^- anation) and was difficult to recrystallize.

The chloride salt was converted into the perchlorate by reprecipitation from aqueous solution (100 mL) with 100 mL of 8 M $NaClO_4$. Precipitation was very slow and was favored by long standing (2–3 days) in a refrigerator. The yellow crystals were collected by filtration, washed with ethanol and ether, and vacuum dried. The yield was about 40%. Recrystallization of the perchlorate was accomplished in the same manner by using smaller amounts of solvent (1 g in 10 mL), as this salt is more soluble in water than the chloride. Anal. Calcd for $[Cr(NH_3)_5(CN)](ClO_4)_2$: Cr, 14.36; NH_3, 23.52; CN, 7.18. Found: Cr, 14.2 ± 0.1; NH_3, 23.5 ± 0.1; CN^-, 7.3 ± 0.2.

Analytical Procedures. The complex salts were decomposed in sodium hydroxide solution. Chromium was determined spectrophotometrically at 374 nm (ϵ 4760 M^{-1} cm^{-1}), following oxidation to chromate ion with alkaline hydrogen peroxide. Ammonia was analyzed by a semimicro Kjeldahl technique, distilling NH_3 from the above alkaline samples. For determination of cyanide, the cyanopentaamminechromium(III) salt was decomposed in 1 M $HClO_4$ at room temperature. The solution was then buffered at pH 10 and was titrated potentiometrically with silver nitrate by using a Radiometer TTT 1c automatic titrator. The free CN^- content of solutions was also measured potentiometrically by use of an Amel Model 201-CN Sens-Ion electrode, coupled with an Amel Model 332 potentiometer. Samples were buffered at pH 12, and standardization plots were run in parallel with each set of measurements by using NaCN. Within the range of concentration 10^{-3}–10^{-5} M, the reproducibility was ±3%.

Ion-exchange experiments were performed with 3 cm × 1 cm columns of Sephadex SP-C25 cationic resin in the sodium form. Elution was with various concentrations of neutral $NaClO_4$. Electrical conductance of aqueous samples was measured at 20 °C by a Philips PW 9501 conductivity meter, connected with a PW 9512 cell. Optical densities of solutions at specific wavelengths were determined with a Beckman DU spectrophotometer. General electronic absorption spectra were recorded with Shimadzu UV 200S and Cary 17 instruments. Luminescence spectra were measured on argon-saturated solutions by using a Perkin-Elmer MPF 44A spectrofluorimeter, equipped with an R 446 photomultiplier. Infrared spectra were taken on a Perkin-Elmer 257 grating spectrophotometer.

Kinetic Procedures. Rates of aquation of cyanopentaamminechromium(III) were determined spectrophotometrically, by recording the decrease in optical density at given wavelengths, as a continuous function of time. Most of the measurements were done at 230 nm (charge-transfer band), where the extinction coefficients for the reactant and for the product are 470 and 18 M^{-1} cm^{-1}, respectively. The 2.5-mL samples, ca. 1×10^{-3} M in complex, were made up in spectrophotometer cells of 1.0-cm path length, held in a thermostated compartment. The solvent was previously brought to the desired temperature, and 10–15 μL of a stock solution of the complex in water (where it is extremely inert; vide infra) was added with stirring, so that reliable absorbance values could be recorded within 5 s from mixing, under the conditions of fastest conversion. The temperature was kept constant to within 0.1 °C. The reaction was generally followed for ca. 3 half-lives, and A_∞ values were read after 8–10 half-lives. Four sets of measurements were carried out, each one for a series of acidities ($HClO_4$) and at a constant ionic strength (μ = 0.5, 1.0, 1.5, 2.0 M) established by means of added sodium perchlorate. Within a given set, the $HClO_4$ concentration generally varied between 0.05 M and a maximum value, corresponding to the whole ionic strength. At 45 °C and μ = 2.0 M, the determinations were extended to lower acid concentrations, down to 5×10^{-4} M. In order to always maintain a large excess (at least 20 times) of the H^+ concentration over that of released cyanide, we followed the optical density changes for the less acidic solutions up to smaller extents of aquation. For this reason, samples with $HClO_4$ concentrations lower than 10^{-3} M were only 2×10^{-4} M in complex and were monitored in cells of 4.0-cm path length (10-mL volume).

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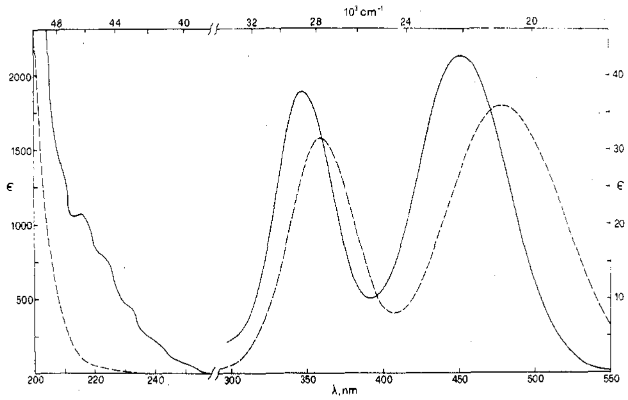

Figure 1. Ligand-field (ε on the right) and charge-transfer (ε on the left) absorption spectra in 10^{-3} M $HClO_4$: solid line, $Cr(NH_3)_5(CN)^{2+}$; broken line, $Cr(NH_3)_5(H_2O)^{3+}$.

A number of rate measurements were performed at 435 nm (first LF band) by using the same general criteria as above. Because of the smaller extinction coefficients (36.6 M^{-1} cm^{-1} for $Cr(NH_3)_5(CN)^{2+}$ and 17.6 M^{-1} cm^{-1} for $Cr(NH_3)_5(H_2O)^{3+}$), the complex concentrations were around 1×10^{-2} M and 3.0-cm cells were employed. Pseudo-first-order rate constants were evaluated from least-squares fits of log $(A_t - A_\infty)$ vs. time.

A few rate constants were obtained by direct determination of released CN^- ion, with the cyanide-sensitive electrode. Solutions were thermostated in Al-foil-wrapped volumetric flasks. Aliquots (3 mL) were withdrawn at intervals, buffered at pH 12, and potentiometrically analyzed. At this pH and at room temperature, thermal CN^- release is so slow that analytical measurements were not affected by the presence of the complex.

Most of the reported rate constants are the average of at least two independent experiments. While the spectrophotometric results were reproducible to ±1.5%, the lower precision of CN^- analysis allowed an average deviation of ±7% for the other data. Whenever a rate constant was measured by different methods, the results agreed within experimental error. Activation enthalpies and entropies were derived from a least-squares analysis of log (k/T) vs. $1/T$.

Results

Preparation. Cyanide anation of (dimethyl sulfoxide)pentaamminechromium(III) takes place smoothly in dimethyl sulfoxide (eq 1), as shown by a progressive shift of the solution

$$Cr(NH_3)_5(Me_2SO)^{3+} + CN^- \rightarrow Cr(NH_3)_5(CN)^{2+} + Me_2SO \quad (1)$$

absorption maxima to shorter wavelengths, during substitution. Access of the CN^- ion to the coordination sphere is considerably favored in a dipolar aprotic medium, with respect to aqueous solutions, by various factors: (i) the enhancement of ion association,[16] (ii) a poorer anion solvation,[17] and (iii) the absence of any hydrolysis. Some role must also be played by the departing ligand. Attempts to anate $Cr(NH_3)_5(H_2O)^{3+}$ either in water or in Me_2SO (as well as in dimethylacetamide)[18] were unsuccessful, as deprotonation of coordinated H_2O by CN^- produced hydroxopentaamminechromium(III), whose decomposition was strongly competitive with ligand replacement. Also, $Cr(NH_3)_5Cl^{2+}$ was found to be extremely resistant to interchange with CN^-. Prolonged reaction periods led to mixtures of products of stepwise coordination of more CN^- groups, as qualitatively evidenced by a further blue shift of the spectrum.

Table I. Electronic Spectrum of $Cr(NH_3)_5(CN)^{2+}$ in Aqueous Solution

obsd features		predicted	
λ, nm	ε, M^{-1} cm^{-1}	max[a] λ, nm	assignt[b]
680[c]			$^2E_g \rightarrow {}^4A_{2g}$[d]
		464	$^4B_1 \rightarrow {}^4B_2$ ($^4T_{2g}$)
451 (max)	42.6		
		440	$^4B_1 \rightarrow {}^4E$ ($^4T_{2g}$)
391 (min)	10.0		
		349	$^4B_1 \rightarrow {}^4E$ ($^4T_{1g}$)
347 (max)	37.7		
		342	$^4B_1 \rightarrow {}^4A_2$ ($^4T_{1g}$)
251 (sh)	60		$t_{2g} \rightarrow t_{1u}$ (π^*)
241 (sh)	200		
232 (sh)	440		
224 (sh)	760		
217 (sh)	1060		
210 (sh)	1330		

[a] According to ref 9. [b] Octahedral parent states in parentheses. [c] Transition observed in emission only. [d] In octahedral approximation.

Spectra. The electronic spectrum of the $Cr(NH_3)_5(CN)^{2+}$ ion in aqueous solution is displayed in Figure 1. In octahedral approximation, the two LF maxima (values in Table I) are assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions, respectively, in order of increasing energy. If comparison is made with $Cr(NH_3)_6^{3+}$, especially the first LF maximum (462 nm for the hexaammine) results to be displaced toward shorter wavelengths, as expected on the basis of the higher spectrochemical position of CN^-, relative to NH_3. Considering the actual C_{4v} complex symmetry, the octahedral $^4T_{2g}$ excited state is split into the ^4E and $^4B_2$ components and, likewise, the $^4T_{1g}$ one gives rise to the $^4A_2$ and ^4E levels.[8,9] The wavelengths of the corresponding transitions from the $^4B_1$ ground state have already been predicted according to LF theory[9] and are compared with the experimental data in Table I. Because of the relatively small energy separation (1200 cm^{-1}) between the sublevels, no splitting is apparent, even in the long-wavelength band, as it is undetectable in many other $Cr(NH_3)_5X^{2+}$ complexes.[1] However, an excellent agreement exists between the observed maxima and the average values of the calculated components, for each band.

In 2.0 M $HClO_4$ (at 0 °C), the first LF maximum is shifted to the red by 3–4 nm. This is congruent with the kinetic evidence for protonation of a significant fraction of the complex under these conditions (vide infra). The HCN ligand is then spectrochemically weaker than CN^-.

It is worthwhile to note that the $Cr(NH_3)_5(CN)^{2+}$ cation is electronically atypical among acidopentaammines of chromium(III). While the acido groups of all other known $Cr(NH_3)_5X^{2+}$ species exert a lower ligand-field strength with respect to NH_3, in the present case the average strength along the z (NH_3–CN^-) axis is higher than that on the xy $(NH_3)_4$ equatorial plane. It follows that the usual energy ordering of the excited sublevels is reversed, and the $^4B_2$ state falls below the ^4E one. Given the important photochemical role of the lowest spin-allowed excited state of chromium(III),[3] this peculiarity bears on the photolytic behavior. The antibonding electron density associated with the $^4B_2$ state is prevalently localized on the $d_{x^2-y^2}$ orbital, so that bond weakening upon LF excitation may be expected to occur preferentially on the equatorial plane rather than on the z axis, as observed in many other tetragonal chromium(III) complexes.[3]

The intense UV absorption with onset at 257 nm is associated with a metal-to-ligand, $t_{2g} \rightarrow t_{1u}$ (π^*, CN^-), charge-transfer (CT) transition. Such an assignment appears reasonable on the grounds of previous spectral interpretation for $Cr(CN)_6^{3-}$ and other hexacyano complexes.[19] A remarkable characteristic of this band is a succession of six shoulders, the wavelengths of which are given in Table I. This clean, organic-type pattern presents a constant separation between

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successive features of ca. 1600 cm^{-1}. Both the constancy and the magnitude of the energy differences suggest that a vibrational sequence is involved. The vibration whose progressions are to be expected on a Laporte-allowed band is the C–N stretch.[19] A C–N stretching frequency for the excited state lower (ca. 25%) than that of the ground electronic state (vide infra) is consistent with an electron being in a π^*(CN) orbital. These observations may be taken as further evidence for a metal-to-ligand nature of the CT excited state. On the contrary, the CT transitions of all other known acidopentaammines of chromium(III) (having π-donor-only acido groups) are recognized as ligand-to-metal electron excitations.

In deaerated (Ar saturated) aqueous solution at room temperature, the complex exhibits moderately intense luminescence, centered at 680 nm. The emission band is assigned as $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence (in O_h approximation). The reverse process, doublet absorption, is barely detectable in the present case.

The infrared spectrum confirms coordination of CN^- with the presence of a sharp band at 2140 cm^{-1}, corresponding to the C–N stretching frequency. The intensity of absorption is fairly low, as already reported in the literature for *cis*-[11,12] and *trans*-$Cr(en)_2(CN)_2{}^+$.[11]

Solution Behavior. The new chromium(III) cation was characterized also in solution by an ion-exchange technique, by conductance measurements, and by its aqueous chemistry.

The complex was completely eluted through the cationic exchanger by 5×10^{-2} M $NaClO_4$. In parallel experiments such a solution displaced dipositive chromium(III) ions, as $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5(NCS)^{2+}$, but not the tripositive $Cr(NH_3)_6{}^{3+}$ species. Upon elution with 2×10^{-2} M $NaClO_4$, the column retained $Cr(NH_3)_5(CN)^{2+}$, whereas the same eluant moved 1+ charged compounds such as $Cr(NH_3)_4(C_2O_4)^+$ and *trans*-$Cr(NH_3)_4Cl_2{}^+$.

The molar conductivity of a 1×10^{-3} M solution of the perchlorate salt of the complex in water at 20 °C is 230 Ω^{-1} cm^2, which is in the range of 1:2 electrolytes. The values for the perchlorates of $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5(NCS)^{2+}$ in the same conditions are 222 and 220 Ω^{-1} cm^2, respectively.

Aqueous samples of $Cr(NH_3)_5(CN)^{2+}$, either at the natural pH (ca. 6.3) or at an alkaline pH, are quite stable at room temperature, as indicated by the constancy of their absorption spectra even after 1 day. In acidic media ($HClO_4$), instead, the cyanide ligand is readily replaced by solvent. Both LF absorption bands undergo a progressive red shift, accompanied by the appearance of increasing amounts of free CN^-. Three sharp isosbestic points are observed at 472 (ϵ 35.2), 395 (ϵ 10.4), and 360 nm (ϵ 31.4), precisely where the spectra of $Cr(NH_3)_5(CN)^{2+}$ and $Cr(NH_3)_5(H_2O)^{3+}$ cross (Figure 1).

At pH <3 the isosbestic points are maintained up to 100% conversion, and the final spectrum exhibits maxima at 480 (ϵ 35.8) and 359 nm (ϵ 31.4), which identify aquopentaamminechromium(III).[1] The simultaneous presence of stoichiometric amounts of uncoordinated CN^- confirms that cyanopentaamminechromium(III) behaves cleanly according to eq 2. In acid solution the spectrum of the aquation product

$$Cr(NH_3)_5(CN)^{2+} + H_2O \rightarrow Cr(NH_3)_5(H_2O)^{3+} + CN^- \quad (2)$$

is fairly stable (further aquation of $Cr(NH_3)_5(H_2O)^{3+}$ is slower by a factor of at least 10^2),[1] so that the aquo complex can be either precipitated as the perchlorate salt or characterized by ion-exchange tests.

At higher pH values, deviation from isosbestic behavior takes place before reaction is completed, due to the combined effects of a slower aquation rate of $Cr(NH_3)_5(CN)^{2+}$ (vide infra) and of a faster secondary decomposition of $Cr(NH_3)_5(H_2O)^{3+}$. The latter phenomenon becomes important at pH >4, since deprotonation of the aquopentaammine complex ($pK_a = 5.3 \pm 0.1$)[1] produces nonnegligible amounts of the more reactive $Cr(NH_3)_5(OH)^{2+}$ complex.

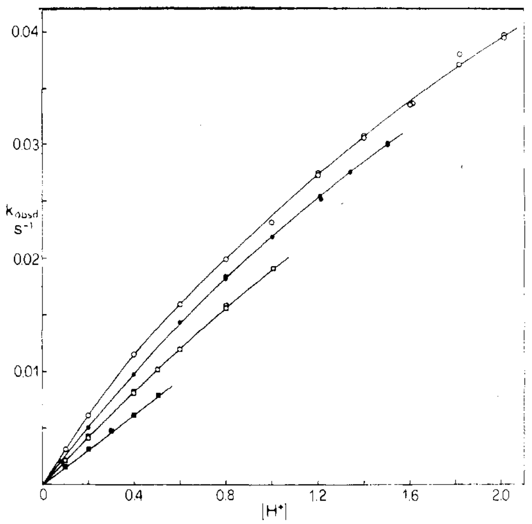

Figure 2. Pseudo-first-order rate constants for aquation of $Cr(NH_3)_5(CN)^{2+}$ as a function of the hydrogen ion concentration, at 45.0 °C and constant ionic strengths of 0.5 M (■), 1.0 M (□), 1.5 M (●), and 2.0 M (○) ($NaClO_4$).

Preliminary kinetic experiments were run with use of sulfate, acetate, and phosphate buffers. In the presence of any of these species, the reaction products, as identified by absorption spectra, were somewhat different than in solutions containing only the perchlorate anion. Also, at a given acidity, the reaction rates changed markedly in different media. Partial anation was clearly occurring, as already noted in the literature for analogous systems.[6] For this reason, the use of such buffers was carefully avoided in kinetic studies.

As a final, qualitative observation, the considerable inertness of $Cr(NH_3)_5(CN)^{2+}$ in alkaline solution contrasts with the fast, base-catalyzed decomposition of other acidopentaammines of chromium(III).[1,2]

Aquation Kinetics. The thermal reactivity of $Cr(NH_3)_5(CN)^{2+}$ was quantitatively studied over a wide range of acidities ((5×10^{-4})–2.0 M $HClO_4$) and ionic strengths (0.5–2.0 M). At pH <3, first-order rate plots were always linear up to 80–90% conversion to $Cr(NH_3)_5(H_2O)^{3+}$. Only for lower acidities was the linearity limited to smaller percentages of reaction (in any case at least 25%), in parallel with the loss of isosbestic behavior, for the reasons mentioned above.

The pseudo-first-order rate constants for aquation, k_{obsd}, are listed in Table II, together with the experimental conditions. The immediate finding is that the reaction is strongly acid catalyzed. At given temperatures and ionic strengths (1.0 M or more), plots of k_{obsd} vs. the hydrogen ion concentration deviate from linearity, especially at high acidities, as exemplified in Figure 2. The downward curvature indicates a less-than-first-order dependence on $[H^+]$. Such a pattern can be accounted for by a scheme involving two pathways for aquation: the first one is acid independent while the other follows fast and reversible equilibrium protonation of a fraction of the reactant (eq 3–5).

$$Cr(NH_3)_5(CN)^{2+} + 2H_2O \xrightarrow{k_0} Cr(NH_3)_5(H_2O)^{3+} + HCN + OH^- \quad (3)$$

$$Cr(NH_3)_5(CN)^{2+} + H_3O^+ \overset{K}{\rightleftharpoons} Cr(NH_3)_5(CNH)^{3+} + H_2O \quad (4)$$

$$Cr(NH_3)_5(CNH)^{3+} + H_2O \xrightarrow{k_H} Cr(NH_3)_5(H_2O)^{3+} + HCN \quad (5)$$

Table II. Pseudo-First-Order Rate Constants for Aquation of $Cr(NH_3)_5(CN)^{2+}$ [a]

$\mu = 2.0$ M[b]			$\mu = 2.0$ M[b]			$\mu = 1.5$ M[b]			$\mu = 1.0$ M[b]			$\mu = 0.5$ M[b]		
T, °C	[H$^+$], M	10^3k_{obsd}, s^{-1}	T, °C	[H$^+$], M	10^3k_{obsd}, s^{-1}	T, °C	[H$^+$], M	10^3k_{obsd}, s^{-1}	T, °C	[H$^+$], M	10^3k_{obsd}, s^{-1}	T, °C	[H$^+$], M	10^3k_{obsd}, s^{-1}
25.0	0.100	0.400	45.0	0.000505	0.0181	45.0	0.0760	2.01	25.0	0.201	5.15	25.0	0.0481	0.0958
	0.200	0.779		0.00101	0.0331		0.201	5.08		0.400	1.02		0.0727	0.148
	0.401	1.46		0.00505	0.170		0.402	9.75		0.501	1.27		0.0963	0.186
	0.600	2.08		0.0101	0.339		0.601	14.4		0.602	1.50		0.489	1.03
	0.800	2.78		0.100	3.11		0.802	18.3		0.807	2.01	35.0	0.0481	0.278
	1.001	3.26		0.200	6.06		1.00	21.9		1.00	2.43		0.0727	0.438
	1.20	3.73		0.401	11.5		1.20	25.3	45.0	0.100	2.09		0.0963	0.500
	1.40	4.08		0.600	16.0		1.34	27.6		0.201	4.18		0.489	2.86
	1.61	4.61		0.801	19.9		1.50	30.0		0.401	8.23	45.0	0.0481	0.729
	1.81	4.87		1.001	23.1					0.501	10.14		0.0727	1.18
	2.01	5.22		1.20	27.4					0.601	11.9		0.0963	1.48
35.0	0.100	1.13		1.40	30.7					0.806	15.8		0.101	1.57
	0.200	2.19		1.61	33.4					1.00	19.1		0.201	3.16
	0.401	4.16		1.81	37.8								0.301	4.74
	0.600	5.98		2.01	39.7								0.401	6.16
	0.801	7.43											0.506	7.90
	1.001	8.99										55.0	0.0481	1.96
	1.20	10.26											0.0727	3.00
	1.40	11.6											0.0963	4.12
	1.61	12.9											0.489	19.1
	1.81	13.9												
	2.01	14.9												

[a] Most of the data are the average of two kinetic experiments. Precision is ±1.5%. [b] Ionic strength maintained constant by means of $NaClO_4$.

Table III. Rate and Equilibrium Constants[a] and Activation Parameters for Aquation of $Cr(NH_3)_5(CN)^{2+}$

		value of const				
μ, M	const	45.0 °C	35.0 °C	25.0 °C	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu
2.0	k_0, s^{-1}	$<1 \times 10^{-6}$		$(<1 \times 10^{-7})$		
	10^3k_HK, M^{-1} s^{-1}	32.1 ± 0.1	11.67 ± 0.02	4.10 ± 0.01	20.0 ± 0.2	20.2 ± 0.6
	10^2k_H, s^{-1}	9.7 ± 0.3	3.9 ± 0.1	1.47 ± 0.04	17.2 ± 0.1	−9.3 ± 0.3
	K, M^{-1}	0.33 ± 0.01	0.297 ± 0.006	0.279 ± 0.009		
1.5	10^3k_HK, M^{-1} s^{-1}	27.0 ± 0.4				
	10^2k_H, s^{-1}	13.0 ± 0.6				
	K, M^{-1}	0.23 ± 0.02				
1.0	10^3k_HK, M^{-1} s^{-1}	21.5 ± 0.3		2.62 ± 0.03	19.2 ± 0.8	
	10^2k_H, s^{-1}	18 ± 2		3.3 ± 0.7	15.3 ± 1.3	−14.0 ± 4.3
	K, M^{-1}	0.12 ± 0.02		0.079 ± 0.017		
0.5	10^3k_HK, M^{-1} s^{-1}	15.5 ± 0.8	5.88 ± 0.27	1.99 ± 0.05	20.1 ± 0.2[b]	19.3 ± 0.5[b]
	10^2k_H, s^{-1}	(26 ± 2)				
	K, M^{-1}	(0.06 ± 0.01)				

[a] Extrapolated values in parentheses (see text). [b] Calculated including $k_HK = 0.041 \pm 0.001$ M^{-1} s^{-1}, at 55.0 °C.

According to this scheme, the experimental data, k_{obsd}, are related through eq 6 to the first-order rate parameters k_0 and k_H for the uncatalyzed and acid-catalyzed reaction modes, respectively.

$$k_{obsd} = (k_0 + k_HK[H^+])/(1 + K[H^+]) \qquad (6)$$

At low acidity values the $K[H^+]$ product can be neglected with respect to unity and k_{obsd} becomes a linear function of $[H^+]$. Linear dependence on the acid concentration is, in fact, observed in the $[H^+] = 0$–10^{-2} M (expanded) range. Extrapolation to $[H^+] = 0$ should yield the rate constant, k_0, for reaction 3. However, because of the above-mentioned experimental limitations, rate constants could not be obtained for acidities lower than 5×10^{-4} M. Even with low-acidity data (i.e., at larger scale expansion), the intercepts of Figure 2 remain very close to zero and the standard deviations for k_0, evaluated by a least-squares analysis, are larger than the k_0 values themselves (e.g., $k_0 = 2 \times 10^{-7} \pm 1 \times 10^{-6}$ s^{-1} at 45 °C). Therefore, only an upper limit could be established for k_0. From particularly accurate data at 45 °C and $\mu = 2.0$ M, k_0 was found to be smaller than k_H by a factor of at least 10^5. On the other hand, any attempt to get a better numerical estimate of k_0 through eq 6 failed, the scatter of results being again larger than the above upper limit. Since it was virtually impossible to determine the actual k_0 value under any condition, the same factor was assumed to separate k_H from k_0 at all temperatures and ionic strengths.

For evaluation of the other parameters, eq 6 may be rearranged in the form of eq 7.

$$\frac{1}{k_{obsd} - k_0} = \frac{1}{k_H - k_0} + \frac{1}{(k_H - k_0)K}\,\frac{1}{[H^+]} \qquad (7)$$

As the contribution of k_0 to the observed rate constant is negligible, plots of $1/k_{obsd}$ vs. $1/[H^+]$ should be linear. This is, in fact, the observation for all conditions, as shown in Figure 3. The reciprocal of the intercept corresponds to k_H, while the ratio of the intercept to the slope gives the equilibrium constant for protonation (eq 4). The values of k_HK, k_H, and K for various ionic strengths and temperatures and the activation parameters are collected in Table III.

It should be noticed that the lower the ionic strength, the less pronounced the curvature of the plots of Figure 2, denoting smaller and smaller extents of protonation in equilibrium 4. As a consequence, a larger uncertainty arises in the compu-

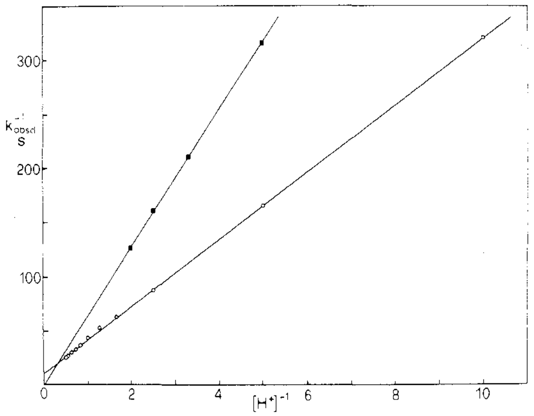

Figure 3. Plot of k_{obsd}^{-1} vs. $[H^+]^{-1}$ for aquation of $Cr(NH_3)_5(CN)^{2+}$ at 45.0 °C. For the sake of clarity, only the data at μ = 0.5 M (■) and μ = 2.0 M (○) are reported.

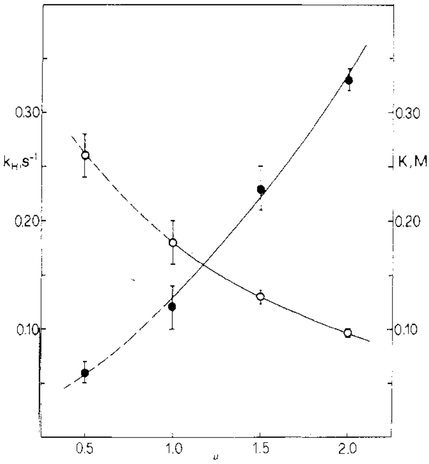

Figure 4. Dependence on the ionic strength of the first-order rate constant, k_H, for reaction 5 (○) and of the equilibrium constant, K, for eq 4 (●). The k_H and K values at μ = 0.5 M are obtained by imposing both smooth extrapolations from data at higher ionic strengths and agreement of their product with the experimentally determined k_HK quantity. Temperature is 45.0 °C.

tation of k_H and K with decreasing μ, due also to the lower acidity region spanned. For μ = 0.5 M the above plots appear essentially linear and the intercepts of eq 7 and Figure 3 tend to zero. Under these circumstances, the individual parameters cannot be calculated and only their product is given. The only way to obtain approximate values for k_H and K at μ = 0.5 M is extrapolation from data at higher ionic strengths and at the same temperature, as illustrated in Figure 4. The k_HK product can then provide a check for the consistency of the extrapolated quantities.

Discussion

The occurrence of an acid-catalyzed pathway (eq 4 and 5) for aquation of $Cr(NH_3)_5(CN)^{2+}$ is undoubtedly related to the high basicity of CN^-. The lability of cyanide is clearly increased by protonation, as removal of the negative charge of the leaving group is expected to cause larger ligand repulsion. Reaction paths of this kind are generally observed when the departing ligand either hydrogen bonds or is strongly basic.[1,2,20] Among other $Cr(NH_3)_5X^{2+}$ ions, acid catalysis was found for X = F,[21] N_3,[22] ONO,[23] and $OCOCCl_3$.[4] For X = CN the acid-dependent pathway predominates completely over the acid-independent one (eq 3) as for X = ONO.[23] However, unlike the cyanide, the nitrito complex exhibits linear first-order dependence on $[H^+]$. This suggests that the equilibrium constant for protonation of the ONO^- ligand is somewhat smaller than that for protonation of coordinated cyanide, in agreement with the lower basicity of ONO^-. In the present case, K is sufficiently large that a considerable fraction of the complex undergoes protonation at high acidities and ionic strengths (e.g., 22–25% at pH 0 and μ = 2.0 M).

Since protonation changes the nature of the acido group, the absorption spectrum should be modified under the conditions of appreciable hydrogen ion uptake. The bathochromic shift observed for the low-energy LF band in 2.0 M $HClO_4$ is consistent with this expectation. Owing to the exceedingly high reactivity in such a medium, the spectrum could be recorded only at 0 °C. Assuming $K \approx 0.2$ at this temperature (by extrapolation from higher temperatures), we estimated the first LF maximum of the pure $Cr(NH_3)_5(CNH)^{3+}$ species to occur at 460–465 nm. Therefore, the spectrochemical position of the HCN ligand results to be lower than that of CN^- and would be located between NH_3 and H_2O. The spectral changes are also manifested by a slight shift of the isosbestic points during aquation in $[H^+]$ = 2.0 M, with respect to lower acidities.

Also, several $Cr(H_2O)_5X^{2+}$ type complexes have been reported to undergo acid-catalyzed aquation, when X = F,[24] N_3,[25] OSO_3,[26] H_2PO_2,[27] $OCOCH_3$,[28] and CN.[29,30] The aquation behavior of $Cr(H_2O)_5(CN)^{2+}$ [30] closely resembles the present results, so that some comparison appears possible. At the same ionic strengths and acidities, both k_{obsd} and k_H are larger for the pentaammine complex than for the pentaaquo one by a factor of 5–6. The difference fits a general trend. A literature survey[2,31] indicates that about one order of magnitude separates the aquation rates of $Cr(NH_3)_5X^{2+}$ ions from those of the $Cr(H_2O)_5X^{2+}$ analogues. The present activation enthalpy for $k_H(\mu = 2.0\ M)$ is virtually identical with that of $Cr(H_2O)_5(CN)^{2+}$ (16.2 ± 2.0 kcal mol^{-1}),[30] while the $\Delta S^{\ddagger}$ values are not very different for the two complexes (−16.0 ± 4.0 eu for the pentaaquo species),[30] suggesting that the same mechanism is operative in both systems for the acid-catalyzed pathway. $\Delta H^{\ddagger}$ is unusually low for chromium(III), providing additional evidence that the acid-assisted reaction mode is highly preferred.

The slightly larger extent of protonation for the pentaammine than for the pentaaquo ion (as inferred from K) may be ascribed to the different ligand environment. Since oxygen is more electronegative than nitrogen, $(H_2O)_5Cr(CNH)^{3+}$ should be a stronger acid than $(NH_3)_5Cr(CNH)^{3+}$.

Concerning the acid-independent reaction path (eq 3), the small magnitude of k_0 should reflect the high nucleophilicity of CN^- and the considerable degree of π bonding which must be overcome on going to the transition state. Here the (partially filled) t_{2g} metal-localized orbitals (in O_h approximation) are π bonding. In all other acidopentaammines, these orbitals are π antibonding and, consistently, higher reactivities are observed.

In the case of $Cr(H_2O)_5(CN)^{2+}$, evidence has been reported for an internal proton transfer from coordinated water to CN^-.[29,30] Loss of cyanide would be facilitated by such a transfer, since the departing ligand would be neutral, while the complex would be left with a 2+ (instead of 3+) charge.

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The absence of this possibility in $Cr(NH_3)_5(CN)^{2+}$ may well account for the much smaller k_0 value found for the pentaammine ion, although its k_H is larger than that of the pentaaquo complex.

For $Cr(NH_3)_5X^{2+}$ [1,6,31] and $Cr(H_2O)_5X^{2+}$,[1,30,31,33] as well as for $Co(NH_3)_5X^{2+}$ complexes,[20,31,32] the rate constants for uncatalyzed aquation have been correlated with the aquation equilibrium constants[20,32] (or their reverse),[6,33] with the base strength of the leaving group,[31] and with the spectrochemical strength of X^-, as deduced from the frequency of the first LF absorption band.[30,32] In general, the rates decrease with decreasing equilibrium constants and with increasing basicity and ligand-field strength of X^-. With exception of some ligands, fairly good linear free-energy relationships were observed. CN^- occupies an extreme position both in the scale of basicities (for complexes known to date) and in the spectrochemical series. It may then be interesting to check whether the results for the new complex conform with the above relations, even though, unfortunately, only a limiting value could be obtained for k_0.

With literature data (for X = I, Br, Cl, F, NCS, N_3),[1,2,31] a plot of log k_0 vs. pK_a for HX yields an extrapolated k_0 value of about 10^{-9} s^{-1} at 25 °C for $Cr(NH_3)_5(CN)^{2+}$. According to the ligand-field strength criterion, the order of magnitude of k_0 would result 10^{-15} s^{-1}. While our finding is in qualitative agreement with both estimates, the k_0 value extrapolated from pK_a data appears more plausible. It has been pointed out that the main determinant of the energy of activation for substitution is the energy of the σ-bonding system, whereas the spectrochemical position of a ligand reflects a mixture of σ and π interactions.[32] The large π-electron involvement in bound cyanide may therefore account for the discrepancy between the two extrapolations; that is, the spectral properties may be affected by π interactions to a much larger extent than the bond strength. As a confirmation of this point, a better agreement between the base-strength predictions and the spectroscopic ones ($k_0 \approx 10^{-10}$–10^{-11} s^{-1}) is found if only the σ parameters of the two-dimensional spectrochemical series[34] are considered.

The most complete set of rate constants was obtained at an ionic strength of 2.0 M, so as to cover the largest possible interval of acidities and, at a given acidity, to maximize the extent of protonation. However, sufficient data were collected for other μ values that some general remarks on the influence of the ionic strength upon the various parameters may be made.

(1) In order to rule out possible medium effects within a given ionic strength, we calculated k_HK, k_H, and K by least-squares fits of eq 7 using different sets of k_{obsd} data (i.e., first, only four experimental points, corresponding to the lowest acidities, then five points, then six, and so on). The results did not present any trend, as the deviations from the values obtained by including all the points and reported in Table III were random and within experimental error. Thus, no effect is apparent when $NaClO_4$ is replaced by $HClO_4$, indicating that the activity coefficients remain essentially constant over the whole range of acidities and that the curvature of the plots of Figure 2 is actually attributable to the presence of different fractions of protonated complex at different $[H^+]$.

(2) Protonation of the complex is favored by the ionic strength; i.e., the concentration equilibrium constant, K, increases with increasing μ, as shown in Figure 4. This is consistent with a decrease of the activity coefficients for the species participating in equilibrium 4. An analogous increase of protonation was reported for $Cr(H_2O)_5(OCOCH_3)_2^{+}$ [28] and $Cr(H_2O)_5(CN)^{2+}$.[30]

(3) At constant H^+ concentration, the pseudo-first-order rate constants, k_{obsd}, increase by a factor of ca. 2, on passing from $\mu = 0.5$ to $\mu = 2.0$ M. From eq 6, such an effect appears to be essentially due to the increment of the k_HK product by about the same factor (it may be noticed that, despite this change, the activation enthalpy for k_HK is independent of μ). On the other hand, the individual rate constant for the acid-assisted pathway, k_H, drops significantly with increasing ionic strength. It follows that the enhancement of the over all reactivity depends on the increase of K, i.e., on the presence of larger equilibrium amounts of protonated complex, although the latter becomes intrinsically less reactive at higher ionic strengths.

We are presently investigating the photochemistry of the $Cr(NH_3)_5(CN)^{2+}$ ion. The excited-state reactivity upon LF band irradiation consists exclusively of NH_3 aquation and is typically "antithermal", as widely established for many other chromium(III) complexes.[3]

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Registry No. $[Cr(NH_3)_5(CN)](ClO_4)_2$, 72509-66-1; $[Cr(NH_3)_5(CN)]Cl_2$, 72509-67-2; $[Cr(NH_3)_5(Me_2SO)](ClO_4)_3$, 65821-32-1; $[Cr(NH_3)_5(H_2O)](ClO_4)_3$, 32700-25-7.

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