Table III. Diffusion Coefficient of Sb(III) in $AlCl_3$–RCl Melts

melt	10^7D, $cm^2\ s^{-1}$	$10^{10}D\eta/T$, $g\ cm\ s^{-2}\ K^{-1}$
slightly basic $AlCl_3$–ImCl	2.65	1.3
slightly acidic $AlCl_3$–ImCl	8.39	4.1
basic $AlCl_3$–BuPyCl[a]		1.3
acidic $AlCl_3$–BuPyCl[a]		3.8

[a] Data taken from ref 11.

do not distinguish here between $SbCl_3$ and $SbCl_3\cdots AlCl_4^-$ or $SbCl_2^+$ and $SbCl_2^+\cdots AlCl_4^-$.

The calculated values of $i{:}i_{tot}$ correspond to the case when chloride ions released during reduction of the Sb(III) complex do not influence the reduction current of Sb(III). However, all the possible reactions of Cl^- ions released at the electrode surface upon reduction of the Sb(III) will cause a *decrease* of this current; the calculated values are the maximum values for each mechanism. For example, if we consider reaction 1 as occurring in solution *prior* to the reduction of Sb(III), then, at $R = 1$, no more than one-third of the Sb(III) will be transformed into its "acidic form", because the stoichiometry of reaction 1 is 1:3 $SbCl_3{:}AlCl_3$. The experimental data indicates the current of the "acidic form" exceeds $^1/_3$ of i_{tot}, thus eliminating this possibility. By analogy, we can also eliminate the second possibility, i.e. $SbCl^{2+}$ formation.

We have treated the starting solute in a neutral melt as $SbCl_3$ (or $SbCl_3\cdots AlCl_4^-$). One can show that the possible partial autodissociation of $SbCl_3$ into $SbCl_2^+$ and $SbCl_4^-$ or even an equilibrium reaction of $SbCl_3$ with $AlCl_4^-$ to form $SbCl_4^-$ and $AlCl_3$, would not affect our analysis because the added $AlCl_3$ would react with $SbCl_4^-$ rather than with $SbCl_2^+$ or $SbCl_3$, since $SbCl_4^-$ is the strongest Lewis base among these three species.

The analysis of the data on the changes of the wave height with the amount of $AlCl_3$ added does not eliminate the existence of $SbCl_3$ in solution. It does indicate that at least some $SbCl_2^+$ must be present in the solution and that it is the species reducing at +0.6—i.e., the first wave that grows in as $AlCl_3$ is added (Figure 3). If one examines the morphology shown in Figure 1 for the reduction of Sb(III) in basic and acidic melts, then the first wave seen in the reduction in the "neutral" melt (Figure 2) at ca. 0 V is absent. We thus conclude that this wave involves a species not present in the basic or acidic melt and that it is most probably $SbCl_3$, perhaps solvated by tetrachloroaluminate. The second wave in Figure 2 involves the reduction of $SbCl_4^-$, the dominant species of Sb(III) in the basic melt, which forms as a result of the increased basic character in the vicinity of the electrode as the $SbCl_3$ is reduced in this unbuffered, neutral melt. (Table III compares $D\eta/T$ values for Sb(III) in acidic and basic melts.) Thus, we conclude that the addition of $AlCl_3$ to Sb(III) in the neutral melt in fact is as per eq 3.

The presence of $SbCl_2^+$ in molten mixtures of $SbCl_3$ with alkali-metal chlorides and/or $AlCl_3$ has been postulated in the literature.[10–12] Raman studies however did not give support for the above species and instead indictaed some interactions between $SbCl_3$ and $AlCl_3$ in their molten equimolar mixtures.[13] However $SbCl_2^+$ has recently been postulated as the species responsible for the chemical oxidation of perylene in molten $SbCl_3$ containing $AlCl_3$.[14]

Acknowledgment. This work was supported by the Air Force Office of Scientific Research.

Registry No. ImCl, 65039-09-0; $SbCl_3$, 10025-91-9; $AlCl_3$, 7446-70-0; W, 7440-33-7; Pt, 7440-06-4; Sb, 7440-36-0.

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Contribution from the Department of Chemistry,
University of California, Santa Barbara, California 93106

Photosubstitution Quantum Yields for Hexacyanorhodate(III), $Rh(CN)_6^{3-}$, and Hexacyanoiridate(III), $Ir(CN)_6^{3-}$

Mark E. Frink and Peter C. Ford*

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It has been shown that the photochemical properties of the $M(CN)_6^{3-}$ (M = Co(III), Rh(III), Ir(III)) complexes are parallel, each giving the pentacyanoaquo complex as the only photoproduct when photolysis is conducted in acidic aqueous media (eq 1).[1]

$$M(CN)_6^{3-} \xrightarrow[H_3O^+]{h\nu} M(CN)_5H_2O^{2-} + HCN \qquad (1)$$

However, of these, only $Co(CN)_6^{3-}$, which displays a wavelength-independent quantum yield for photoaquation of 0.31 ± 0.02 mol/einstein, has had its solution photosubstitution properties quantitatively characterized.[2–8] Reported here are quantitative investigations of the photosubstitutions displayed by the $Rh(CN)_6^{3-}$ and $Ir(CN)_6^{3-}$ ions in acidic aqueous solution at 25 °C. Also reported are the low-temperature (77 K) luminescence spectra and emission lifetimes of these species and of the photoproducts $M(CN)_5H_2O^{2-}$.

Experimental Section

Materials and Synthesis. Reagent grade compounds were used for all preparations described in this work. Water used for syntheses and experimental determinations was deionized and then distilled in an all-glass apparatus.

Potassium hexacyanorhodate(III), $K_3[Rh(CN)_6]$, and potassium hexacyanoiridate(III), $K_3[Ir(CN)_6]$, were prepared from $RhCl_3{\cdot}xH_2O$ and $IrCl_3{\cdot}xH_2O$, respectively, according to previously published procedures.[9,10] (*Caution* must be exercised in these syntheses since HCN gas is generated!) Purification of the Rh(III) salt by recrystallization proved insufficient, so the method described by Geoffroy employing alumina and silica gel column chromatography was used.[1] A constant electronic absorption spectrum was obtained after several chromatography runs. The electronic absorption band maxima were in agreement with the literature values; however, the extinction coefficient of the longest wavelength band (260 nm) was found to be significantly lower than reported[1,9] (see below). The infrared spectrum of purified samples agreed with published values.[1,11] The Ir(III) complex was purified by repeated recrystallizations. In agreement with reported results, the spectrum of $Ir(CN)_6^{3-}$ in aqueous solution showed no measurable absorption bands between 700 and 270 nm.[1,10] Below 270 nm the absorption increases (without structure) and goes off scale at ~230 nm. The infrared spectrum was in close agreement with published results.[1,11]

Electronic absorption spectra were recorded on a Cary 118 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer. A Radiometer PHM 84 pH meter was used for all pH measurements. A specific-ion electrode (Gam Rad PHI 93100), sensitive to 1×10^{-6} M, was used to detect free CN^- in solution via millivolt readings on the pH meter.

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Table I. Electronic Absorption Properties

complex	λ_{max} (ϵ_{max})^b	ref
$Co(CN)_6^{3-}$	312 (243), 260 (180), 198 (35400)	*c*
$Co(CN)_5(H_2O)^{2-}$	380 (250)	*d*
$Rh(CN)_6^{3-}$	255 (280), 225 (527)	9
	260 (170), 225 sh (555)	1a
	265 (110), 224 sh (600)	this work
$Rh(CN)_5(H_2O)^{2-}$	265 (605)	1a
	265 (650)	this work
$Ir(CN)_6^{3-}$	no spectral features	1a and this work
$Ir(CN)_5(H_2O)^{2-}$	270 sh (180), 235 (790)	1a
	270 sh (198), 235 (940)	this work

^{a}Acidic aqueous solution; 25 °C. ^{b}Absorbance wavelength in nm; ϵ in M^{-1} cm^{-1}. ^{c}Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4260. ^{d}Haim, A.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1961**, *83*, 509.

Photolysis and Luminescence. Photolyses were carried out at 25 °C by methods previously described for rhodium(III) and iridium(III) ammine complexes.[12-14] The 254-nm irradiation was generated by employing a low-pressure Hg penlight (Oriel C-13-61) with a short-wave filter (Oriel C-13-00-32) mounted on an optical rail with a manual shutter and thermostated cell holder. Irradiation with 229- and 214-nm light was accomplished on a photolysis train with interchangeable resonance, Cd (Philips 26-2873) and Zn (Philips 93106E), respectively. Light intensities at all wavelengths were determined by ferrioxalate actinometry.[14] Photoaquation quantum yields (ϕ_s) were determined by three separate techniques (Table II). Spectral changes were monitored at the wavelength of irradiation, at the λ_{max} of the starting material, and at the λ_{max} of the major photoproduct. Independent measurement of the photolysis-induced changes in the solution pH were used to determine ϕ_s. The release of 1 equiv of CN^- neutralizes 1 equiv of acid, and the resulting pH change can be used to evaluate the extent of cyanide ligand loss. In separate experiments, labilized CN^- concentrations were accurately determined from millivolt values matched with standard concentration values from a calibration curve. Parallel experiments showed no dark reactions observed spectrally or pH changes, consistent with the thermal inertness of these complexes. The spectra of the hexacyano complexes appeared independent of pH over the range 2–9.

The excited-state lifetimes and emission spectra of these rhodium(III) and iridium(III) cyanide complexes were measured in a KBr pellet or in a 4/1 $MeOH/H_2O$ glass solution at 77 K on a Nd-YAG laser system and by using techniques previously described.[15]

Results and Discussion

In acidic aqueous solution, ligand field (LF) excitation of $M(CN)_6^{3-}$ complexes leads to photosubstitution of one of the coordinated CN^- ligands by H_2O (eq 1).[1-4] The electronic absorption characteristics of these $M(CN)_6^{3-}$ complexes, and of the photoaquation products $M(CN)_5H_2O^{2-}$, are listed in Table I. For $Rh(CN)_6^{3-}$, the band at 225 nm has been assigned as the lowest energy, singlet ligand field absorption $^1T_1 \leftarrow {}^1A_1$. The electronic absorption characteristics of the Co(III) analogues are included for comparative purposes. The feature reported at 260 nm in the absorption spectrum of $Rh(CN)_6^{3-}$ is an enigma, given that the reported extinction coefficient of this band varies significantly among investigators (Table I). However, since the $Rh(CN)_6^{3-}$ ion readily undergoes photoaquation to give $Rh(CN)_5(H_2O)^{2-}$, which has an absorption maximum at 265 nm, it appears likely that the higher extinction coefficients reported earlier reflect the contributions by the latter species as an impurity.

Table II. Photosubstitution Quantum Yields (ϕ_s) of $Rh(CN)_6^{3-}$ and of $Ir(CN)_6^{3-}$ in Aqueous Solution^a

λ_{irr}^{b}	pH	ϕ_s($Rh(CN)_6^{3-}$)^c	$\phi_s$$Ir(CN)_6^{3-}$)^c
214	0.0	0.18 ± 0.03	0.43 ± 0.03
	1.0	0.15 ± 0.03 (0.17)^d	(0.40)^d
	3.0	0.19 ± 0.03 (0.16)^e	0.36 ± 0.03 (0.38)^e
229	0.0	0.19 ± 0.04	0.37 ± 0.04
	1.0	0.26 ± 0.04	
	3.0	0.23 ± 0.04	0.40 ± 0.04
254	0.0	0.07 ± 0.01	0.02 ± 0.01
	1.0	0.06 ± 0.01 (0.06)^d	0.01 (0.01)^d
	3.0	0.07 ± 0.01 (0.07)^e	(0.01)^e

^{a}25 °C; acidic ($HClO_4$) solutions; ϕ_s in mol/einstein. ^{b}Irradiation wavelength in nm. ^{c}Spectrally determined from optical density changes at 265 nm for $Rh(CN)_6^{3-}$ and at 270 nm for $Ir(CN)_6^{3-}$. ^{d}ϕ_s determined by CN^--specific electrode technique (±0.03). ^{e}ϕ_s determined by ΔpH (±0.03).

The photoaquation quantum yields measured for aqueous $Rh(CN)_6^{3-}$ under various conditions show good agreement between values determined by spectral changes and those measured by pH changes or cyanide-specific electrode measurements (Table II). Isosbestic points were observed in the absorption spectrum at 217 and 241 nm in each photolysis run monitored. Irradiation at either 214 or 229 nm gave the same quantum yield, 0.20 ± 0.03 mol/einstein. There was no apparent dependence of ϕ_s values on solution pH. However, 254-nm irradiation led to a significantly smaller photoaquation quantum yield, 0.07 ± 0.01 mol/einstein. Given that the photoproduct (λ_{max} 265 nm) absorbs much more strongly at 254 nm ($\epsilon_{254} = 580$ M^{-1} cm^{-1}) than does $Rh(CN)_6^{3-}$ ($\epsilon_{254} \leq 90$ M^{-1} cm^{-1}), the smaller quantum yield value reported at 254 nm may be the result of a significant inner-filter effect owing to the photoproduct.[16]

Quantum yields for $Ir(CN)_6^{3-}$ photoaquation determined by the three techniques described (Table II) gave similar results. Irradiations at 214 nm and at 229 nm each gave $\phi_s = 0.40 \pm 0.03$ mol/einstein. However, as in the Rh(III) case, 254-nm excitation gave a much smaller quantum yield value of ~0.01 mol/einstein. Again, the photoproduct ($\epsilon_{254} = 250$ M^{-1} cm^{-1}) absorbs much more strongly at this wavelength than does $Ir(CN)_6^{3-}$ ($\epsilon_{254} \leq 50$ M^{-1} cm^{-1}).

The homologous hexacyano complexes $M(CN)_6^{3-}$ (M = Co(III), Rh(III), Ir(III)) each are quite photoactive toward labilization of a single CN^-. For $Co(CN)_6^{3-}$ the pattern of wavelength-independent quantum yields has been interpreted in terms of very efficient internal conversion/intersystem crossing from initially formed ligand field (LF) excited states to the lowest energy triplet LF state ($^3T_1$), from where reactive deactivation to products and nonradiative and radiative deactivation to ground state are competitive processes. A similar model has been proposed to explain the ligand field photochemistry of rhodium(III) and iridium(III) ammine complexes.[17] Given the large spin–orbit constants of Rh(III) and Ir(III), interconversion of higher energy LF states to the lowest energy triplet LF state would be expected to be comparably efficient for the heavier $M(CN)_6^{3-}$ complexes. In this context the smaller ϕ_s values found for the longest wavelength photolysis (254 nm) of the $Rh(CN)_6^{3-}$ and $Ir(CN)_6^{3-}$ ions are puzzling. We believe this is probably due to inner-filter effects owing to the strong absorption by photoproducts at this wavelength and/or to the presence of photoinactive impurities not completely removed by repeated recrystallization. Attempts to correct for the inner-filtering phenomenon by extrapolating to 0% reaction were frustrated by the much stronger absorption of the photoproducts. An obvious alternative, but unsubstantiated, possibility would be that absorption at 254 nm represents excitation into photoinactive states (e.g., a charge-transfer or triplet LF state) while the higher energy excitation populates singlet LF states, which themselves are the reactive states or undergo internal conversion/intersystem crossing to reactive states not accessible by 254-nm excitation. The question is not fully resolved.

The luminescence properties of the $Rh(CN)_6^{3-}$ and $Ir(CN)_6^{3-}$ salts at 77 K are summarized in Table III along with some data

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Table III. Emission Properties of Rhodium(III) and Iridium(III) Cyanide Complexes at 77 K[a]

complex	τ, μs	ν_{max}, μm^{-1}	$\Delta\nu_{1/2}$, μm^{-1}	ν_{0-0}, μm^{-1}
$K_3[Co(CN)_6]$[b]	680	1.44	~0.44	~2.0
$K_3[Rh(CN)_6]$[c]	84 ± 10	1.96[d]	0.45	2.5
$[Rh(CN)_6{}^{3-}]$[e]	103 ± 10	1.85		
$[Rh(CN)_5H_2O^{2-}]$[e]	~4	1.85	0.50	2.5
$K_3[Ir(CN)_6]$[c]	39 ± 4	1.95	0.55	2.65
$[Ir(CN)_5H_2O^{2-}]$[e]	0.8 ± 0.1	1.90	0.48	2.5

[a] Experimental uncertainties: ν_{max} and $\Delta\nu_{1/2}$, $\pm 0.05\ \mu m^{-1}$; ν_{0-0}, $\pm 0.15\ \mu m^{-1}$. The 0–0 transition energies were estimated from $\nu_{0-0} = \nu_{max} + 1.29\Delta\nu_{1/2}$.[13] [b] Emission spectra A measured as crystalline salts by: Mungardi, M.; Porter, G. B. *J. Chem. Phys.* **1966**, *44*, 4354. ν_{0-0} estimated by: Miskowski, V. M.; Gray, H. B.; Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1979**, *18*, 1410. [c] Sample in KBr pellet (1–4%). [d] This value is in agreement with a previous report of the emission maximum from $K_3[Rh(CN)_6]$: Wolpl, A.; Oelhrug, D. *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 394. [e] Potassium salt as solution in 4/1 $MeOH/H_2O$ glass.

for the $M(CN)_5H_2O^{2-}$ photoproducts and for $Co(CN)_6{}^{3-}$. Emission from the $Co(CN)_6{}^{3-}$ ion has been assigned to the $^3T_1 \rightarrow {}^1A_1$ ligand field transition.[18] A similar assignment would be consistent with the broad Gaussian shapes of the emission bands seen for $Rh(CN)_6{}^{3-}$ and $Ir(CN)_6{}^{3-}$ as well as with the higher 0–0 energies of these latter transitions, given the larger ligand field splitting of Rh(III) and Ir(III). Luminescence lifetimes follow the descending order $Co(CN)_6{}^{3-} >> Rh(CN)_6{}^{3-} > Ir(CN)_6{}^{3-}$, consistent with the ascending values of the spin–orbit coupling constants of the central metal atom. Attempts to measure excited-state lifetimes of $Rh(CN)_6{}^{3-}$ and $Ir(CN)_6{}^{3-}$ in ambient-temperature, aqueous solutions were unsuccessful owing to the very weak emissions under these conditions.

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Registry No. $Rh(CN)_6{}^{3-}$, 19356-46-8; $Ir(CN)_6{}^{3-}$, 19356-47-9; $Rh(CN)_5(H_2O)^{2-}$, 42892-92-2; $Ir(CN)_5(H_2O)^{2-}$, 42893-00-5.

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Contribution from the Chemistry Department,
Royal Veterinary and Agricultural University,
Thorvaldsensvej 40, DK-1871 Copenhagen V, Denmark,
and Department of Inorganic Chemistry,
H. C. Ørsted Institute, University of Copenhagen,
DK-2100 Copenhagen Ø, Denmark

Evidence for "Classical" Hydroxo-Bridged Polymers in Hydrolyzed Hexaaquachromium(III) Solutions

L. Mønsted,[1a] O. Mønsted,[1b] and J. Springborg*[1a]

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Polymerization of hexaaquachromium(III) in aqueous solution yields hydroxo-bridged polynuclear complexes, which have been the subject of intensive studies. A dimeric species, $Cr_2(OH)_2{}^{4+}$, a trimeric species, $Cr_3(OH)_4{}^{5+}$, and two isomeric tetrameric species, $Cr_4(OH)_6{}^{6+}$, have been isolated and characterized in solution, but failure to obtain suitable crystalline salts of any of these species has prevented direct structure determinations.[2-5]

Table I. Acid Dissociation Constants of Chromium(III) Monomers and Oligomers in 1 M $NaClO_4$ at 25 °C

cation	pK_a[a]	ref
$[Cr(H_2O)_6]^{3+}$	4.29[b]	4
$[Cr(NH_3)_5(H_2O)]^{3+}$	5.18	28
$[(H_2O)_5Cr(OH)Cr(H_2O)_5]^{5+}$	1.6[c]	2
$[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$	3.68[d]	4
$Cr_3(OH)_4(aq)^{5+}$	4.35	4
$Cr_4(OH)_6(aq)^{6+}$ (isomer IA)[e]	3.53	5
$Cr_4(OH)_6(aq)^{6+}$ (isomer IIA)[e]	0.89	5
cis-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$	3.5	23
cis,cis-$[(H_2O)(NH_3)_4Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$	1.75	7
Δ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)]^{5+}$	0.48	6,7
trans-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(H_2O)]^{4+}$	6.0	21
cis-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH_2)]^{4+}$	3.9	35

[a] pK_a = −log (K_{a1}/M), where K_{a1} is the concentration equilibrium constant. [b] p$K_a \approx 4.15$ in 0.1 M $NaClO_4$ at 20 °C.[29] [c] Determined from kinetic data; 2 M $(Li,H)ClO_4$. p$K_a \approx 1.3$–1.6 has recently been reported in an independent study.[24] [d] p$K_a \approx 3.5$ in 0.1 M $NaClO_4$ at 20 °C.[29] [e] Cf. Figure 2.

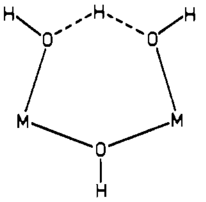

Figure 1. Hydrogen-bond stabilization of deprotonated monohydroxo-bridged "*cis,cis*"-diaqua polymers. Cf. the α-type interaction in Figure 3. This type of bond between a terminal water and hydroxide ligands is a pronounced feature in many systems,[6-8,25-27,36-39] and a $H_3O_2{}^-$-bidentate ligand has even been suggested.[36-39]

Acid-induced reaction of the blue $Cr_2(OH)_2{}^{4+}$ cation gives initially a green dimeric species, and the kinetic and thermodynamic data for the interconversion reactions between these dimers[2] are very similar to data obtained for the corresponding ammonia system, $[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]^{4+}$, and related amine systems.[6-9] This similarity suggests that the blue and green dimers are dihydroxo- and monohydroxo-bridged species, respectively, and implies that the ammine and amine hydroxo-bridged polynuclear systems[6-21] can be used as models for the polynuclear aqua

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