in part the nonidealized pseudo-16-line pattern. The presence of more than 16 lines in the EPR spectra of the mixed-valence porphyrin complexes can also be explained on this basis. Other factors that may contribute to the differences between the experimental spectra and the idealized intensity ratios and positions of the hyperfine lines based on the simple coupling scheme (i.e. $|A_{\mathrm{Mn(III)}}| = |2A_{\mathrm{Mn(IV)}}|$) include (1) anisotropic coupling of the electron spin to the manganese nuclei, (2) g-value anisotropy, (3) second-order hyperfine interactions since for manganese the hyperfine interactions are not small compared to the Zeeman interactions,[9] and (4) line widths that are approaching the splitting between adjacent hyperfine lines. The magnitude of the EPR line widths in the porphyrin complexes may in large part be due to unresolved ^{14}N superhyperfine splittings, as has been proposed for the bis(μ-oxo) complexes.[10]

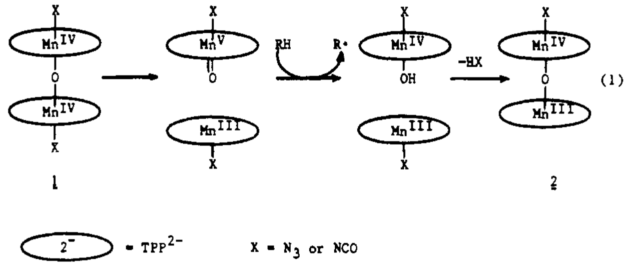
The average separation of the hyperfine lines in the porphyrin mixed-valence complexes, assuming a 16-line pattern, is 69.3 ± 0.7 G for both complexes. There are, however, small differences between the anisotropies of the hyperfine lines in the two complexes that may be due to electronic differences between the NCO and N_3 ligands. Electronic differences between the NCO and N_3 ligands have also been observed in the EPR spectra of the monomeric complexes $(N_3)_2Mn^{IV}TPP$ and $(OCN)_2Mn^{IV}TPP$.[5] The average hyperfine coupling to the manganese nuclei in the porphyrin complexes is significantly smaller than the average hyperfine coupling observed in the bis(μ-oxo)-bridged mixed-valence complexes, suggesting the presence of less manganese-centered spin density in the porphyrin complexes (the average separation of hyperfine lines in the bis(μ-oxo) complexes is ~81 G).[9,10] This is consistent with greater manganese–ligand covalency in the porphyrin complexes.

The proposed mono(μ-oxo) structure of **2** is reasonable on the basis of the known mono(μ-oxo) structure of the starting material,[3] the known 5-coordinate structures of $XMn^{III}TPP$ complexes,[12] and the known pseudooctahedral coordination about the manganese in the related monomeric complexes $X_2Mn^{IV}TPP$ ($X = N_3$, OCN, CH_3O).[5,13] The inequivalence of the two manganese ions in the mixed-valence porphyrin complexes is not surprising since only one manganese is likely to be coordinated by a sixth anionic ligand. Since the occupation of the antibonding d_{z^2} orbital in manganese(III) porphyrin complexes is known to induce long axial bond lengths[12] whereas manganese(IV) porphyrin complexes have short axial bond lengths,[3,5,13] large barriers to vibrationally allowed intramolecular electron transfer are expected for these complexes.

The similarity of the EPR spectra of the mixed-valence bis(μ-oxo)-bridged complexes, where the Mn–O–Mn angle is near 97°,[11] and the mono(μ-oxo)-bridged porphyrin complexes, where the Mn–O–Mn angle is expected to be near 180°, indicates that the EPR spectra of oxo-bridged mixed-valence Mn(III)/Mn(IV) dimers are not very sensitive to the number or the geometry of the bridging oxo groups. The magnitude of the antiferromagnetic coupling between the Mn(III) and Mn(IV) ions may be more sensitive to the number and geometry of the oxo bridges, but our inability to isolate the mixed-valence porphyrin dimers in a pure form has precluded the determination of J in these complexes by magnetic susceptibility measurements.

The EPR spectra of the mixed-valence complexes described here are similar to the EPR spectrum observed when spinach chloroplasts are flashed with one pulse of light and then frozen.[10] However, Dismukes and co-workers have recently suggested that some additional weak transitions observed outside the field range where the Mn(III)/Mn(IV) dimers show absorptions can be explained by the presence of a 3Mn(III)/Mn(IV) tetramer. This EPR-active tetranuclear cluster was proposed to be the water oxidation site of photosystem II.[10]

A potential mechanism for the formation of the mixed-valence porphyrin complexes, **2**, from the starting complexes, **1**, is as follows (eq 1): first, one (IV/IV) dimer disproportionates into Mn(III) and $O{=}Mn^V$ fragments, and the $O{=}Mn^V$ complex then abstracts a hydrogen atom from the solvent to form an alkyl radical and a hydroxo Mn^{IV} porphyrin. Evidence for this portion of this mechanism has been presented elsewhere.[4,14] The recombination of the hydroxo Mn(IV) complex and a Mn^{III} porphyrin with elimination of HX gives the mixed-valence complex.



The free radical that was formed can undergo inner-sphere attack on the coordinated pseudohalide of a second molecule of **1** to yield an alkyl pseudohalide product, RX, and a second molecule of **2**. The formation of alkyl radicals and the formation of alkyl azide products during the reaction of the complex $[(N_3)Mn^{IV}TPP]_2O$ with cyclohexane have been demonstrated previously.[4] The appearance of signals near $g = 7$ in the EPR spectra when the samples of **1** are decomposed for greater than 1 h is consistent with the formation of some $Mn^{II}TPP$ by attack of the alkyl radicals on the $XMn^{III}TPP$ species that build up late in the reaction. The formation of $Mn^{II}TPP$ has been demonstrated previously during the functionalization of hydrocarbons by other high-valent manganese porphyrin complexes.[4]

Acknowledgment. We thank Dr. John McCracken for assistance with the EPR spectrometer. Funding for this research was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (Grant No. CHE 79-09730), and Chevron Research Corp.

Registry No. **1** ($X = N_3$), 79775-62-5; **1** (X = NCO), 81602-67-7; **2** ($X = N_3$), 90064-42-9; **2** (X = NCO), 90064-43-0; Mn, 7439-96-5.

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Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Preparation and Aquation Kinetics of (Acetonitrile)pentaaquochromium(III)

D. Jordan, W. C. Kupferschmidt, and R. B. Jordan*

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Metal complexes of organic nitriles, of the general type $L_5M\text{-}NC\text{-}R^{3+}$, are known for many of the kinetically inert metal ions.[1,2] These complexes show kinetic stability toward simple aquation typical for the particular metal ion and present no unusual problems in preparation and isolation. The complexes do hydrolyze to the corresponding carboxamide complex in neutral and alkaline solutions.[2-4]

It is noteworthy however that the chromium(III) complexes of the type $(H_2O)_5Cr{-}NC{-}R^{3+}$ have not been characterized. There have been fleeting references to the 1,4-dicyanobenzene[5] and fumaronitrile[6] complexes. Both were tentatively identified as the product of the chromium(II) reduction of the corresponding $(NH_3)_5Co^{3+}$ complex. These products were observed to aquate in 2–3 min in aqueous acid. This rapid aquation is surprising in view of the normal kinetic inertness of chromium(III) and the stability toward aquation of the $(NH_3)_5Co^{3+}$ complexes. Commonly, aquation rates of $(NH_3)_5CoX$ and $(H_2O)_5CrX$ complexes are within a factor of 10 of each other.[7,8] The unusual kinetic lability might lead one to question the identification of the products of the chromium(II) reduction reaction.

It might be suggested that the $(H_2O)_5CrNCR^{3+}$ complexes undergo rapid carboxamide formation, rather than simple aquation. However, terephthalonitrile and fumaronitrile were identified as the final reaction products,[6,9] and $Cr(OH_2)_6^{3+}$ was identified in the latter system.

This paper describes two methods of preparation of $(H_2O)_5CrNCCH_3^{3+}$ and a study of its aquation kinetics.

Results and Discussion

The characterization of $(H_2O)_5CrNCCH_3^{3+}$ presents the usual problems for $(H_2O)_5Cr^{III}$ complexes, namely high solubility, and the difficulties in applying the usual spectroscopic methods to dilute aqueous solutions of paramagnetic species. The desired species has been prepared by two very different methods and characterized from the fact that the product from both methods has the same aquation kinetics. In addition, the aquation products have been shown to be $Cr(OH_2)_6^{3+}$ and CH_3CN.

The reaction of iodoacetonitrile and chromium(II) in aqueous acid has been proposed[10] to proceed as

$$2Cr^{2+} + ICH_2CN \rightarrow \underset{100\%}{(H_2O)_5CrI^{2+}} + \underset{25\%}{(H_2O)_5CrCH_2CN^{2+}} + \underset{75\%}{(H_2O)_5CrNCCH_3^{3+}} \quad (1)$$

The first two products have been separated and characterized previously.[10] In the present study the third product was separated from the first two by ion-exchange chromatography at 5 °C on Dowex 50W-X2. The electronic spectrum has maxima at 566 and 397 nm with extinction coefficients of 15.7 and 21.2 $M^{-1}\ cm^{-1}$, respectively.[11]

Table I. Aquation Kinetics of $(H_2O)_5CrNCCH_3^{3+\,a}$

temp, °C	[H⁺], M	$10^4 \times k_{obsd}$, s^{-1}	temp, °C	[H⁺], M	$10^4 \times k_{obsd}$, s^{-1}
25.0	0.30	4.45	25.0	0.045	4.71
25.0	0.25	4.14	25.0	0.20	4.0[b]
25.0	0.20	3.88	25.0	0.14	4.18[c]
25.0	0.15	4.30	20.0	0.14	2.70[c]
25.0	0.10	4.28	14.6	0.14	1.45[c]

[a] Unless otherwise indicated, solutions contain ~1 mL of CH_3CN in 26 mL of $LiClO_4$-$HClO_4$-H_2O at 1.0 M ionic strength with total [chromium(III)] ≈ 3.5×10^{-3} M = [cobalt(II)]. Reaction was monitored at 404–406 nm. Results are averages of at least two determinations. [b] Ion-exchanged product from Cr(II) + $NCCH_2I$, in 0.2 M $HClO_4$-1.0 M $NaClO_4$ monitored at 258 nm. [c] Ionic strength 0.17 M.

The aquation of the tripositive product of eq 1 was found to yield $Cr(OH_2)_6^{3+}$, identified by its electronic spectrum. The organic product of the aquation was identified by allowing the reaction to proceed for 5–6 h at ambient temperature and collecting ~60% of the solution by vacuum distillation into a trap at liquid-N_2 temperature. The ^{13}C NMR spectrum of the distillate showed only the $-CN$ and $-CH_3$ resonances in the same positions as that of an authentic sample of acetonitrile in water. The aquation rate was followed at 258 nm in 0.2 M $NaClO_4$–1.0 M $HClO_4$ at 25 °C and gave a pseudo-first-order rate constant of $4.0 \times 10^{-4}\ s^{-1}$.

Another preparative method was developed in order to confirm the product assignment of eq 1 and to provide a more convenient source for kinetic studies. It was found that oxidation of chromium(II) by $(NH_3)_4Co(OH_2)_2^{3+}$ in 50% aqueous acetonitrile produces a mixture of $Cr(OH_2)_6^{3+}$ and a species with properties expected for $(H_2O)_5CrNCCH_3^{3+}$. This method is more convenient than eq 1, but the product mixture is difficult to separate by ion exchange, because both chromium products have a tripositive charge. Since $Co(OH_2)_6^{2+}$ and $Cr(OH_2)_6^{3+}$ should not affect the aquation rate of $(H_2O)_5CrNCCH_3^{3+}$, this method was used for the kinetic studies.

The kinetic results are summarized in Table I. From the standpoint of identifying the reactant, the most important results from Table I are the nearly identical rates of reaction of the products from the two preparative methods. This observation and the fact that the reaction products are CH_3CN and $Cr(OH_2)_6^{3+}$ provide very strong evidence that the reaction being followed kinetically is

$$(H_2O)_5CrNCCH_3^{3+} + H_2O \rightarrow Cr(OH_2)_6^{3+} + NCCH_3 \quad (2)$$

The reaction rate is independent of $[H^+]$ with an average rate constant of $4.3 \times 10^{-4}\ s^{-1}$ at 25 °C in 1 M $LiClO_4$–$HClO_4$.

Since the reaction medium for most of the kinetic studies contained 1 mL of acetonitrile in 26 mL of H_2O–$HClO_4$–$LiClO_4$, the effect of added acetonitrile on the kinetics was explored. When the reaction solution contained 3, 6, and 11 mL of acetonitrile in a total of 27 mL, the rate constants were 3.9×10^{-4}, 3.3×10^{-4}, and $3.2 \times 10^{-4}\ s^{-1}$, respectively. This rate constant variation is not significant until the medium is >20% acetontrile.

The temperature dependence of the rate was studied in 0.14 M $HClO_4$, and the results (Table I) give $\Delta H^{*} = 16.1 \pm 1.2$ kcal mol^{-1} and $\Delta S^{*} = -20.2 \pm 3.5$ cal $mol^{-1}\ deg^{-1}$. A comparison of these parameters to those for other $(H_2O)_5CrX$ complexes[7] shows that ΔH^{*} is substantially below the usual range of 22–26 kcal mol^{-1}. This low ΔH^{*} is responsible for the unexpectedly high rate of aquation of $(H_2O)_5CrNCCH_3^{3+}$.

The aquation rate of $(NH_3)_5CoNCCH_3^{3+}$ has been studied in 0.50 M $HClO_4$ at ambient temperature (25 ± 2°) and found to have a rate constant of $2.2 \times 10^{-7}\ s^{-1}$. Clearly the acetonitrile complexes of $(H_2O)_5Cr^{3+}$ and $(NH_3)_5Co^{3+}$ do not have the rather similar aquation rates noted above for other com-

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(11) This solution probably contains 5–10% $Cr(OH_2)_6^{3+}$ due to aquation of $(H_2O)_5CrNCCH_3^{3+}$ during sample preparation for the spectrophotometric measurement.

plexes of these metal species. The nitrile complexes of $(H_2O)_5Cr^{3+}$ can be expected to aquate much more rapidly than the $(NH_3)_5Co$ analogues, consistent with the observations here and previous work with 1,4-dicyanobenzene and fumaronitrile.[5,10]

Experimental Section

The chromium(II) solutions were prepared by zinc amalgam reductions of $Cr(OH_2)_6(ClO_4)_3$ stored under argon and handled by syringe techniques. General procedures, chemical sources, and analytical methods are described elsewhere.[6,10,12]

The reaction with iodoacetonitrile was done by adding aqueous Cr(II) to a deoxygenated solution of iodoacetonitrile so that initial reaction concentrations were 6.98×10^{-2} M Cr(II), 0.138 M $NCCH_2I$, and 0.50 M $HClO_4$ in a total volume of 20.0 mL. After 30 s, the solution was exposed to air and rapidly cooled in a dry ice–acetone slush. The solution was diluted to 60 mL with ice-cold water and charged onto a column of Dowex 50W-X2 (H^+ form) in a cold room at 5 °C. The unwanted products ($(H_2O)_5CrI^{2+}$, $(H_2O)_5CrCH_2CN^{2+}$) were eluted as quickly as possible with 0.20 M $HClO_4$–0.50 M $HClO_4$. Then, the desired product was eluted with 0.2 M $HClO_4$–1.0 M $NaClO_4$.[13] A portion of the eluent was transferred to a 10-cm path length cell to record the electronic spectrum and monitor the decomposition rate.

In the second preparative method a stock solution of 15 mL of 2.34 M $HClO_4$ and 15 mL of CH_3CN was prepared. To a 10-mL aliquot of this solution was added 0.14 g of $[(NH_3)_4CoCO_3]ClO_4$,[14] and the solution was sealed with a serum cap and deoxygenated with argon. Then, 1.0 mL of 0.49 M $Cr(ClO_4)_2$ solution was added and the reaction allowed to proceed for 2 min. Then, a 2.0-mL aliquot was taken and placed in a 10-cm path length cell containing appropriate amounts of $HClO_4$ and $LiClO_4$ solutions and water to give a final ionic strength of 1.0 M. To account for evaporation losses during degassing, a second 10-mL aliquot of the stock solution was treated in the same way except for the omission of reactants. Then, 2.0 mL of this solution was titrated with standard NaOH to determine the acidity, and the amounts of $HClO_4$ and $LiClO_4$ to be added to the spectrophotometer cell were calculated accordingly. For the temperature studies in 0.14 M H^+, the preparative solution contained 2 mL of CH_3CN in 9 mL of $HClO_4$–H_2O and a 2-mL aliquot of this was diluted to 13 mL with $HClO_4$–H_2O in a 5-cm path length cell.

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Registry No. $(H_2O)_5CrNCCH_3^{3+}$, 89936-34-5.

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(13) A small amount of a red product remained on the column. This product, which aquates to $Cr(OH_2)_6^{3+}$ and $(H_2O)_5CrCH_2CN^{2+}$, is tentatively identified as $(H_2O)_5CrNCCH_2Cr(OH_2)_5^{5+}$ and accounts for ~2% of the iodoacetonitrile.

(14) Since $[(NH_3)_4CoCO_3]ClO_4$ decarboxylates rapidly in acid, the actual oxidant is $(NH_3)_4Co(OH_2)_2^{3+}$. Problems were encountered at one stage because this reactant contained some nitrate salt impurity. It is recommended that the perchlorate is prepared by addition of aqueous $NaClO_4$ to a solution of $[(NH_3)_4CoCO_3]Cl$: Schlessinger, G. G. "Inorganic Laboratory Preparations"; Chemical Publishing Co., Inc.: New York, 1962.

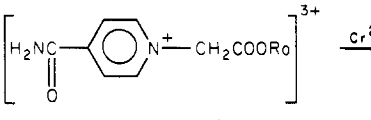
Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 68. Mediation by N-Substituted Isonicotinoyl Derivatives[1]

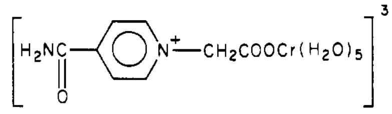
M. S. Ram, J. R. Barber, Jr., and E. S. Gould*

Received June 30, 1983

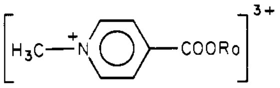
A report in 1979 described the reductions of such cobalt(III) complexes as the *N*-carboxymethyl derivative I, in which conjugation between $-COOCo^{III}$ and a pyridine ring activated by a γ-C(=O)NH– function was interrupted by a saturated unit.[2] It was found that reduction of I by Cr^{2+} proceeded about 700 times as rapidly as that of complex II, in which conjugation is unbroken. Since this acceleration did not persist when the $-CONH_2$ group was moved to the poorly activating β position (III), and since the primary oxidation product was found to be a $-COOCr^{III}$ complex (IV), it was proposed that the reduction of oxidant I proceeded through a doubly bridged intermediate of type V, in which the incoming chromium interacted with both the ring and the carboxyl function. Reductions, by Eu^{2+}, of both the cobalt complex I and its parent carboxylic acid exhibited similar enhancements. It was therefore suggested, at the same time, that an intermediate analogous to V might intervene in these reactions also.



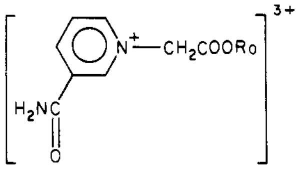
I, $k_{Cr} = 660$[3]



IV

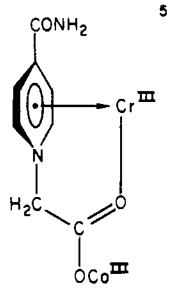


II, $k_{Cr} = 0.93$



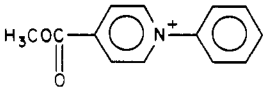
III, $k_{Cr} = 0.059$

Ro = "roseo" = $(NH_3)_5Co^{III}$



V

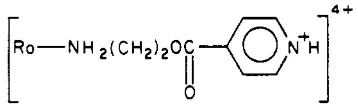
It was subsequently noted, however, that rapid Eu^{2+} reduction of the ligand did not require the *N*-carboxymethyl function,[4] i.e., that marked enhancement remained when the latter unit was replaced by a number of strongly electron-attracting N-bound aryl groups (e.g., VI). Moreover, it was



VI, $k_{Eu} = 580$[6]

$[Ro—NH_2(CH_2)_2OH]^{3+}$

VII, $k_{Eu} = 0.0085$



VIII, $k_{Eu} = 7.4$

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(1) Support of this work by the National Science Foundation (Grant No. 8022881) is gratefully acknowledged.

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0020-1669/84/1323-1988$01.50/0