Cluster A   Cluster B

Similarities of the absorption and MCD spectra between Co(II) complexes of cysteine-containing peptides and Co(II) metallothioneins suggest the presence of a similar type of cluster, postulated by Otvos and Armitage[35b] for the Co(II) complexes of cysteine-containing peptides.

The calculated ligand field parameter Δ_t (4780 cm^{-1}) for Co(II)-substituted rabbit metallothionein[65] is comparable to those of **3** and Co(II) complexes of cysteine-containing peptides, indicating cluster formation (Table III). Using the ligand field parameters (Δ_t = 4780 cm^{-1} and B = 624 cm^{-1}) and the lowest charge-transfer energy (ν_{obsd} = 17 240 cm^{-1}) estimated from the MCD band at 580 nm for rabbit metallothionein,[6b] we obtained the optical electronegativity, χ_L, of cysteine thiolate (*terminal* and *bridging*) for the metallothionein as 2.1. This value is in agreement with those of **3** and Co(II) complexes of Z-Cys-Ala-Ala-Cys-OMe and Z-

Ala-Cys-OMe (Table IV) and is significantly smaller than the χ_L value, 2.40, for *terminal* cysteine thiolate previously reported.[5b] This fact also indicates the presence of *bridging* thiolates.

Next, let us consider CD spectra of Co(II) metallothioneins in comparison with those of Co(II) complexes of cysteine-containing peptides. Much stronger Cotton effects have been observed in the *charge-transfer transition region* for Co(II) metallothionein than in the $^1A_2(F) \rightarrow {}^4T_1(P)$ transition region.[6b] This is consistent with the CD spectral feature found for the Co(II) complex of Z-Cys-Ala-Ala-Cys-OMe shown in Figure 3c. These are presumably due to the chelating effects of Cys-X-Cys and/or Cys-X-Y-Cys units on the metal ion since the Co(II) complex of Z-Ala-Cys-OMe exhibited weak Cotton effects at the charge-transfer region.

Finally, we have demonstrated through this work that the combination of CD and MCD spectroscopies is superior to sole utilization of absorption spectroscopy for elucidation of the geometry around the metal ion and that CD spectra provide interesting information about the dynamic contribution of ligand conformations to the electronic states of metal ions. The model studies using optically active peptide ligands are important to the understanding of active site structures of metalloenzymes.

Synthesis, Kinetics, and Photochemistry of the Chromium(III) Dicyano–Aquo–Ethylenediaminetetraacetate Complex
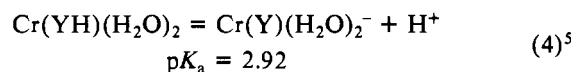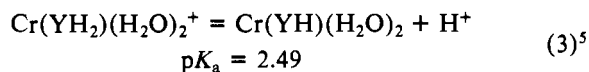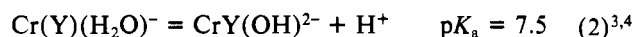
ZHONG CHEN,[1] MARC CIMOLINO, and ARTHUR W. ADAMSON*

A new EDTA complex of Cr(III) is described, Na$_3$[Cr(Y)(CN)$_2$(H$_2$O)]·4H$_2$O, where Y denotes ethylenediaminetetraacetate or EDTA. The EDTA ligand is terdentate in this complex, three of the carboxyl groups being uncoordinated. The complex undergoes pH-dependent aquation of the cyano groups, the rate-determining step being the reaction of Cr(YH)(CN)$_2$(H$_2$O)$^{2-}$, followed by rapid loss of the second cyano group. The acid dissociation constant of the YH complex is 2.55 × 10^{-6} M at 20 °C and 1 M ionic strength, and the rate constant at 20 °C and activation parameters for the slow step are 2.55 × 10^{-2} M^{-1} s^{-1}, $\Delta H^{o\ast}$ = 18.9 kcal mol^{-1}, and $\Delta S^{o\ast}$ = -1.4 cal mol^{-1} K^{-1}. It is suggested that internal hydrogen bonding of the protonated carboxyl group in Cr(YH)(CN)$_2$(H$_2$O)$^{2-}$ may assist the aquation. The complex Cr(Y)(CN)$_2$(H$_2$O)$^{3-}$ undergoes photoaquation of cyanide with a quantum yield of 0.018 at 20 °C and pH 7.6, with 514-nm excitation. The pH dependence of ϕ indicates that the protonated form cannot be significantly more photoactive than the unprotonated one. Emission from aqueous solution is weak and of lifetime less than 15 ns at 10 °C. The photochemical and emission behavior is compared with expectations from the photochemistry and emission rules for Cr(III) complexes.

Introduction

A complex of Cr(III) and EDTA, ethylenediaminetetraacetate or Y^{4-}, was first reported by Brintzinger et al.[2] in 1943. The complex was later shown not to be sexidentate but rather to have the formula Cr(YH)(H$_2$O),[3] YH denoting the EDTA ligand with one of the carboxyl groups unattached and protonated. Later, Hamm[4] studied the acid–base equilibrium Cr(YH)(H$_2$O) = Cr(Y)(H$_2$O)$^-$. That the water in Cr(YH)(H$_2$O) is indeed coordinated has been confirmed by a crystal structure determination.[5] Although the existence of the sexidentate complex has been proposed, Thorneley et al.,[6]
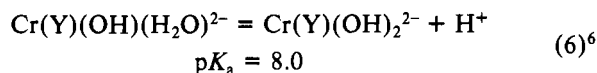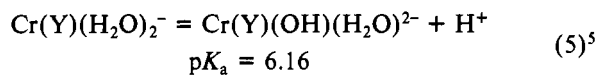
in an extensive study of acid–base and related equilibria, were unable to find evidence for the CrY$^-$ species.

The EDTA complexes of Cr(III) are interesting because of the several states of partial coordination that are found. Some of the associated equilibrium constants are given as follows:

$$Cr(YH)(H_2O) = CrY(H_2O)^- + H^+ \qquad pK_a = 3.1 \quad (1)^4$$

$$Cr(Y)(H_2O)^- = CrY(OH)^{2-} + H^+ \qquad pK_a = 7.5 \quad (2)^{3,4}$$

$$Cr(YH_2)(H_2O)_2^+ = Cr(YH)(H_2O)_2 + H^+$$
$$pK_a = 2.49 \qquad (3)^5$$

$$Cr(YH)(H_2O)_2 = Cr(Y)(H_2O)_2^- + H^+$$
$$pK_a = 2.92 \qquad (4)^5$$
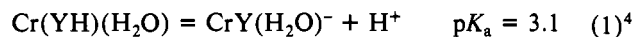
(1) Permanent address: Shandong University, Jinan, Shandong, China.
(2) Britzinger, H.; Thiele, H.; Müller, U. *Z. Anorg. Allg. Chem.* **1943**, *251*, 285.
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$$Cr(Y)(H_2O)_2^- = Cr(Y)(OH)(H_2O)^{2-} + H^+$$

$$pK_a = 6.16 \tag{5}^5$$

$$Cr(Y)(OH)(H_2O)^{2-} = Cr(Y)(OH)_2^{2-} + H^+$$

$$pK_a = 8.0 \tag{6}^6$$

Also

$$Cr(Y)(OH)^{2-} + H_2O = Cr(Y)(OH)_2^{3-} + H^+$$

$$pK_a = 12.2 \tag{7}^7$$
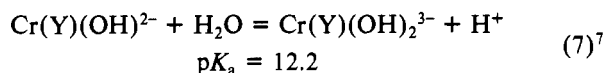
Diacido complexes have also been reported, $Cr(YH_3)$-$(X)_2(H_2O)$ (X = Cl, Br) and $Cr(YH_2)(Cl)_2(H_2O)^-$;[6] although the pK_a's were not determined, the YH_3 forms were thought to dominate only in very acidic solutions. The diaquo, hydroxy–aquo, and diacido species have all been considered to be in the cis form, apparently without proof. In the case of the YH_3-containing species, it was thought that one nitrogen and the two associated carboxyl groups were unattached, rather than three carboxyl groups.[6] The aquation kinetics of the dichloro complex is apparently one of slow loss of one chloride, followed by rapid loss of the second, to give Cr-$(YH_x)(H_2O)^{x-1}$ (x undetermined).[6] The only photochemistry reported is that of $Cr(YH)(H_2O)$, found to be photoinert ($\phi < 10^{-4}$) to radiation of wavelengths longer than 214 nm.[8] The reverse of reaction 7 is apparently fast,[6] however, and the low ϕ might not be intrinsic, but rather the net of photoaquation annulled by rapid back-reaction.

There has been some interest in the aquation kinetics,[9-14] photochemistry,[15,16] and emission properties[17] of cyano and dicyano ammine and aquo complexes of Cr(III), and it seemed worthwhile to extend these kinds of study to a cyano–EDTA species. This would allow some comparisons of kinetic behavior, as well as additional applications of the photolysis[18] and emission[19] rules. An added interest was that cyano–EDTA complexes of Cr(III) had not previously been reported, so that a synthetic challenge was also involved.

Experimental Section

Preparation of the Complexes. $Cr(YH)(H_2O)$ was prepared by the method of Hamm.[4] The absorption spectrum in 0.1 M perchloric acid solution showed maxima at 540 and 390 nm, with respective extinction coefficients of $\epsilon = 146$ and 113 M^{-1} cm^{-1}, in reasonable agreement with the reported values of 540 nm (147 M^{-1} cm^{-1}) and 390 nm (106 M^{-1} cm^{-1}).[4]

$Na_3[Cr(Y)(CN)_2(H_2O)]\cdot4H_2O$ was synthesized as follows. To a hot, concentrated sodium cyanide solution (1.5 g/8 mL of water) was added 1.0 g of $Cr(YH)(H_2O)$, and the mixture was held at 65–70 °C for several minutes. The deep red solution was then cooled and treated with 40 mL of methanol, whereupon a reddish salt slowly precipitated out. This was filtered off, washed with methanol and then with ethanol and ether, and air-dried. The yield was 1.2 g or 78%. The crude product could be recrystallized from concentrated aqueous solution by the addition of methanol containing a small amount of sodium cyanide and was washed and dried as before, the
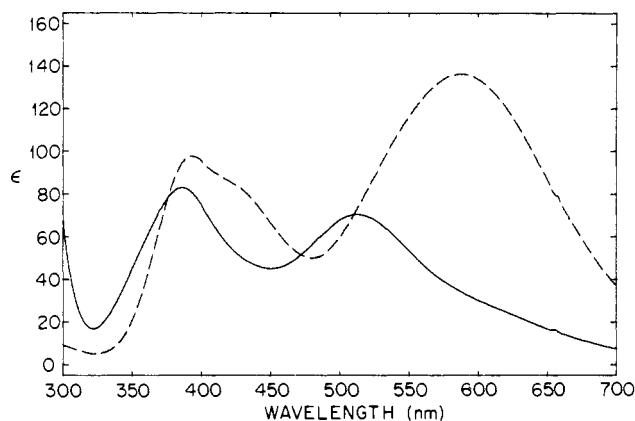
Figure 1. Absorption spectra for $Na_3[Cr(Y)(CN)_2(H_2O)]\cdot4H_2O$ in sodium hydroxide solution (solid line) and for $Cr(YH)(H_2O)$ (dashed line). Both spectra are for 20 °C and pH 12.07 solution.[20]

Table I. Absorption Features of $Cr(Y)(CN)_2(H_2O)^{3-}$ in Aqueous pH 12.07 Solution

feature		
λ, nm	ϵ, M^{-1} cm^{-1}	assignment[a]
512 (max)	70.40	$^4B_1 \rightarrow {}^4B_2$ $(^4T_{2g})$
450 (min)	45.00	
386 (max)	83.01	$^4B_1 \rightarrow {}^4E$ $(^4T_{2g})$
322 (min)	16.89	

[a] Octahedral parent states in parentheses.

ethanol washing being continued until there was no test for cyanide in the effluent. It was important that some sodium cyanide be present since otherwise impure product was obtained. The yield was 0.79 g or 66%. Anal. Calcd: C, 26.14; H, 4.02; N, 10.16; CN, 9.43; Cr, 9.43; water of crystallization, 13.06. Found: C, 26.21; H, 3.93; N, 10.53; CN, 9.29; Cr, 9.37; water of crystallization, 12.96. The absorption spectrum is shown in Figure 1[20] and is characterized in Table I.

All reagents and solvents used were of reagent grade.

Analytical Procedures. Chromium was determined spectrophotometrically at 372 nm ($\epsilon = 4815$ M^{-1} cm^{-1}) following oxidation of the Cr(III) in the complex to chromate ion with alkaline hydrogen peroxide.[21] Cyanide was found by titration with standard silver nitrate solution.[22,23] In this determination, a solution of the complex in 0.1 M perchloric acid was allowed to aquate fully at room temperature. The solution was then adjusted to pH ≥ 10 with 1 M sodium hydroxide solution before carrying out the titration.

Carbon, hydrogen, and nitrogen analyses were carried out by Elek Microanalytical Laboratories. Finally, water of crystallization was obtained from the weight loss on drying for 24 h in a 105 °C oven.

Kinetic Measurements. The thermal aquation rate of $Cr(Y)(CN)_2(H_2O)$ was studied in phosphate–citrate buffer solutions[24] made up to an ionic strength of 1.0 M with potassium chloride and over the pH range of 2.0–7.0. The concentration of the complex was generally 2×10^{-3} M, and the pH remained essentially constant during the reaction, the increase after complete aquation being less than 0.05 pH unit. The degree of reaction was followed by monitoring the absorbance, A, at 586 nm, a region of maximum change, as shown in Figure 1. The spectrophotometer was an HP Model 8450.

The reaction was rapid at low pHs, necessitating the following procedure. A measured volume of buffer solution was placed in a 1 cm square spectrophotometer cell held in an HP 89100A temperature control unit, which maintained temperature to ±0.1 °C as monitored by means of an HP 89102A temperature probe. The solution was stirred in situ by means of a magnetically driven stir bar. After the

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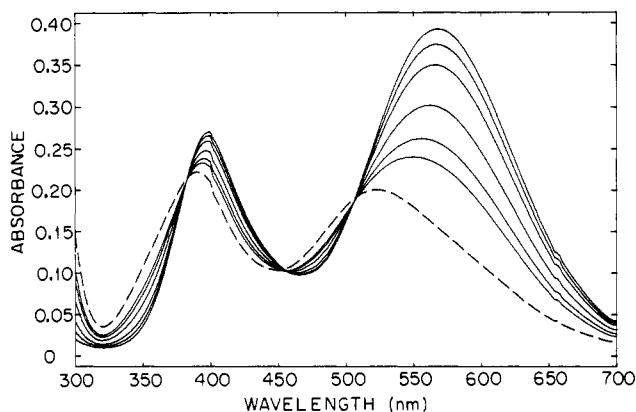
Figure 2. Spectral changes during aquation of 2 × 10^{-3} M Cr-(Y)(CN)$_2$(H$_2$O)$^{3-}$ in phosphate–citrate buffer at pH 6.379 and 1.0 M ionic strength (KCl), 25 °C:[20] dashed line, initial spectrum; solid lines, spectra at successive times of 100, 150, 250, 450, 650, and 1000 s.

desired temperature was reached, the cell was removed from the holder, the requisite amount of solid complex added, the mixture shaken vigorously, and the cell replaced in the holder. It was possible to begin recording absorbance vs. time within about 10 s after the addition of the complex.

Aquation was followed over 3–4 half-lives, and the absorbance at complete reaction, A_∞, was taken to be the constant value reached after 10–15 half-lives. This A corresponded to the value for a corresponding solution of Cr(YH)(H$_2$O). Plots of ln $(A_\infty - A_t)$ vs. time were quite linear, and the apparent first-order rate constants, k_{th}, were obtained from the best least-squares slope for data out to about 3 half-lives.

Photolysis Measurements. The HP 8450 spectrophotometer allowed spectral measurements to be made during irradiation. The photolyzing light was the 514-nm output beam of a Coherent Radiation Model 52B HD argon laser, this wavelength being very close to the isosbestic point of the thermal aquation reaction; see Figures 1 and 2.

The physical arrangement was one in which the laser beam was reflected downward so as to enter the 1 cm square spectrophotometer cell from the top; the concentration of the complex, 1.05 × 10^{-2} M, was such that the beam was fully absorbed in the solution, and separate tests with layered colored solution showed that the stir bar mixed top and bottom layers of solution on less than a 30 s time scale (compared with typical photolysis times of about 10 min). The same temperature control unit and probe were used as for the kinetic studies.

The incident light intensity was around 1 × 10^{-6} einstein s^{-1} and was monitored by the laser power meter, calibrated by Reineckate actinometry carried out both before and after the irradiation.[25] Even at this relatively high light intensity and small volume of solution (ca. 3 mL), the thermal reaction rate limited the measurements to pHs above about 7. For this pH region, it was better to use the more specialized buffer system based on mixtures of the acid and base form of tris(hydroxymethyl)aminomethane, total concentration about 0.5 M. The buffer materials were obtained from Sigma Chemical Co., under the trademark "Trisma".

Because it was preferable not to rely on the separate thermal rate studies and also because a different buffer was used, the dark reaction rate was determined with each photolysis run. The solution was divided into two fractions immediately after mixing, and one fraction was cooled rapidly in an ice bath, in the dark, while the photolysis measurements were made on the other fraction. At the conclusion of the photolysis, the dark solution was brought to the photolysis temperature and the thermal rate measured. The time lags involved in handling the dark solution were not critical because the thermal reaction rates were small at 0 °C at the pHs involved. Both the photolytic and the dark reactions were followed, as before, by means of the absorbance change at 586 nm. For both, apparent first-order rate constants were obtained from the best least-squares slopes of the plots of ln $(A_\infty - A_t)$ vs. time.

Emission Behavior. Sodium hydroxide solutions of the complex, pH 12, were tested for possible room-temperature emission, by using

the amplified pulsed Nd layser system previously described.[19] Emission monitoring was at several wavelengths in the 640–740-nm region, and only a weak emission could be detected of maximum intensity around 650 nm and of less than about 15-ns lifetime even at 10 °C.

Results and Discussion

The Complex Cr(Y)(CN)$_2$(H$_2$O)$^{3-}$. It was at first thought that indirect means would be needed to obtain the subject complex from a Cr(III)–EDTA species. Anation of Cr(Y-H)(H$_2$O) with hydrochloric or hydrobromic acid led to Cr-(YH$_3$)(X$_2$)(H$_2$O), for example, and only by means of a solid-state reaction was it possible to prepare a complex such as Cr(Y)(NCS)$^{2-}$.[26,27] Alternatively, cyano ammine complexes have been prepared via the dimethyl sulfoxide containing complex, as in the case of Cr(NH$_3$)$_5$(Me$_2$SO)$^{3+}$.[12] We were unable to convert Cr(YH)(H$_2$O) to Cr(YH)(Me$_2$SO), however, so this approach failed. It appears that coordinated water in Cr(III)–EDTA complexes is firmly held. The direct reaction described in the Experimental Section works well, somewhat surprisingly.

The EDTA ligand in Cr(Y)(CN)$_2$(H$_2$O)$^{3-}$ is evidently terdentate; the water is assumed to be coordinated, since it is not removable with 24 h of 105 °C heating. The two cyanides are released only as aquation occurs. The above formulation is thus indicated, presumably with three uncoordinated carboxyl groups. It would be of interest to have the pH titration curve for the complex, but it undergoes rapid aquation of the cyano groups in just the pH region of likely interest, thus distorting any pH titration curve. In future work, it may be possible to obtain crystals suitable for an X-ray structure determination of a salt of the complex.

The absorption spectrum of aqueous Cr(Y)(CN)$_2$(H$_2$O)$^{3-}$ at pH 12.07 is shown in Figure 1, and the positions of the maxima and minima are detailed in Table I, along with what seem to be reasonable assignments for the transitions (note ref 14). The complex undergoes aquation in acidic media, as noted above, with a red shift in the absorption spectrum, and release of 2 mol of cyanide/mol. The final spectrum of Cr-(YH)(H$_2$O) is included in Figure 1 and agrees closely with that of our separate preparation of Cr(YH)(H$_2$O).

The infrared absorption spectrum of Na$_3$[Cr(Y)(CN)$_2$-(H$_2$O)]·4H$_2$O shows a Cr–COO carbonyl stretching frequency of 1635 cm^{-1}, which is at the same position as reported for Cr(YH)(H$_2$O)[28] but of larger intensity. There is no peak for COOH in our compound, but there is a weak cyanide stretching peak, at 2160 cm^{-1}, analogous to that reported for *cis*- and *trans*-Cr(en)$_2$(CN)$_2$$^+$.[29,30] There is also a broad band around 3450 cm^{-1}, corresponding to water of crystallization.

Thermal Aquation Kinetics. Figure 2 shows a typical sequence of rapid-scan spectra[20] obtained during the aquation of Cr(Y)(CN)$_2$(H$_2$O)$^{3-}$. Good isosbestic points are maintained, indicating that no appreciable buildup of any intermediate occurs during the reaction. The sequence in the figure is for pH 6.38 at 25 °C; the isosbestic points vary somewhat with pH, as might be expected. Not only should the degree of protonation of the reactant vary with pH, but also that of the product, as indicated by eq 2 and 3.

As noted in the Experimental Section, the degree of reaction was followed quantitatively from the increase in A at 586 nm, and a typical semilog plot of $(A_\infty - A_t)$ vs. time is shown in Figure 3. The set of apparent first-order rate constants, k_{th},

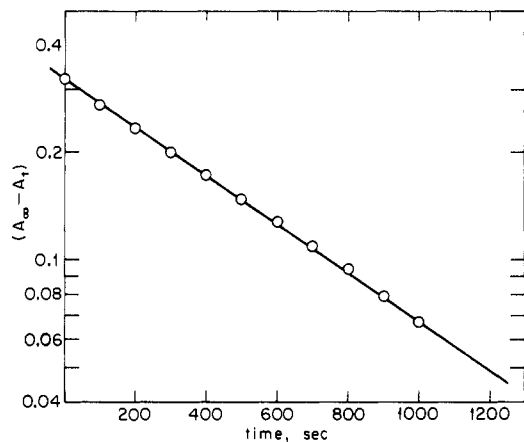(25) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

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Figure 3. First-order plot for the aquation of $Cr(Y)(CN)_2(H_2O)^{3-}$ in phosphate–citrate buffer at pH 7.00 and ionic strength 1.0 M (KCl), 25 °C.

Table II. Apparent First-Order Rate Constants for the Aquation of $Cr(Y)(CN)_2(H_2O)^{3-}$

	$10^2 k_{th},^b$ s⁻¹		
pH^a	15 °C	20 °C	25 °C
2.061	1.50 ± 0.01	2.56 ± 0.01	4.72 ± 0.01
2.672	1.45 ± 0.03	2.55 ± 0.05	4.68 ± 0.02
3.773	1.37 ± 0.01	2.55 ± 0.01	4.55 ± 0.02
4.720	1.33 ± 0.01	2.22 ± 0.04	3.79 ± 0.01
5.214	1.06 ± 0.00	1.64 ± 0.01	2.85 ± 0.01
5.324	0.91 ± 0.01	1.37 ± 0.01	2.04 ± 0.04
5.638	0.67 ± 0.02	1.27 ± 0.03	1.49 ± 0.01
6.043	0.48 ± 0.01	0.76 ± 0.01	1.16 ± 0.02
6.379	0.21 ± 0.006	0.24 ± 0.01	0.37 ± 0.01
7.070	0.074 ± 0.002	0.091 ± 0.002	0.15 ± 0.02

^{a} Phosphate–citrate buffer solutions at 1 M ionic strength (KCl).
^{b} The average of two or more independent runs.

Table III. Parameters for the Aquation of $Cr(Y)(CN)_2(H_2O)^{3+a}$

	value		
quantity	15 °C	20 °C	25 °C
$10^2 k_1$, s⁻¹	1.44 ± 0.05	2.55 ± 0.07	4.65 ± 0.05
$10^6 K_1$, M	2.56 ± 0.09	2.86 ± 0.07	3.69 ± 0.04

$$\Delta H^{\circ \ddagger} = 18.88 \pm 0.01 \text{ kcal mol}^{-1};$$
$$\Delta S^{\circ \ddagger} = -1.39 \pm 0.03 \text{ cal mol}^{-1} \text{ K}^{-1}$$

^{a} Phosphate–citrate buffer solution at 1.0 M ionic strength (KCl).

is given in Table II. The variation of k_{th} with pH is shown in Figure 4, for 20 °C. Qualitatively, k_{th} is essentially constant below a pH of about 3.5; above this pH there is a rapid decrease, with k_{th} approaching zero above pH 7. The appearance of the plot is that of a titration curve, and the data do, in fact, fit expression 8.

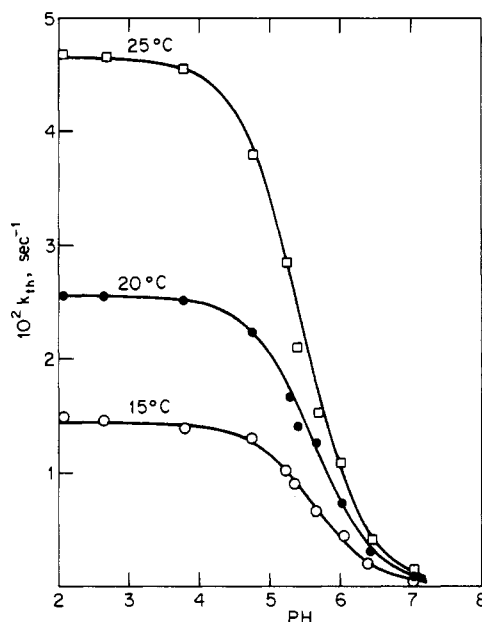$$k_{th} = \frac{k_1(H^+)}{K_1 + (H^+)} \quad (8)$$

According to eq 8, a plot of $1/k_{th}$ vs. $1/(H^+)$ should be linear, the values of the slope and intercept allowing calculation of k_1 and K_1. This linearity was indeed observed; the best-fitting calculated curves are given by the solid lines in Figure 4, and the corresponding k_1 and K_1 values are listed in Table III.
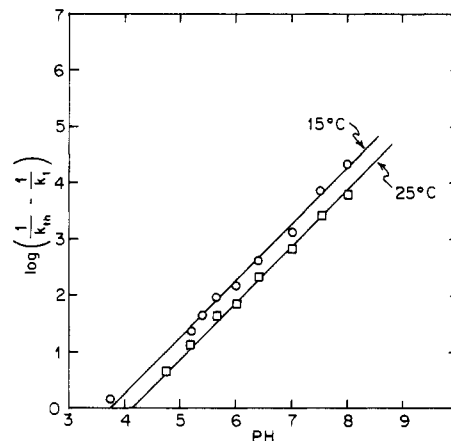
The actual fitting procedure was first to determine k_1 from the intercept of the plot of $1/k_{th}$ vs. $1/(H^+)$ and then to obtain the value of K_1 from a plot according to the equation

$$\log (1/k_{th} - 1/k_1) = \log (K_1/k_1) + pH \quad (9)$$

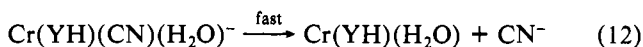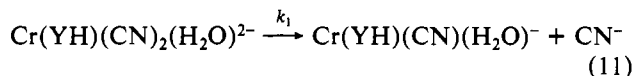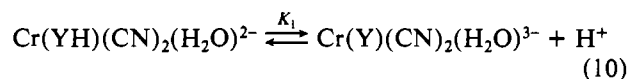Such plots were accurately linear, with unit slope, as illustrated in Figure 5.

Figure 4. Variation of k_{th} with pH for the aquation of $Cr(Y)(CN)_2(H_2O)^{3-}$ in phosphate–citrate buffers at ionic strength 1.0 M (KCl). Solid lines are calculated from best fits of eq 8.
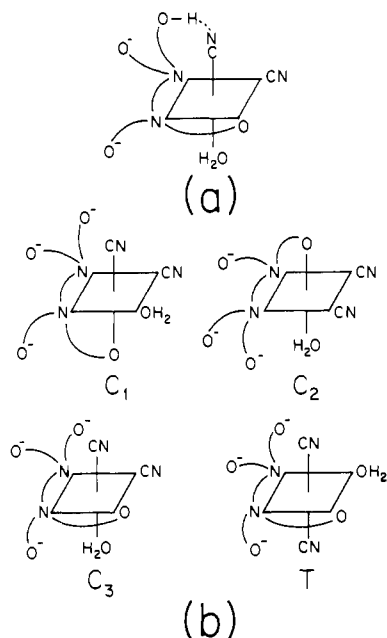

Figure 5. Aquation of $Cr(Y)(CN)_2(H_2O)^{3-}$. Data were plotted according to eq 9.

Equation 8 anticipates the simple mechanistic scheme shown by eq 10–13. The similar sequence of a slow–fast two-step

$$Cr(YH)(CN)_2(H_2O)^{2-} \underset{}{\overset{K_1}{\rightleftharpoons}} Cr(Y)(CN)_2(H_2O)^{3-} + H^+ \quad (10)$$

$$Cr(YH)(CN)_2(H_2O)^{2-} \xrightarrow{k_1} Cr(YH)(CN)(H_2O)^- + CN^- \quad (11)$$

$$Cr(YH)(CN)(H_2O)^- \xrightarrow{fast} Cr(YH)(H_2O) + CN^- \quad (12)$$

$$H^+ + CN^- = HCN \quad (13)$$

aquation was suggested for the dichloro Cr(III)–EDTA complex.[7] As in the dichloro case, we cannot distinguish different sets of degrees of protonation; that is, YH could be YH_x (1 ≤ x ≤ 3) and Y could be YH_{x-1}. It seems clear, however, that only *one* stage of acid–base equilibrium is present over the pH range 2–7, and we make the analogy to eq 1 and 4. The higher negative charges in our case could reasonably lower the acid dissociation constant of a YH-containing complex from around 10^{-3} M for the aquo–EDTA species to our value of around 10^{-6} M.

The complexes $Cr(NH_3)_5(CN)^{2+}$ and *cis*- and *trans*-$Cr(NH_3)_4(CN)_2^+$ undergo an acid-catalyzed aquation,[12,14] pre-
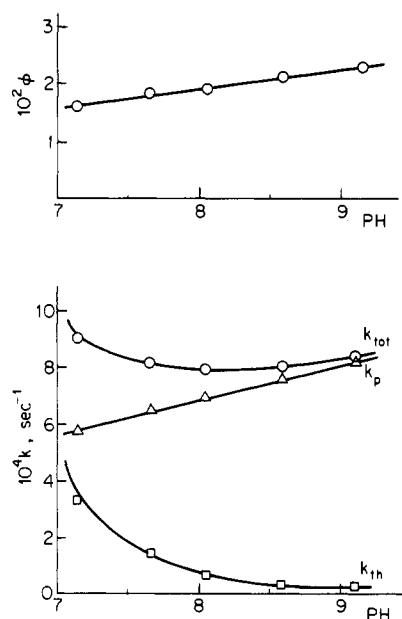
Figure 6. Possible isomeric formulations of Cr(Y)(CN)$_2$(H$_2$O)$^{3-}$: (a) illustration of hydrogen bonding to a cyanide; (b) possible cis and trans isomers.

Figure 7. Variation of k_{tot}, k_{th}, and k_p with pH for aqueous Cr-(Y)(CN)$_2$(H$_2$O)$^{3-}$ in tris(hydroxymethyl)aminomethane buffer solutions at 20 °C (lower figure) and variation of ϕ with pH (upper figure).

sumably via protonation of a cyano ligand. No saturation in rate is reached, however, the –CNH moiety being an acid with an estimated K_a of ca. 0.1 M.[11] We assume that this is also the case here and, for this reason, do not assign K_1 to an acid–base equilibrium of coordinated cyanide, but rather to the process of eq 10. If there were, in addition, an acid-catalyzed aquation of Cr(YH)(CN)$_2$(H$_2$O)$^{2-}$ through a –CNH intermediate, a square dependence on (H$^+$) would appear in the numerator of eq 8, contrary to observation. A possibility, illustrated in Figure 6a, is essentially an internal acid catalysis via hydrogen-bond formation between a cyano ligand and the protonated free carboxyl group of the EDTA ligand.

The activation enthalpy for k_1 was determined from a plot of ln (k_1h/kT) vs. $1/T$, where k is the Boltzmann constant, h is Planck's constant, and the activation entropy was determined from the relationship $k_1 = (kT/h) \exp(\Delta S^*/R) \exp(-\Delta H^{o*}/RT)$. least-squares analysis gives ΔH^{o*} = 18.9 ± 0.01 kcal mol^{-1} and ΔS^{o*} = –1.4 ± 0.03 cal mol^{-1} K^{-1}. This activation enthalpy is similar to that found for aquation of Cr(NH$_3$)$_5$CN^{2+},[15] although the activation entropy is different, as might be expected from the difference in detail of the acid catalysis. K_1 was less precisely determinable than k_1, but the set of values for the three temperatures suggests that ΔH^o for eq 10 is small, consistent with the small ΔH^o of dissociation of a carboxylic acid.[31]

Photochemistry. Cr(Y)(CN)$_2$(H$_2$O)$^{3-}$ undergoes photoaquation of cyanide, but because of the low quantum yield, ϕ, the process could be studied only in relatively alkaline solution. Even so, it was generally necessary to make substantial correction for the concomitant thermal aquation reaction.

This correction was facilitated because of the following circumstances. Regardless of mechanistic detail, the overall process may be written as R → P, both photochemically and thermally, where R denotes reactant Cr(Y)(CN)$_2$(H$_2$O)$^{3-}$ and all species in rapid acid–base equilibrium with it, and P denotes the product Cr(YH)(H$_2$O) and similarly related species. That is, the product of the photoaquation is observed spectrally to

Table IV. Rate Constants for the Photolysis and Dark Reaction of Cr(Y)(CN)$_2$(H$_2$O)$^{3-}$ and Quantum Yields (20 °C)^a

quan-tity^b	value^c				
	pH 7.143	pH 7.655	pH 8.043	pH 8.581	pH 9.130
$10^4 k_{tot}$	9.03 (11)	8.15 (13)	7.92 (29)	8.10 (17)	8.43 (16)
$10^4 k_{th}$	3.26 (09)	1.47 (07)	0.69 (04)	0.39 (02)	0.29 (03)
$10^4 k_p$	5.79 (10)	6.48 (27)	6.92 (31)	7.70 (17)	8.14 (18)
ϕ	0.0163	0.0183	0.0190	0.0213	0.0230
ϕ/F^d	0.0168	0.0185	0.0191	0.0213	0.0230

^{a} In tris(hydroxymethyl)aminomethane buffer solutions. ^{b} Rate constants in s^{-1}. ^{c} Numbers in parentheses are the decimal deviations of the average of three or four independent runs. ^{d} F denotes fraction of complex present in unprotonated form.

be identical with the production of the thermal aquation reaction at any given pH. The product species is photoinert, and further, the irradiation wavelength of 514 nm is close enough to the reaction isosbestic wavelength that $\epsilon_R = \epsilon_P$ is a reasonable approximation over the pH range involved. Finally, the absorbance of the solution used was such that all incident light was absorbed.

Under the above conditions and assumptions, we can write

$$d(R)/dt = -(k_{th} + k_p)(R) = -k_{tot}(R) \qquad (14)$$

where k_p is the pseudo-first-order rate constant given by $k_p = I_0\phi/C_0$. Here, I_0 is the incident light intensity in einstein L^{-1} s^{-1}, and C_0 is the total Cr(III) concentration (and the initial concentration of R). The experimental procedure was to determine k_{tot} under 514-nm irradiation by the same method as used for the thermal reaction and, in a separate experiment, to determine k_{th} on an aliquot of the solution not under irradiation, as described in the Experimental Section. The difference in the two k values gave k_p and, from measurement of I_0 and knowledge of C_0, ϕ could be calculated.

Figure 7 shows the variation of k_{tot}, k_{th}, and k_p over the pH range 7–9, and the date are summarized in Table IV. The data were not extended to pHs lower than 7 because of the rapidly increasing imprecision of obtaining k_p from the difference $(k_{tot} - k_{th})$. Note that in the range of pH studied, Cr(Y)(CN)$_2$(H$_2$O)$^{3-}$ is the dominant species; at pH 7, for example, only 3.8% of R is present as Cr(YH)(CN)$_2$(H$_2$O)$^{2-}$, and at pH 9, the percentage drops to 0.04%.

(31) Rossini, F. D., Wagman, D. D., Evans, W. H., Eds. "Selected Values of Chemical Thermodynamic Constants"; U.S. National Bureau of Standards: Washington, DC; 1952.

Since ϕ is nearly pH independent in the pH 7–9 range, $Cr(YH)(CN)_2(H_2O)^{2-}$ clearly is not the primary photoactive form. We conclude that most if not all of the photochemistry is due to $Cr(Y)(CN)_2(H_2O)^{3-}$. That is, the photoaquation yield for the former complex could be comparable to that for the latter one but cannot be very much larger. There is a small increase in ϕ values between pH 7 and 9, even after correction for the fraction present in unprotonated form. This increase appears to be outside of our experimental error. Possibly, some further deprotonation occurs, e.g. of the coordinated water, to give a more photoactive species. No detailed studies were made, but qualitative results indicate that ϕ is not highly temperature dependent.

It is of interest to consider the application of the photolysis[18] and emission[19] rules for Cr(III) complexes. Figure 6 shows the four possible geometric isomers if the EDTA ligand in $Cr(Y)(CN)_2(H_2O)^{3-}$ is coordinated through two nitrogens and one carboxyl group. In three of these, C_1, C_2, and C_3, the cyano groups are cis, and in the fourth, T, they are trans. For all four cases, the photolysis rules predict the yield for cyanide aquation to be small, as observed, since the cyano group does not lie on the weak-field axis. In cases C_1, C_3, and T, the labilized group should be a coordinated nitrogen, for which permanent detachment and consequent net photolysis seem unlikely. In case C_2, either water exchange or aquation of a carboxyl group would be predicted, processes that we would not have been able to observe. According to the emission rules, the emission lifetime for C_1 might be observable since neither grop on the weak-field axis is substitutionally very labile. For C_2, C_3, and T, however, the emission lifetime should be short,

as observed, since the weak-field axis contains a coordinated carboxyl group, which is substitutionally labile in the Cr-(III)–EDTA family. The cis isomers seem to be preferred in this family, and our tentative conclusion is that the complex is in the form C_2 or C_3.

Summary

The complex $Cr(Y)(CN)_2(H_2O)^{3-}$ resembles the various cyano–aquo and cyano–ammine complexes of Cr(III) in that the thermal reaction is one of cyanide aquation, the rate increasng with decreasng pH. Unlike the other cases, however, there does not appear to be appreciable contribution to the rate from a path involving –CrCNH. It is possible that the aquation is assisted by internal protonation of a cyano group through hydrogen bonding from a noncoordinated but protonated carboxyl group.

While the cyano–ammine complexes show primarily *ammonia* photoaquation, the photochemistry of our complex is one of *cyanide* aquation only. A likely explanation, however, is that labilization of other ligands either is blocked or, if it does occur, is unobservable under our conditions. Both the quantum yield behavior and the emission behavior are consistent with the photolysis and emission rules proposed for Cr(III) complexes.

Registry No. $Na_3[Cr(Y)(CN)_2(H_2O)]$, 86900-67-6; Cr(Y-H)(H_2O), 15955-81-4.

Contribution from the Nuclear Research Centre Negev, Beer-Sheva, Israel, Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel, and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Reaction of ·CH₂C(CH₃)₂OH Radicals with Cobalt(II) Tetrasulfophthalocyanine in Aqueous Solutions. A Pulse Radiolytic Study[1]
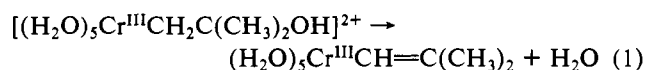
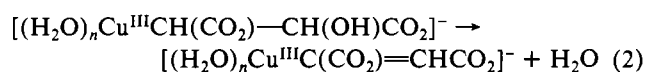YACOV SOREK,[2a] HAIM COHEN,[2a] WILLIAM A. MULAC,[2b] KLAUS H. SCHMIDT,[2b] and DAN MEYERSTEIN*[2a–c]

The reaction of cobalt(II) tetrasulfophthalocyanine, $[Co^{II}(tspc)]^{4-}$, with ·CH₂C(CH₃)₂OH free radicals was studied. The results indicate that the first product formed is $[(tspc)Co^{III}CH_2C(CH_3)_2OH]^{4-}$. This product loses water via β elimination to yield $[(tspc)Co^{III}CH=C(CH_3)_2]^{4-}$. The decomposition of the latter compound yields $[Co^I(tspc)]^{5-} + OCHCH(CH_3)_2$ at pH ≥ 9.5, $[Co^{III}(tspc)]^{3-} + CH_2=C(CH_3)_2$ at pH ~ 6, and mainly $[Co^{II}(tspc)]^{4-}$ plus equal amounts of $CH_2=C(CH_3)_2$ and $OCHCH(CH_3)_2$ at pH ~ 3. The results suggest that a pK of the water molecule trans to the aliphatic residue affects the mechanism of hydrolysis. A further reaction is observed, the exact nature of which is not fully understood. For comparison purposes the oxidation of $[Co^{II}(tspc)]^{4-}$ by $Br_2^-\cdot$ and its reduction by $CO_2^-\cdot$ were studied.
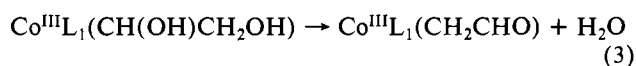
Introduction

Pulse radiolysis is a powerful technique for the study of the properties of short-lived intermediates with metal–carbon bonds formed in reactions of aliphatic free radicals with low-valent transition-metal complexes.[3–6] Of special interest is the possibility to measure the rate of β elimination of hydroxyl groups. Three reactions of this type have been studied so far in aqueous solutions:[7a]

$$[(H_2O)_5Cr^{III}CH_2C(CH_3)_2OH]^{2+} \rightarrow$$
$$(H_2O)_5Cr^{III}CH=C(CH_3)_2 + H_2O \quad (1)$$
$$k_{obsd} = 1.0 \times 10^2 + (1.1 \times 10^3)[H_3O^+] \text{ s}^{-1} \text{ }^4$$

$$[(H_2O)_nCu^{III}CH(CO_2)-CH(OH)CO_2]^- \rightarrow$$
$$[(H_2O)_nCu^{III}C(CO_2)=CHCO_2]^- + H_2O \quad (2)$$
$$k = 2 \times 10^2 \text{ s}^{-1} \text{ }^5$$

$$Co^{III}L_1(CH(OH)CH_2OH) \rightarrow Co^{III}L_1(CH_2CHO) + H_2O \quad (3)$$

$$k = 4 \text{ s}^{-1} \text{ at pH 5.0 and } k = 15 \text{ s}^{-1} \text{ at pH 3.5}^6$$

where $L_1 \equiv$ 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-

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