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Acid Hydrolysis and Linkage Isomerism of the *cis*-Dicyanobis(ethylenediamine)chromium(III) Ion

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Despite the continuing interest in amine [1, 2] and cyano [3, 4] compounds of chromium(III), examples of mixed cyano-amine complexes are presently restricted to *cis*- and *trans*-dicyanobis(ethylenediamine)chromium(III), $Cren_2(CN)_2^+$, and some hydrolysis derivatives [5, 6]. No kinetic study on the substitution behaviour of these complexes has as yet been reported. We present here the results of a kinetic investigation of acid-catalysed aquation of the first coordinated cyanide group from the species *cis*-$Cren_2(CN)_2^+$. These data provide a useful comparison with those reported earlier by Wakefield and Schaap [7–9] for the corresponding cyano-aquo complexes $Cr(H_2O)_5CN^{2+}$, *cis*-$Cr(H_2O)_4(CN)_2^+$ and *fac*-$Cr(H_2O)_3(CN)_3^0$. In addition we present evidence for an interesting example of Ag^+ ion promoted cyano–isocyano linkage isomerism, in which a crystalline perchlorate salt of the isocyano isomer has been isolated.

Experimental

Materials

Commercially available chemicals of reagent grade quality were used without further purification. Two dissimilar synthetic routes to *cis*-$[Cren_2(CN)_2]ClO_4$ have been recently described [5, 6]. The method of Schaap and co-workers [6] was preferred because of the isomeric purity of the product; and in our hands has proven the more reliable method. The twice recrystallized perchlorate salt yielded an ultraviolet–visible absorption spectrum in excellent agreement with literature values. The method of Schaap and co-workers [6] was also adopted for resolution of the parent complex into $(+)_{589}$ and $(-)_{589}$-$[Cren_2(CN)_2]I$ optical isomers their circular dichroism (CD) spectra matching closely those reported [5, 6].

Kinetic Measurements

Reaction was carried out directly in a 5-cm thermostatted silica cell and followed spectrally using a Cary 118 CX spectrophotometer. Complex concentrations of 1.5×10^{-3} *M* and 7.5×10^{-4} *M* were used for kinetic runs with acid concentrations in the range 0.05–0.3 *M* and 0.015–0.025 *M*, respectively. This ensured a large excess of acid and pseudo first-order kinetics. Although substitution of the two cyanide groups by water occurs stepwise, preliminary studies showed that loss of the second cyanide group proceeded at a rate somewhat comparable to that of the first. Thus, in order to follow the first substitution step without significant interference from the second, absorbance changes were monitored at 366 nm – an isosbestic point for the second stage reaction. Observed pseudo first-order rate constants, k_{obs}, were obtained from the slopes of $\ln(A_\infty - A_t)$ *versus* time plots. Reaction was generally followed for 1½–2 half-lives and data were discarded for runs where correlation coefficients were less than 0.998. Reproducibility was generally better than ±4 percent. Due to the limited solubility of *cis*-$Cren_2(CN)_2^+$ in $HClO_4/NaClO_4$ media, we found it necessary to employ HCl as the acid source for most kinetic studies. The ionic strength was generally adjusted to unity using NaCl as the backing electrolyte. Despite the presence of Cl^- ion in solution, spectral data confirmed sole formation of the diaquo complex as the initial reaction product. Under our experimental conditions subsequent anation to form coordinated chloride species proceeds at a sufficiently slow speed so as to present no apparent complications. This view is supported by the very close correspondence in k_{obs} values for kinetic runs performed in 0.1 *M* HCl and 0.10 *M* $HClO_4$ in the absence of backing electrolyte. The activation parameters Ea and $\Delta S^{\ddagger}$ were obtained from the Arrhenius plot of $\ln k_{obs}$ *versus* 1/T. The optical activity of the product species in acid hydrolysis studies employing the parent complex $(-)_{589}$-$[Cren_2(CN)_2]I$ was determined from optical rotation and CD spectral measurements using a Bendix automatic polarimeter (model 1144) and a Jasco ORD/uv-5/CD-1 spectropolarimeter, respectively.

Linkage Isomerism. Isolation of cis-$[Cren_2(NC)_2Ag](ClO_4)_2$

Solid *cis*-$[Cren_2(CN)_2]ClO_4$ (0.2 g, 6.2×10^{-4} mole) was added to a 8 ml solution of 0.1 *M* $AgNO_3$ (8×10^{-4} mole). After dissolution of the complex the solution was allowed to stand at room temperature for five minutes. Solid $NaClO_4$ (2.0 g) was then added with stirring, and a yellow-orange precipitate was obtained on cooling in an ice-bath for several minutes. The product was washed with 10 ml of 50% ethanol, 20 ml of 90% ethanol, 40 ml ether and sucked dry (yield 0.25 g). *Anal*: Calcd. for $[Cren_2(NC)_2Ag](ClO_4)_2$: C, 13.57; H, 3.04; N, 15.83; Cl 13.55%. Found: C, 13.45; H, 3.18; N, 15.38; Cl 13.28%. The yield according to this product formulation was 76 percent.

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Results and Discussion

Acid Hydrolysis

In agreement with Schaap and co-workers [6], we observe that in the presence of excess acid the parent complex is converted completely to the *cis*-diaquo product. No evidence was found for concomitant labilization of a Cr(III)–ethylenediamine bond – a substitution pathway prominent in many *trans*-$Cren_2X_2^+$ systems [10]. Our observations are consistent with the following two step reaction sequence:

$$cis\text{-}Cren_2(CN)_2^+ + H_3O^+ \rightarrow cis\text{-}Cren_2(CN)(H_2O)^{2+} + HCN \quad (1)$$

$$cis\text{-}Cren_2(CN)(H_2O)^{2+} + H_3O^+ \rightarrow cis\text{-}Cren_2(H_2O)^{3+} + HCN \quad (2)$$

The dependence of the observed rate constant for reaction (1) on H^+ concentration is presented in Table I. A plot of k_{obs} at 25 °C *versus* $[H^+]$ ($\mu = 1.0$, HCl/NaCl) yields a straight line with a correlation coefficient of 0.9985 and a near-zero intercept, indicating a simple first order dependence on $[H^+]$. Thus the analytical expression for k_{obs} is of the form:

$$k_{obs} = k_0 + k^1[H^+] = k^1[H^+] \quad (3)$$

(since no hydrolysis is observed in neutral solution). The 25 °C value of k^1 obtained from the slope of the k_{obs} *versus* $[H^+]$ plot is $1.99 \times 10^{-2}\ M^{-1}\ sec^{-1}$ (Table II). A two step mechanism consistent with expression (3) is given in reactions (4) and (5).

$$cis\text{-}Cren_2(CN)_2^+ + H^+ \xrightleftharpoons{K,\ fast} cis\text{-}Cren_2(CN)(CNH)^{2+} \quad (4)$$

$$cis\text{-}Cren_2(CN)(CNH)^{2+} \xrightarrow[slow]{k_1} cis\text{-}Cren_2(CN)(H_2O)^{2+} + HCN \quad (5)$$

TABLE I. Observed Rate Constants for *cis*-$Cren_2(CN)_2^+$ Acid Hydrolysis.

Temp, (°C)	μ = 1 (HCl, NaCl)		[HCl] = 0.10 *M*, 25 °C	
	$[H^+]$, *M*	10^4k_{obs}, (sec^{-1})	μ	10^4k_{obs}, (sec^{-1})
25.0	~0[a]	0	0.5 (NaCl)	16.9
	0.015	3.59	1.0 (NaCl)	21.8
	0.025	6.21	2.0 (NaCl)	26.2
	0.05	10.8		
	0.10	21.8	1.0 (LiCl)	21.4
	0.15	30.0	1.0 (KCl)	18.6
	0.20	42.9		
	0.30	59.3		
15.0	0.05	3.02		
35.0	0.05	26.8		
45.0	0.05	70.1		

[a] Parent complex dissolved in 1.0 *M* NaCl solution.

This mechanism is essentially identical to that suggested by Wakefield and Schaap [7–9] in their corresponding study of several cyano-aquo Cr(III) compounds. The first step involves a rapid and reversible protonation of the parent complex (represented by the equilibrium constant K) and is followed by the slow, rate-determining aquation of the protonated species with a rate constant k_1. This mechanism yields a theoretical rate law of the form:

$$\text{rate} = \frac{k_1K[H^+]}{1 + K[H^+]}[\text{complex}]$$

Provided K and/or $[H^+]$ are small then $1 \gg K[H^+]$, and the rate reduces to an expression first order in $[H^+]$ as experimentally observed. *i.e.* $k_{obs} = k_1K[H^+] = k^1[H^+]$. However, if K is not small an eventual flattening in the k_{obs} *versus* $[H^+]$ plot is predicted at high $[H^+]$. Up to the highest $[H^+]$ employed in the present study (0.30 *M*) no such curvature was apparent, which necessitates a relatively small value for K. This seems reasonable in view of the net positive charge of the parent complex, and is in accord with the K value of 0.21–0.55 (25 °C, μ = 2.0) reported for the analogous *cis*-$Cr(H_2O)_4(CN)_2^+$ species [8]. It was possible to employ higher $[H^+]$ in this latter study (up to 1.4 *M* at 25 °C) due to the much smaller hydrolysis rate constant k^1 (Table II). Down-

TABLE II. Comparison of Rates and Activation Parameters for Acid Hydrolysis of Cyano–Cr(III) Complexes.[a]

Complex	10^5k_0 (sec^{-1})	10^4k_1K ($M^{-1}\ sec^{-1}$)	Ea (kJ $mole^{-1}$)	$\Delta S^\ddagger$ ($JK^{-1}\ mole^{-1}$)
$Cr(H_2O)_5CN^{2+}$	1.1	5.9	87 ± 0.5	−27 ± 1[b]
cis-$Cr(H_2O)_4(CN)_2^+$	<0.6	8.4	86 ± 1	−23 ± 3[c]
fac-$Cr(H_2O)_3(CN)_3^0$	<0.3	6.6	82 ± 3	−23 ± 5[d]
cis-$Cren_2(CN)_2^+$	0	199	78 ± 2	−16 ± 4[e]

[a] Rate constants at 25 °C. [b] Ionic strength 2.0, reference 7. [c] Ionic strength 2.0, reference 8. [d] Ionic strength 2.0, reference 9. [e] Ionic strength 1.0, this work.

ward curvature in the k_{obs} *versus* $[H^+]$ plot was thus observed, from which individual k_1 and K values were determined. Furthermore, spectral differences between the protonated and unprotonated parent complex enabled an independent evaluation of K to be made. The greater reactivity of *cis*-$Cren_2(CN)_2^+$ and the relative insensitivity of its spectrum to $[H^+]$ have prevented extraction of individual values of k_1 and K in the present study.

A comparison between *cis*-$Cren_2(CN)_2^+$ and the cyano-aquo species of Wakefield and Schaap [7–9] is thus restricted to k_1K (or k^1) values and the corresponding activation parameters (see Table II). Furthermore, the ionic strengths employed differ in the two studies [11]. It is noteworthy that the ionic strength dependence shown by k_{obs} in Table I is in keeping with the postulated reaction mechanism, since K increases with increasing ionic strength [12]. Two general comments may be made concerning the comparative data presented in Table II:

1. *The non-catalysed pathway* (k_0) is absent for the cyano-amine system while being significant for the cyano-aquo systems. This observation supports the mechanism previously proposed for the k_0 pathway, which has been attributed to intramolecular proton transfer from a H_2O ligand *cis* to the leaving CN^- group [7–9]. Since *cis*-$Cren_2(CN)_2^+$ has only an amine *cis* to the leaving CN^- proton transfer is far less likely (ethylenediamine being less acidic than H_2O).

2. *The acid-catalysed pathway* for the cyano-amine system has a rate constant k_1K (or k^1) approximately 25 times greater than that for the correspondingly charged cyano-aquo complex, *cis*-$Cr(H_2O)_4(CN)_2^+$. This may be attributed to both a smaller activation energy and less negative entropy of activation than for the cyano-aquo system. An additional factor may be an increased value for the protonation equilibrium constant K, although this effect is not expected to be large.

Finally, it is of considerable interest to examine the stereochemistry of the acid hydrolysis reaction under investigation. Polarimetric measurements at 589 nm and 546 nm indicate that the *levo*-dicyano parent hydrolyses to the *levo*-diaquo product. The corresponding CD spectra for parent and product are shown in Fig. 1. The product spectrum matches closely that reported by Kindred and House [13] for $(-)_{589}$-*cis*-$Cren_2(H_2O)_2^{3+}$, and indicates that both substitution steps proceed with $\geqslant 97$ percent retention of optical activity [14]. Retention of configuration is also inferred from an analysis of the CD spectra in Fig. 1, which cover the region of the longest wavelength spin-allowed ligand field absorption band. For such complexes of C_2 symmetry two CD bands are anticipated in this region, but it is generally observed that the E band dominates [13]. Since both compounds have a negative sign for their dominant CD band they are both tentatively assigned the same absolute configuration, Δ [13]. The absence of stereochemical change during octahedral substitution is a rather general phenomenon for Cr(III) systems in aqueous solution [13, 15]. It is regarded as a characteristic of an associative interchange (I_a mechanism) for the rate determining step, in accordance with *cis* rather than remote attack by incoming group relative to the displaced ligand. In contrast, stereochemical change is normally associated with a dissociative type mechanism (I_d or D) [15].

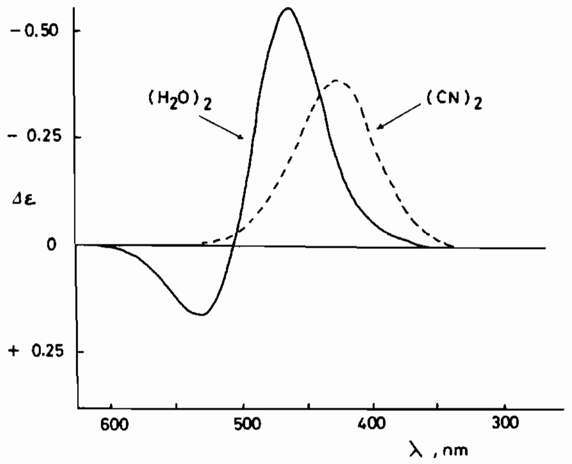


Fig. 1. Circular dichroism spectra of $(-)_{589}$-*cis*-[$Cren_2$-$(CN)_2$]I in H_2O (– – – –); hydrolysis product in 0.8 *M* HCl (——).

Linkage Isomerism

The addition of Ag^+ (as $AgNO_3$) to aqueous solutions of *cis*-$Cren_2(CN)_2^+$ results in a rapid change in the visible absorption spectrum. On further prolonged standing (12–16 hours, 25 °C) hydrolysis to the diaquo product occurs accompanied by precipitation of AgCN. The initial spectral shifts are observed until $[Ag^+]/[Cr(III)]$ is equal to 1.0, with spectra remaining essentially invariant for ratios exceeding unity. New absorption maxima are observed at 458 nm and 351 nm (*Solution* A), compared with peaks for the parent complex at 434 nm and 339 nm (Table III). Similar spectral movements have been noted previously for several cyano-aquo Cr(III) species on addition of Hg^{2+} or Ag^+, and have been attributed to intramolecular cyano → isocyano linkage isomerism about the Cr(III)–cyanide bond [16, 17]. A general representation for such processes involving Ag^+ is given in reaction (6).

$$Cr{-}CN + Ag^+ \rightleftharpoons Cr{-}NCAg^+ \tag{6}$$

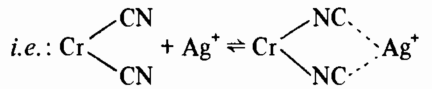
If linkage isomerism occurs in *cis*-$Cren_2(CN)_2^+$ for both cyanide groups the resultant silver adduct will contain a N_6 chromophore about Cr(III). The very close correspondence of the spectrum of Solution A with that of several N_6 model compounds (Table III) provides strong support for such an isomerism process.

TABLE III. UV–Visible Spectral Data.

Complex	Absorption Maxima[a]	Chromophore	Reference
cis-$Cren_2(CN)_2^+$	339(62); 434(70)	N_4C_2	6
$Cren^{3+}$	351(61); 457(76)	N_6	21
cis-$Cren_2(NH_3)_2^{3+}$	351(54); 460(66)	N_6	21
Solution A	351 ; 458	N_6	this work
Solid adduct	351(64); 458(79)	N_6	this work

[a] Wavelengths in nm. Values in parentheses are the molar absorptivities.

Although the Ag^+ species is believed to exist predominantly as the 1:1 (Ag^+:Cr(III)) adduct [18], the typical N_6 spectrum indicates interaction of Ag^+ with both CN^- ligands. This is in accord with maintenance of an overall *cis* geometry for the complex.



(7)

The CD spectrum observed for this silver adduct provides confirmation of its *cis* configuration. A structure of this type also rationalizes the marked resistance to acid hydrolysis displayed in even strongly acidic solution.

A unique feature of the present system is the isolation of the 1:1 adduct as a solid, crystalline perchlorate salt, with the empirical formula $[Cren_2(NC)_2Ag](ClO_4)_2$. In agreement with this formulation, a 10^{-3} *M* aqueous solution of the salt at 25 °C has a molar conductance of 230 ohm^{-1} cm^2 $mole^{-1}$ [19]. Except for the absence of NO_3^- absorption, a 10^{-4} *M* aqueous solution of the solid displays a visible spectrum identical with that of Solution A (Table III) indicating a very large equilibrium constant for reaction (7) [18]. The CN stretching frequency appears in the infrared spectrum (KBr disk) of the solid adduct and *cis*-$[Cren_2(CN)_2]ClO_4$ parent at 2128 cm^{-1} and 2130 cm^{-1}, respectively. However, the intensity of this band is an order of magnitude larger in the silver adduct, an observation consonant with more extensive Cr–cyanide π-bonding [20]. The presence of Ag^+ in the adduct should result in stronger Cr–CN σ- and π-bonds, which will have compensating effects on the CN bond strength. These factors may thus provide an explanation for the near equivalency of the CN stretching frequencies [20].

Finally, it is noteworthy that addition of excess NaI to Solution A or an aqueous solution of the solid adduct causes precipitation of AgI and regeneration of the original parent spectrum (maxima at 338 nm and 432 nm). This observation demonstrates the critical stabilizing role of Ag^+ for the isocyano isomer.

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