

ected in the sample of **2**. The absence of **1** was confirmed by the IR spectrum, which lacked the band at 2220 cm⁻¹ assigned as a CN absorption. Strong bands at 2380 and 1680 cm⁻¹ confirmed the B—C and C=O functionalities, the latter being absent in the spectrum of **1**.

Exposure of samples of **2** to the atmosphere for short periods produced no obvious changes in the solid. Upon being heated to its melting point, **2** decomposed rapidly, releasing copious

quantities of gas.

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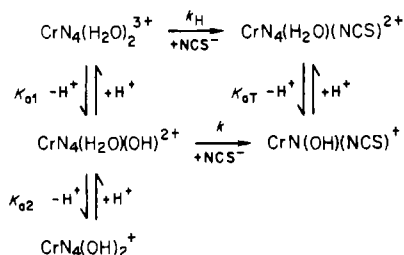
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Kinetic and Equilibrium Studies on Reactions of the Diaquachromium(III) Complex Containing a Saturated Tetradentate Tetraaza 15-Membered Macrocyclic Ligand

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Air oxidation of CrCl₂·4H₂O in an aqueous solution of the macrocyclic ligand [15]aneN₄ gives the diaquachromium(III) complex [Cr([15]aneN₄)(H₂O)₂]³⁺, which is eluted as a single band from a Sephadex SP C-25 column. Reactions studied can be represented by



A sample of the aqua thiocyanato complex was prepared from the diaqua complex (1.0 M NCS⁻, pH 6, 1 week) followed by Sephadex SP C-25 separation. From UV-visible spectrophotometric changes pK_{a1} = 2.9, pK_{a2} = 7.8, and pK_{aT} = 4.6 at 25 °C, I = 1.0 M (LiClO₄). Ion-pair formation constants for CrN₄(H₂O)₂³⁺ and CrN₄(H₂O)(OH)²⁺ with NCS⁻ are 1.2 and 0.7 M⁻¹, respectively. First-order rate constants, k_{obsd}, for the 1:1 substitution of NCS⁻ (0.10 M) are dependent on pH, with CrN₄(H₂O)(OH)²⁺ the much more reactive form. At pH > 7 rate constants k_{obsd} give a pK_{a2} (8.0) in agreement with that obtained from spectra. However, kinetic plots do not give good linearity (30–75% depending on pH), and over the range pH 1–7 there is a mismatch of dependences of k_{obsd} and absorbance (of CrN₄(H₂O)₂³⁺) on pH. These effects are attributed to the existence of configurational (NH) or cis isomers of the trans [15]aneN₄ macrocyclic complex.

Introduction

Cobalt(III) complexes of saturated tetraaza macrocyclic ligands from [12]aneN₄ through [16]aneN₄ have been studied, and a correlation of macrocyclic ring size with geometry of the isolated product reported. Thus, [12]aneN₄ gives cis products only, [13,14]aneN₄ give cis and trans isomers, and [15,16]aneN₄ give trans forms.^{1–4} For a series of Co[15]aneN₄X₂⁺ complexes, Busch and colleagues⁴ have obtained evidence in support of configurational isomers resulting from the different orientations of the NH group. With chromium(III) as the central metal, Swisher et al.⁵ have demonstrated a similar dependence on macrocyclic ring size, with only the cis isomer for [12]aneN₄, cis and trans for [14]aneN₄, and trans for [15]aneN₄. Existing evidence therefore favors the trans isomer

of the [15]aneN₄ complex as the dominant form. We thought it of interest to examine in some detail the solution chemistry of [Cr([15]aneN₄)(H₂O)₂]³⁺ with emphasis on kinetic and equilibration processes. Thiocyanate was selected as an appropriate complexing anion because it can be used over a wide pH range and has strong nucleophilic properties. Samuels and Espenson⁶ have previously reported studies on the reactivity of the [Cr([15]aneN₄)(H₂O)₂]²⁺ complex, which is a strong reducing agent (–0.58 V). Since the latter has potential use as an inner-sphere reductant for the identification of binding sites in electron-transfer reactions of metalloproteins,⁷ it was also of interest to explore substitution properties of the Cr(III) complex over a wide range of pH.

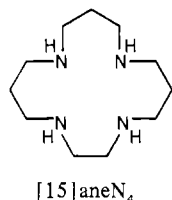
Experimental Section

Preparation of CrN₄(H₂O)₂³⁺. The diaqua(1,4,8,12-tetraazacyclo-pentadecane)chromium(III) complex, [Cr([15]aneN₄)(H₂O)₂]³⁺,

- (1) Collman, J. P.; Schneider, P. W. *Inorg. Chem.* 1966, 5, 1380.
- (2) Poon, C. K.; Tobe, M. L. *J. Chem. Soc. A* 1967, 2069.
- (3) Poon, C. K.; Tobe, M. L. *J. Chem. Soc. A* 1968, 1549.
- (4) Hung, Y.; Martin, L. Y.; Jackels, S. C.; Tait, A. M.; Busch, D. H. *J. Am. Chem. Soc.* 1977, 99, 4029.
- (5) Swisher, R. G.; Brown, G. A.; Smierciak, R. C.; Blinn, E. L.; *Inorg. Chem.* 1981, 20, 3947.

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- (7) Adzamlı, I. K.; Henderson, R. A.; Ong, H.; Sykes, A. G. *Biochem. Biophys. Res. Commun.* 1982, 105, 1582. Adzamlı, I. K.; Henderson, R. A.; Sinclair-Day, J. D.; Sykes, A. G. *Inorg. Chem.*, following paper in this issue.

here abbreviated to $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$, was obtained by 1:1 addition of the 15-membered macrocycle ligand [15]ane N_4



(Strem Chemicals) to $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ (0.05 M)⁸ in O_2 -free H_2O . Following air oxidation, the Cr(III) complex was exchanged onto a Sephadex SP C-25 column. On elution with 0.10 M HClO_4 a yellow-brown band, probably a 2+ chloro complex, was first obtained. The orange $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$ complex was then eluted with 0.10 M HClO_4 + 0.30 M LiClO_4 . The concentration of complex (3–6 mM) was determined from the known spectrum,⁶ showing peaks at 377 nm (ϵ 88 $\text{M}^{-1} \text{cm}^{-1}$) and 454 (ϵ 87). Solutions were stored at pH 1. Adjustment of the pH to the 5–6 range was carried out by addition of 1.0 M NaOH, from a 0.05-mL capacity Micromaster pipet (V. A. Howe Co.), to the stirred solution. Use of carbonate was avoided, because slow changes in spectra resulted; CO_2 -free water was used.

Preparation of $\text{CrN}_4(\text{H}_2\text{O})(\text{NCS})^{2+}$. A mixture of $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$ (1 mM) and sodium thiocyanate (1.0 M) was maintained at pH 6 for 1 week at $\sim 20^\circ\text{C}$. The product was then loaded onto a Sephadex SP C-25 column. After the product was washed with 0.01 M HClO_4 , two bands were formed, the first of which (pink-orange) was eluted with 0.10 M HClO_4 , corresponds to $\text{CrN}_4(\text{H}_2\text{O})(\text{NCS})^{2+}$, and shows absorption maxima at 306, 376, and 464 nm and a shoulder at ~ 500 nm. The second (orange) band eluted with 0.10 M HClO_4 + 0.30 M LiClO_4 was unreacted $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$. After 1–4 weeks, solutions (5 mM) gave orange-red orthorhombic crystals. Anal. Calcd for $\text{Cr}(\text{C}_{11}\text{H}_{26}\text{N}_4)(\text{H}_2\text{O})(\text{NCS})_3$: C, 36.7; H, 6.11; N 21.4. Found: C, 36.4; H, 5.9; N 21.5. Analyses are consistent with a formula $[\text{Cr}(\text{N}_4)(\text{H}_2\text{O})(\text{NCS})](\text{NCS})_2$. After the powdered crystals were dissolved in 0.10 M HClO_4 , the spectrum of $\text{CrN}_4(\text{H}_2\text{O})(\text{NCS})^{2+}$ was obtained (absorbance maxima/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)): 306 (3610), 376 (105), 464 (91). Solutions (0.5 mM) do not aquate or react further with NCS^- (0.25 M) at pH 1 over 5 days.

Other Reagents. Sodium thiocyanate (BDH, Analar) and lithium thiocyanate (BDH, reagent grade) were recrystallized from ethanol and dried to constant weight over silica gel. Aqueous solutions were standardized by the Volhard method.⁹ Lithium perchlorate prepared by addition of HClO_4 (Analar) to Li_2CO_3 (BDH, reagent grade) was recrystallized and standardized by exchanging H^+ for Li^+ using an Amberlite IR 120H resin column.

Buffers. Sodium acetate trihydrate with acetic acid (pK_a 4.7; pH range 3.4–6.8) (BDH, Analar), sodium cacodylate (pK_a 6.3; pH range 5.0–7.0) (BDH, Analar), morpholino ethanesulfonic acid, MES (pK_a 6.1; pH range 4.0–7.0) (Sigma), and tris(hydroxymethyl)aminomethane, Tris (pK_a 8.0; pH range 7.0–9.0) (Sigma) were used without further purification. Fresh solutions (0.20 M) were made as required, and 0.010 M buffer was used in run solutions. All pHs were measured with a Russell (CWR/322) narrow-stem combination-glass electrode with the KCl filling solution replaced by saturated NaCl to enable perchlorate solutions to be studied. The Radiometer PHM 62 pH meter was calibrated against standard solutions at $I = 1.0 \text{ M}$ (LiClO_4).

Kinetic Studies. Absorbance changes were monitored at 306 nm by using a Perkin-Elmer 554 UV-visible spectrophotometer, with an automatic cell changer for overnight runs. The NCS^- reactant was in large excess and the ionic strength adjusted to $I = 1.0 \text{ M}$ with LiClO_4 . No difference in behavior was apparent on substituting NaNCS for LiNCS , and the former was used in most runs. First-order rate constants, k_{obsd} , were obtained from the slope of plots of absorbance (A) changes (306 nm), $\ln(A_\infty - A_t)$, against time, where A_∞ was calculated from known spectra, due allowance being made for absorbance changes due to ion pairing (see Results). The Keszdy-Swinbourne method,¹⁰ which does not require knowledge of A_∞ , was also used. Although rate constants differed by as much as 25% for

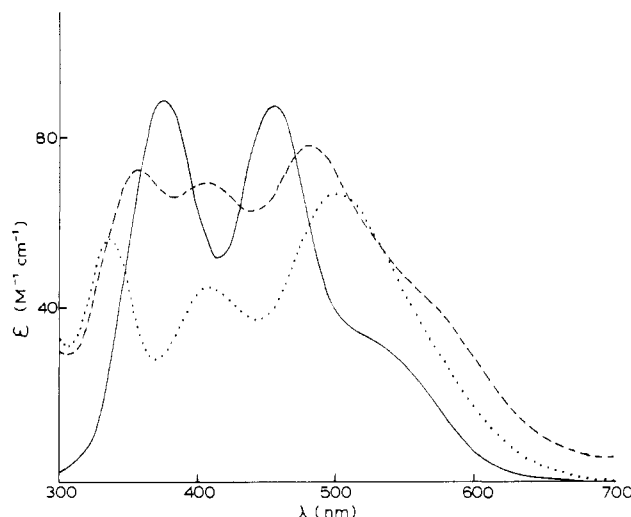


Figure 1. UV-visible spectra of [15]ane N_4 complexes of Cr(III): $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$ (—); $\text{CrN}_4(\text{H}_2\text{O})(\text{OH})^{2+}$ (---); $\text{CrN}_4(\text{OH})_2^+$ (···).

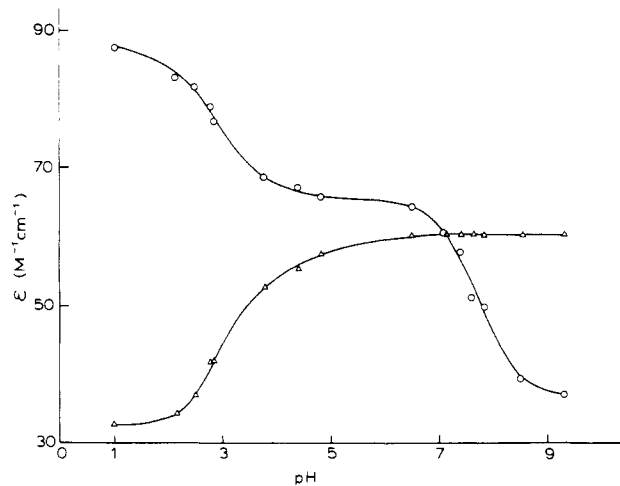


Figure 2. Effect of increasing pH on the absorbance of $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$ (25°C ; $I = 1.0 \text{ M}$ (LiClO_4)): 454 nm (O); 520 nm (Δ). Buffers are as indicated in Table II.

the two procedures, the general trend of values (e.g., in Figure 6) was the same. The linearity of plots was to 75% completion at $\text{pH} > 7.5$ but at other pHs was generally much less (as little as 25%). At pH 1 this was partly due to the decomposition of NCS^- over the extended run times (5 days), and the smell of H_2S was noted. However, this decomposition is not apparent at $\text{pH} > 3$, and the poor linearity of plots is attributed to the complexity of the reactions as will be discussed.

Considerable care was required to eliminate contributions to absorbance changes due to complexing of the buffer to the Cr complex. It was necessary to keep buffers at a low level of concentration (0.010 M) and make extensive comparisons with other buffers in overlap regions to ensure that there were no meaningful contributions. Since the $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$ complex was eluted with 0.10 M HClO_4 , it was necessary to neutralize to $\text{pH} > 6.0$ prior to addition of buffer. It was not possible to do this with carbonate, which coordinated to the Cr and gave spuriously high (factor $\times 2$) rate constants. Careful addition of 1 M NaOH with thorough stirring was found to be satisfactory. Complexation by phosphate was also significant, and this buffer was not used. At $\text{pH} > 7$, use of Tris was found to be satisfactory. Most difficulties were experienced in the pH 3–7 range. For example, in a run with 0.010 M acetate at pH 6.5 (no NCS^-), an acetate complex was formed that was separated on a Sephadex SP C-25 column. The $t_{1/2}$ of > 5 days, $k_{\text{obsd}} < 1.6 \times 10^{-6} \text{ s}^{-1}$, corresponds to a rate process 30 times slower than for the reaction with thiocyanate (0.10 M). From a series of studies, $[\text{NCS}^-] = 0.10 \text{ M}$, at pH 5.2 it was found that MES gave the greatest linearity of kinetic plots: MES (55%) $>$ cacodylate (40%) $>$ acetate (25%). With the precautions taken, we believe that effects directly attributed to buffers have been minimized ($< 10\%$ contribution to rate constants) so that these can be ignored.

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 (9) Vogel, A. I. "A Textbook of Quantitative Inorganic Analysis", 4th ed.; Longmans, Green and Co.: New York, 1978; p 340.
 (10) Keszdy, F. J.; Kaz, J.; Bruylants, A. *Bull. Soc. Chim. Belg.* **1958**, *67*, 687. Swinbourne, E. S. *J. Chem. Soc.* **1960**, 2371.

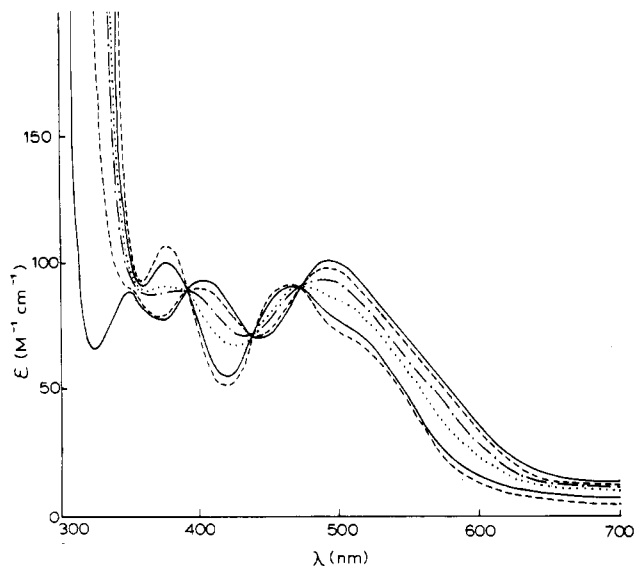


Figure 3. Effect of increasing pH on the UV-visible spectrum of the [15]aneN₄ complex CrN₄(NCS)(H₂O)₂²⁺. Successive spectra at pH 3.18 (---) (lower absorbance at 600 nm), 3.76, 4.75, 5.06, 5.81, and 7.81 (—) are shown (*I* = 1.0 M (LiClO₄)).

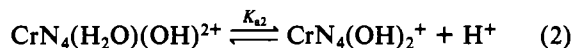
Moreover, as a check, runs in the crucial pH ~3.0 and ~5.5 regions were carried out with no buffer present.

Results

Determination of Acid Dissociation Constants. UV-visible spectra obtained for CrN₄(H₂O)₂³⁺ (pH <2.0), CrN₄(H₂O)(OH)₂²⁺ (pH 5.0–6.5), and CrN₄(OH)₂⁺ (pH >9.0) are shown in Figure 1. Spectra at pH 1.0, 2.8, 4.8, and 6.3 gave isosbestic points at 358, 399, 432 and 471 nm. At pH >7 isosbestic points at 341 and 520 nm were noted. All changes were reversible over 10-min periods necessary to carry out these manipulations. Changes in absorbances at 454 and 520 nm over the range pH 1–9 are shown in Figure 2. A p*K*_{a1} of 2.9 ± 0.1 is obtained for (1). When the pH is increased through



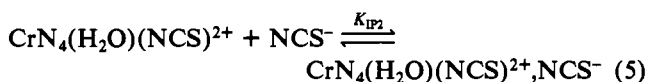
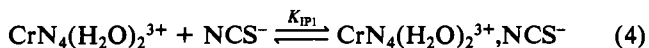
to 9.0, a further acid dissociation (2), giving a p*K*_{a2} of 7.8 ± 0.1, is obtained. No further changes were observed when the pH was maintained at 9.0 for several days.



Similar experiments were carried out for the CrN₄(H₂O)(NCS)₂²⁺ and CrN₄(OH)(NCS)₂⁺ forms (3), and spectra are as shown in Figure 3. Changes at 306 and 412 nm (Figure 4) gave a p*K*_a of 4.6 ± 0.1.



Determination of Ion-Pairing Constants. Rapid increases in absorbance, complete within mixing time, are observed in the visible range on addition of NCS⁻ to CrN₄(H₂O)₂³⁺ and CrN₄(H₂O)NCS₂²⁺. At pH 1, for example, with [NCS⁻] = 1.0 M, *I* = 1.0 M, absorbances are (in both cases) doubled in the 460-nm region. Assuming 1:1 ion-pair formation as in (4) and (5), the expression (6) can be derived, where ε_{obsd} and



$$\frac{1}{\epsilon_{\text{obsd}} - \epsilon_0} = \frac{1}{K_{IP}(\epsilon_{IP} - \epsilon_0)} \frac{1}{[\text{NCS}^-]} + \frac{1}{\epsilon_{IP} - \epsilon_0} \quad (6)$$

ε₀ (with no NCS⁻ present) are known. Linear plots of

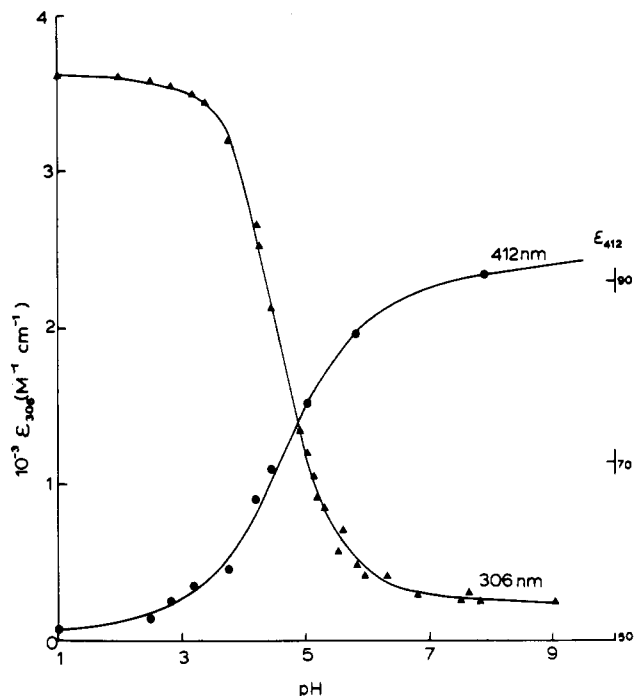


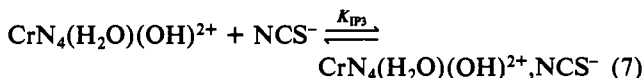
Figure 4. Effect of increasing pH on the absorbance of CrN₄(NCS)H₂O₂²⁺ (25 °C; *I* = 1.0 M (LiClO₄)): 306 nm (▲); 412 nm (●).

Table I. Dependence of Rate Constants, *k*_{obsd}, for the 1:1 Anation of the Cr(III) Complex Cr([15]aneN₄)(H₂O)₂³⁺ ^a

pH	[NCS ⁻], M	10 ⁵ <i>k</i> _{obsd} , s ⁻¹
4.0 (acetate)	0.05	0.33
	0.10	0.63
	0.15	0.86
	0.25	1.29
5.2 (cacodylate)	0.05	0.69
	0.10	1.39
	0.15	2.28
	0.20	2.78
5.3 (acetate)	0.05	0.98
	0.10	1.49
	0.15	2.23
	0.25	4.1
6.3 (acetate)	0.05	2.86
	0.10	4.3
	0.15	5.7
	0.20	6.2
7.65 (Tris)	0.25	7.2
	0.05	2.36
	0.10	3.60
	0.15	4.5
	0.25	5.7

^a Concentration (4–10) × 10⁻⁴ M of thiocyanate at 25 °C, *I* = 1.0 M (LiClO₄), λ = 306 nm; concentration of buffer 1.0 × 10⁻² M.

(ε_{obsd} - ε₀)⁻¹ against [NCS⁻]⁻¹ are obtained at pH 1 from which *K*_{IP}(25 °C) = 1.2 ± 0.1 M⁻¹ and ε_{IP} = 227 M⁻¹ cm⁻¹ for the diaqua complex (λ = 454 nm) and *K*_{IP}(25 °C) = 1.6 ± 0.1 M⁻¹ and ε_{IP} = 312 M⁻¹ cm⁻¹ for the aqua thiocyanato complex (λ = 464 nm). At pH 6.3 the much smaller absorbance changes are assigned to ion-pair formation as in (7), and *K*_{IP3} = 0.7 ± 0.5 M⁻¹ and ε_{IP} = 118 M⁻¹ cm⁻¹ (λ = 481 nm). No change in absorbance was observed on addition of NCS⁻ to solutions of CrN₄(OH)₂⁺ and CrN₄(OH)(NCS)₂⁺.



Kinetic Studies. The dependence of rate constants, *k*_{obsd}, on NCS⁻ was investigated. Rate constants (Table I) obtained at pH 5.2 (cacodylate) and pH 5.3 (acetate) are in satisfactory

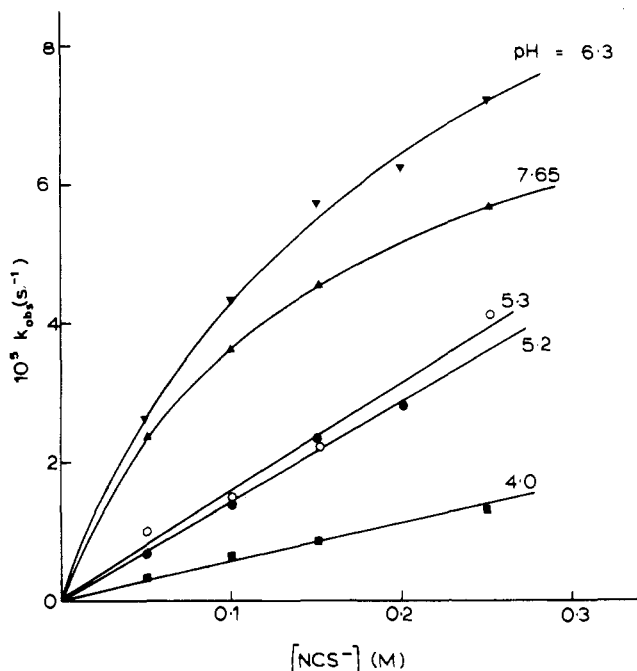


Figure 5. Dependence of rate constants k_{obsd} (25 °C) for the 1:1 reaction of the [15]aneN₄ complex $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$, at low pH, on $[\text{NCS}^-]$, at different pHs, $I = 1.0 \text{ M}$ (LiClO_4).

agreement, showing no dependence on buffer (0.010 M) (Figure 5). At pH 4.0 and 5.2 (and 5.3) linear dependences on $[\text{NCS}^-]$ are observed, and second-order rate constants ($\text{M}^{-1} \text{ s}^{-1}$) can be obtained from the slopes: $(5.0 \pm 0.1) \times 10^{-5}$ (pH 4.0); $(1.43 \pm 0.36) \times 10^{-4}$ (pH 5.2); $(1.60 \pm 0.22) \times 10^{-4}$ (pH 5.3). Similar series of runs at pH 6.3 (acetate) and pH 7.95 (Tris) give nonlinear dependences on $[\text{NCS}^-]$ (Figure 5). A good fit is obtained to the dependence (8), which can be de-

$$k_{\text{obsd}} = \frac{k_1 k_2 [\text{NCS}^-]}{k_{-1} + k_2 [\text{NCS}^-]} \quad (8)$$

rived from the sequence (9)–(10) by applying the station-



ary-state approximation for C^* , where C represents the dominant form of the complex and C^* a more reactive form. At pH 6.3 rate constants (as defined) are $k_1 = (1.17 \pm 0.08) \times 10^{-4} \text{ s}^{-1}$, $k_2/k_{-1} = 6.1 \pm 0.8 \text{ M}^{-1}$, and at pH 7.65 $k_1 = (8.8 \pm 0.02) \times 10^{-5} \text{ s}^{-1}$ and $k_2/k_{-1} = 7.1 \pm 0.3 \text{ M}^{-1}$.

Rate constants, k_{obsd} , obtained over the range pH 1–9 at $[\text{NCS}^-] = 0.10 \text{ M}$ are summarized in Table II. From a fit of data at pH 1–7 to (11), rate constants at pH ~ 1 ($k_{\text{H}} =$

$$k_{\text{obsd}} = \frac{k + k_{\text{H}} K_{\text{a1}} [\text{H}^+]}{1 + K_{\text{a1}} [\text{H}^+]} \quad (11)$$

$4 \times 10^{-7} \text{ s}^{-1}$) are $\sim 10^2$ times smaller than at pH 7.0 ($k = 4.5 \times 10^{-5} \text{ s}^{-1}$). The "p K_{a1} " of 5.3 ± 0.2 obtained does not reproduce that from spectra, p $K_{\text{a1}} = 2.9$. Above pH 7 the profile (Figure 6) gives a p K_{a2} of 8.0 ± 0.2 , which is in satisfactory agreement with the p K_{a2} of 7.8 from spectra and a rate constant $(0.32 \pm 0.48) \times 10^{-5} \text{ s}^{-1}$ (i.e., $\rightarrow 0$) at high pH. Additional runs with no buffer added at pH 3.16 and 5.56, $[\text{NCS}^-] = 0.10 \text{ M}$, gave rate constants 0.76×10^{-5} and $3.6 \times 10^{-5} \text{ s}^{-1}$, respectively, from initial slopes, which are in satisfactory agreement ($\sim 10\%$ higher) than values illustrated in Figure 6.

Table II. Variation of Rate Constants, k_{obsd} , with pH for the 1:1 Thiocyanate (0.10 M) Anation of the Cr(III) Complex $\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})_2^{3+}$ ^a

pH	$10^5 k_{\text{obsd}}, \text{ s}^{-1}$	pH	$10^5 k_{\text{obsd}}, \text{ s}^{-1}$
1.00	0.06	5.52 (acetate)	2.82
1.99	0.12	5.92 (acetate)	3.75
3.38 (acetate)	0.68	6.80 (acetate)	4.72
4.00 (acetate)	0.57 ^b	7.53 (Tris)	4.40
4.26 (MES)	1.08	7.81 (Tris)	2.73
4.26 (acetate)	1.05	8.05 (Tris)	2.18
4.92 (acetate)	1.50	8.58 (Tris)	0.83
5.16 (MES)	1.96	9.05 (Tris)	0.17
5.20 (cacodylate)	1.43 ^b		
5.30 (acetate)	1.60 ^b		

^a Concentration $(4\text{--}10) \times 10^{-4} \text{ M}$; at 25 °C; $I = 1.0 \text{ M}$ (LiClO_4); $\lambda = 306 \text{ nm}$; concentration of buffer $1.0 \times 10^{-2} \text{ M}$. ^b Four runs were carried out at each of these pH values. Rate constants listed are those obtained from a least-squares treatment.

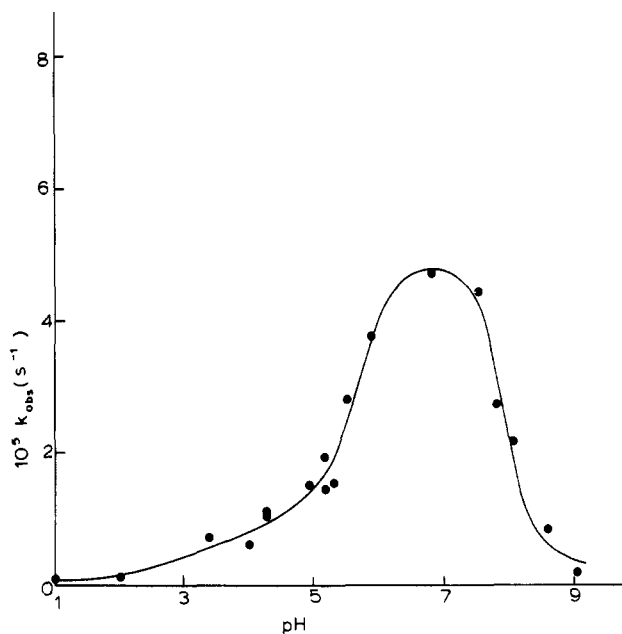


Figure 6. Variation of k_{obsd} (25 °C) with pH for the 1:1 reaction of the [15]aneN₄ complex $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$, with thiocyanate at low pH, $I = 1.0 \text{ M}$ (LiClO_4).

Discussion

It is assumed that the [15]aneN₄ ligand gives octahedral Cr(III) complexes and, from earlier studies on the effect of varying the N₄ macrocycle ring size,^{4,5} that trans complexes are dominant. Consistent with these observations, Samuels and Espenson⁶ have reported a trans structure from an X-ray investigation on the complex, $[\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})(\text{Cl})] \cdot 2\text{H}_2\text{O}$. A crystalline sample of $[\text{Cr}([\text{15}] \text{ane})(\text{H}_2\text{O})(\text{NCS})](\text{NCS})_2$ has been obtained in the present study, and this has now been confirmed as the trans-aqua-thiocyanato complex, in which the N–H bonds all point toward the coordinated thiocyanate. The effect of pH 1–9 on the UV–visible spectrum of $\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})_2^{3+}$ has resulted in the ready identification of three forms, here written as $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$, $\text{CrN}_4(\text{H}_2\text{O})(\text{OH})^{2+}$, and $\text{CrN}_4(\text{OH})_2^+$. The existence of configurational (NH) isomers could give rise to further detail. The sort of influence configurational effects can have is illustrated by the observation that the tetramethyl-substituted [14]aneN₄ complex of Ni(II) is 5- and not 6-coordinate.¹¹ A further possibility is that cis isomers may

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participate in some way and provide a facile rate for complexation.

The acid dissociation pK_a values obtained from spectrophotometric changes for $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$ (2.9), $\text{CrN}_4(\text{H}_2\text{O})(\text{OH})^{2+}$ (7.8) and $\text{CrN}_4(\text{H}_2\text{O})(\text{NCS})^{2+}$ (4.6) are acceptable in terms of known Cr(III) chemistry. However, it should be noted that the pK_{a1} value of 2.9 for $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$ is small compared to values 5.2, 4.1, 4.8, and 6.0 quoted for the complexes $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$,¹⁴ *cis*- and *trans*- $\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$,¹⁵ and $\text{Cr}(\text{en})(\text{NCS})_2(\text{H}_2\text{O})_2^+$,¹⁶ respectively, and that there is an unusually big difference in pK_{a2} and pK_{aT} (4.6) for the 2+-charged complexes. The agreement of pK_{a2} determined kinetically (8.0) and spectrophotometrically (7.8) for $\text{CrN}_4(\text{H}_2\text{O})(\text{OH})^{2+}$ is encouraging. Information from $[\text{H}^+]$ dependences as in (11), and relating to Figure 6, indicate that $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$ reacts 10^2 times more slowly than $\text{CrN}_4(\text{H}_2\text{O})(\text{OH})^{2+}$ and that $\text{CrN}_4(\text{OH})_2^+$ makes little or no contribution. The latter is consistent with it being difficult to replace a negative ligand (OH^-) by another negative ligand (NCS^-).¹⁷ We do not however understand fully the behavior of $\text{CrN}_4(\text{H}_2\text{O})(\text{OH})^{2+}$ and its reactivity with NCS^- . Had there been a similar correspondence of rate constants with spectrophotometric observations to give a pK_{a1} of 2.9 then the rate constant profile (Figure 6) would have looked somewhat different, with no increase in k_{obsd} over the range pH 5–7. Even without buffers (which have presented some difficulties), it has been demonstrated that k_{obsd} from the initial absorbance changes, with the initial pH adjusted to 5.5, is far greater than the values of k_{obsd} determined at pH 3–4. Since buffer effects have been minimized in all the runs reported, it is necessary

to account for the variation in k_{obsd} at pHs in the range 5–7.

The view that configurational and/or *cis* isomers are relevant is supported by the observation that a nonlinear dependence on NCS^- is observed at pH 6.3 and 7.65 (but not at pH <5.3). There are a number of possible explanations for kinetic behavior of this kind. The possibility that ion-pair formation is relevant seems unlikely since the value $K_{\text{IP}} = 7.1 \text{ M}^{-1}$ required by the kinetics is not in agreement with the spectrophotometrically determined value of 0.7 M^{-1} (which is perfectly reasonable in terms of electrostatic models for a 2+,1- interaction).¹⁸ An interpretation in terms of (9)–(10), where C^* represents a more reactive form resulting from an isomerization process ($k_1 = 1.17 \times 10^{-4} \text{ s}^{-1}$), seems more likely. A further possibility, that C^* is a 5-coordinate complex, seems unlikely in terms of known Cr(III) chemistry.

The orientation of N–H groups or participation of *cis* geometric isomers is expected to have an effect on rate constants, since metal-to-ligand bond distances as well as pK_a values will be affected. Of further interest is the observation that at pHs 1.0–3.0, $\text{CrN}_4(\text{H}_2\text{O})(\text{NCS})^{2+}$ does not appear to react with a second thiocyanate. Indeed, over 1 week, the only changes observed are the formation of crystals of $[\text{Cr}(\text{N}_4)(\text{H}_2\text{O})(\text{NCS})](\text{NCS})_2$; in addition we did not observe aequation of thiocyanate in $\text{CrN}_4(\text{NCS})\text{H}_2\text{O}^{2+}$ and $\text{CrN}_4(\text{NCS})\text{OH}^+$.

Details of the crystal structure will be published elsewhere.¹⁹

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Registry No. $\text{CrN}_4(\text{H}_2\text{O})_2^{3+}$, 70832-95-0; $\text{CrN}_4(\text{H}_2\text{O})(\text{OH})^{2+}$, 91208-72-9; $\text{CrN}_4(\text{H}_2\text{O})(\text{NCS})^{2+}$, 91202-09-4; NCS^- , 302-04-5.

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Kinetic Studies on Reactions of Iron–Sulfur Proteins. 8. Inner-Sphere Reductions of Parsley [2Fe-2S] and *Clostridium pasteurianum* 2[4Fe-4S] Ferredoxins with a Chromium(II)–Macrocycle Complex

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Stopped-flow kinetic studies have been carried out on the reduction of parsley [2Fe-2S] and *Clostridium pasteurianum* 2[4Fe-4S] ferredoxins with the 1,4,8,12-tetraazacyclopentadecane complex of Cr(II), $\text{Cr}(\text{15-aneN}_4)^{2+}$, $I = 0.10 \text{ M}$ (NaCl). The [2Fe-2S] protein is one-electron active, and the two one-electron-active clusters in the 2[4Fe-4S] protein react in an equivalent (statistical) manner. Product analyses have demonstrated that the Cr(III) is attached to the protein and that the reactions fall within the definition of inner-sphere electron transfer. Both reactions exhibit pH effects in the 7.0–8.0 region, the proteins becoming more reactive on protonation. The more detailed study with 2[4Fe-4S] gives a pK_a of 7.46 for the protein in its oxidized form, in accordance with a previously reported value of 7.4 from potentiometric studies. Rate constants (25 °C) and activation parameters at pH 8.0 for 2[Fe-2S] are $k = 1.03 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H^\ddagger = 4.7 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -29.4 \text{ cal K}^{-1} \text{ mol}^{-1}$ and for 2[4Fe-4S] are $k = 6.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H^\ddagger = 3.2 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -31.0 \text{ cal K}^{-1} \text{ mol}^{-1}$. When the Cr(III) is bound to the reduced protein, it has little or no effect on rate constants for the $[\text{Co}(\text{NH}_3)_6]^{3+}$ oxidation. For both proteins, addition of redox-inactive $[\text{Cr}(\text{en})_3]^{3+}$ does not give competitive inhibition with $\text{Cr}(\text{15-aneN}_4)^{2+}$ as reductant. Instead, an acceleration is observed with the [2Fe-2S] protein and no effect with the 2[4Fe-4S] protein. The implications of these results with regard to binding site(s) on the protein are considered. Electrostatics do not appear to have the same controlling influence in reactions of $\text{Cr}(\text{15-aneN}_4)^{2+}$ with the [2Fe-2S] and 2[4Fe-4S] proteins as in previous studies.

Introduction

Inorganic complexes are used extensively as probes for assessing the reactivity of electron-transport metalloproteins. Of interest, but at present little explored, is the possibility that

inner-sphere electron transfer can be demonstrated for reactions of this kind. If the inorganic product is substitution inert so that it remains attached to the protein, this can also help define more precisely the lead-in group (or groups) for electron