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Equilibrium and Kinetic Studies of the Reactions of *N*-Substituted (Ethylenediamine-*N,N',N'*-triacetato)aquachromium(III) with Several Anions

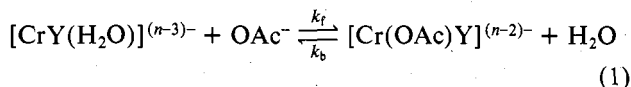
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The reactions $[\text{CrY}(\text{H}_2\text{O})]^{(n-3)-} + \text{X}^- \rightleftharpoons [\text{CrXY}]^{(n-2)-} + \text{H}_2\text{O}$ were investigated at 25.0 °C and $I = 1.0$ (NaClO_4); Y represents ethylenediamine-*N,N,N',N'*-tetraacetate (edta), *N*-(hydroxyethyl)ethylenediamine-*N,N',N'*-triacetate (hedtra), ethylenediamine-*N,N',N'*-triacetate (edtra), and *N*-methylethylenediamine-*N,N',N'*-triacetate (medtra); n is 4 for edta and 3 for hedtra, edtra, and medtra. The equilibrium constants of the reactions were $13.6 \pm 1.2 \text{ M}^{-1}$ ($\text{X}^- = \text{NCS}^-$), $1.9 \pm 0.2 \text{ M}^{-1}$ ($\text{X}^- = \text{ONO}^-$), and $110 \pm 15 \text{ M}^{-1}$ ($\text{X}^- = \text{N}_3^-$) for $[\text{CrX}(\text{hedtra})]^-$, $12.3 \pm 1.0 \text{ M}^{-1}$ for $[\text{Cr}(\text{NCS})(\text{edtra})]^-$, $2.1 \pm 0.3 \text{ M}^{-1}$ for $[\text{Cr}(\text{ONO})(\text{medtra})]^-$, $21.8 \pm 0.4 \text{ M}^{-1}$ for $[\text{Cr}(\text{NCS})(\text{hedtra})]^-$, and $0.57 \pm 0.07 \text{ M}^{-1}$ for $[\text{Cr}(\text{NCS})(\text{edta})]^{2-}$. The observed pseudo-first-order rate constants of the reactions (k_0) were found to be expressed as $k_0 = k_f[\text{X}^-] + k_b$, except for the reactions of $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ with NCS^- and of $[\text{Cr}(\text{medtra})(\text{H}_2\text{O})]^-$ with ONO^- . The rate constants of the forward reaction ($k_f, \text{M}^{-1} \text{ s}^{-1}$) and of the backward reaction (k_b, s^{-1}) were $k_f = 3.32 \pm 0.11$ and $k_b = 0.244 \pm 0.019$ for the reaction with $\text{X}^- = \text{NCS}^-$ and Y = hedtra, $k_f = (2.95 \pm 0.10) \times 10^{-2}$ and $k_b = (2.40 \pm 0.17) \times 10^{-3}$ for the reaction with $\text{X}^- = \text{NCS}^-$ and Y = edtra, $k_f = 12 \pm 2$ and $k_b = 6.24 \pm 0.32$ for the reaction with $\text{X}^- = \text{ONO}^-$ and Y = hedtra, and $k_f = 19.8 \pm 1.2$ and $k_b = 0.189 \pm 0.012$ for the reaction with $\text{X}^- = \text{N}_3^-$ and Y = hedtra, respectively. The k_0 values for the reaction of $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ with NCS^- could be expressed as $k_0 = \{K^{\text{H}}k_1 + k_2[\text{H}^+]\}[\text{NCS}^-]/\{K^{\text{H}} + [\text{H}^+]\} + \{K^{\text{H}}_{\text{Cr}(\text{NCS})\text{Y}}k_{-1} + k_{-2}[\text{H}^+]\}/\{K^{\text{H}}_{\text{Cr}(\text{NCS})\text{Y}} + [\text{H}^+]\}$, where $k_1 = 13.7 \pm 0.6 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} = 26.8 \pm 1.9 \text{ s}^{-1}$, $k_2 = 0.773 \pm 0.042 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-2} = (3.17 \pm 0.33) \times 10^{-2} \text{ s}^{-1}$, $K^{\text{H}} = [\text{H}^+][\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-/[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})] = (1.54 \pm 0.16) \times 10^{-2} \text{ M}$, and $K^{\text{H}}_{\text{Cr}(\text{NCS})\text{Y}} = [\text{H}^+][\text{Cr}(\text{NCS})(\text{edta})]^{2-}/[\text{Cr}(\text{NCS})(\text{hedtra})]^- = (4.08 \pm 0.55) \times 10^{-4} \text{ M}$. The k_0 values (s^{-1}) for the reaction of $[\text{Cr}(\text{medtra})(\text{H}_2\text{O})]^-$ with ONO^- were found to conform to the equation $k_0 = \{(1.7 \pm 0.9) \times 10^{-3} + (0.856 \pm 0.065)[\text{HNO}_2]\}[\text{ONO}^-] + (8 \pm 3) \times 10^{-4} + (0.41 \pm 0.02)[\text{HNO}_2]$. The mechanisms of the reactions are presented.

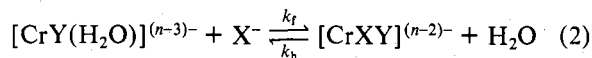
Introduction

In the previous work, $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ and $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]^-$ were found to undergo unexpectedly rapid substitution reactions with acetate (eq 1),^{1,2} where Y^{n-} denotes

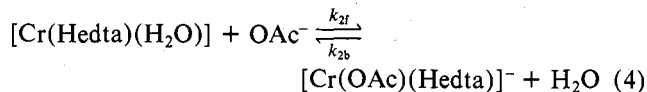
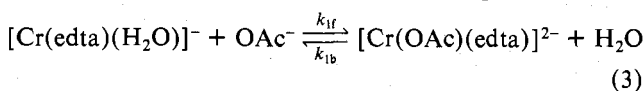


aminopolycarboxylate and n the number of negative charges on Y. The unusual lability has been interpreted by postulating that the transient coordination of the uncoordinated *N*-carboxymethyl or *N*-hydroxyethyl group existing in the complex ion assists the ligand substitution at the sixth coordination position of the chromium(III) center.² Quite recently, Matsubara and Creutz reported that $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ shows unusually rapid substitution reactions.³ Yoshino and his colleagues also made a similar observation on $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$.⁴ Matsubara and Creutz pointed out that labilization of metal-water bonds in EDTA complexes may be a rather general phenomenon.³ In connection with this, it was found in this laboratory that $[\text{Fe}(\text{hedtra})(\text{H}_2\text{O})]$ and $[\text{Fe}(\text{nta})(\text{H}_2\text{O})_2]$ react very rapidly with thiocyanate ions to give $[\text{Fe}(\text{NCS})(\text{hedtra})]^-$ and $[\text{Fe}(\text{NCS})(\text{nta})(\text{H}_2\text{O})]^-$, respectively (the rate constants were $>10^7 \text{ M}^{-1} \text{ s}^{-1}$).⁵

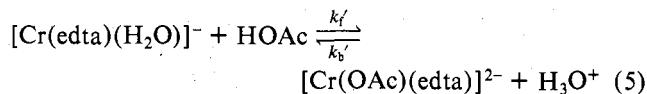
As part of our continuing interest in the rapid substitution reactions of the chromium(III) complexes, the equilibrium and kinetic studies of reaction 2 are carried out by changing the



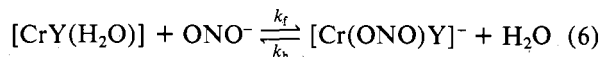
nature of the entering ligand X^- . As reported in the previous paper,² the rates of the reactions of $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]^-$, $[\text{Cr}(\text{edtra})(\text{H}_2\text{O})]$, and $[\text{Cr}(\text{medtra})(\text{H}_2\text{O})]$ with acetate were independent of the hydrogen ion concentrations. On the other hand, the pseudo-first-order rate constants of the reaction of $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ with acetate increased linearly with the increase of the hydrogen ion concentrations. This acid dependency of the rates was assigned tentatively to the occurrence of the two simultaneous reactions in eq 3 and 4. The



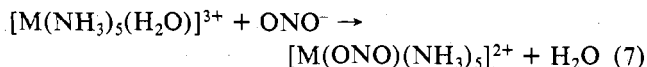
k_{1f} and k_{2f} values were determined to be $3.3 \text{ M}^{-1} \text{ s}^{-1}$ and $3.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, respectively. As proposed later by Sulfab et al.,⁶ reaction 4 may be formulated as reaction 5 which is the



complex-forming reaction between $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ and the weak acid HOAc. The k'_f value could be estimated to be $5.5 \text{ M}^{-1} \text{ s}^{-1}$ from the k_{2f} value and pK value of HOAc. Reactions 4 and 5 cannot be differentiated by the kinetic studies and constitute a so-called proton ambiguity in the mechanism. In order to avoid the problem of "proton ambiguity" and to know the reactivity of $[\text{Cr}(\text{Hedtra})(\text{H}_2\text{O})]$, we attempt a study at various hydrogen ion concentrations for the reaction of $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ with thiocyanate which is one of the strong-acid anions. In addition to this, the reactions of $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]$ and $[\text{Cr}(\text{edtra})(\text{H}_2\text{O})]$ with thiocyanate are examined. Furthermore, the reactions of $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]$ and $[\text{Cr}(\text{medtra})(\text{H}_2\text{O})]$ with nitrite (eq 6) are in-



vestigated in this work. It is known that the kinetics of the nitrosation reactions of $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ (eq 7) show the rate law given by eq 8, where M represents cobalt(III),



$$\text{rate} = k[\text{aqua complex}][\text{HNO}_2][\text{ONO}^-] \quad (8)$$

rhodium(III), iridium(III), and chromium(III).⁷ The interpretation given for eq 8 is that N_2O_3 is the active agent which reacts with $[\text{M}(\text{OH})(\text{NH}_3)_5]^{2+}$ without M-O bond cleavage. It was previously considered that reaction 1 proceeded through the cleavage of the chromium(III)-oxygen bond.² If this holds for reaction 6, the rate law of reaction 6 would not conform to eq 8 but would conform to eq 9. The

$$\text{rate} = (k_f[\text{ONO}^-] + k_b)[\text{CrY}(\text{H}_2\text{O})] \quad (9)$$

Table IV. Rate Constants of the Anation Reactions (k_f , $M^{-1} s^{-1}$) of $[Cr(H_2O)_6]^{3+}$, $[Cr(NH_3)_5(H_2O)]^{3+}$, and $[CrY(H_2O)]^{(n-3)-}$ Complexes at 25 °C and $I = 1 M$

complex	X ⁻					
	N ₃ ⁻	OAc ⁻	ONO ⁻	NCS ⁻	Cl ⁻	Br ⁻
$[Cr(H_2O)_6]^{3+}$				1.8×10^{-6} ^a	3.1×10^{-8} ^b	8.6×10^{-9} ^c
$[Cr(NH_3)_5(H_2O)]^{3+}$	9.0×10^{-6} ^d	1.0×10^{-5} ^d		1.5×10^{-3} ^{d,e}	8.4×10^{-5} ^{d,e}	7.3×10^{-5} ^f
$[Cr(edtra)(H_2O)]$		$(2.88 \pm 0.14) \times 10^{-2}$ ^g		$(2.95 \pm 0.10) \times 10^{-2}$ ^h		
$[Cr(medtra)(H_2O)]$		$(7.31 \pm 0.35) \times 10^{-4}$ ^g	$(1.7 \pm 0.9) \times 10^{-3}$ ^h			
$[Cr(hedtra)(H_2O)]$	19.8 ± 1.2 ^{h,i}	7.60 ± 0.61 ^g	12 ± 2 ^h	3.32 ± 0.11 ^h	<0.1 ^j	<0.2 ^j
$[Cr(aedtra)(H_2O)]$		4.5 ± 0.7 ^k				
$[Cr(Hedta)(H_2O)]$				0.773 ± 0.042 ^h		
$[Cr(edta)(H_2O)]^-$	98 ± 5 ^l	3.3 ± 0.4 ^g		13.7 ± 0.6 ^h		

^a C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955). ^b T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965); C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967). ^c F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964); J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960). The original references should be consulted for the details of the values of I . ^d D. A. House, *Coord. Chem. Rev.*, **23**, 223 (1977). ^e $I = 0.11 M$. ^f T. Ramasami and A. G. Sykes, *Inorg. Chem.*, **15**, 2885 (1976). ^g Reference 2. ^h This work. ⁱ $\Delta H^\ddagger = 48.1 \pm 1.2$ kJ mol⁻¹, $\Delta S^\ddagger = -57 \pm 4$ J mol⁻¹ K⁻¹. ^j Reference 9. ^k Reference 10. ^l Reference 6.

equilibrium and kinetic studies of the reaction of $[Cr(hedtra)(H_2O)]$ with azide are also reported in this work. The results will be compared with those reported in the previous papers.^{2,6,8-10}

Experimental Section

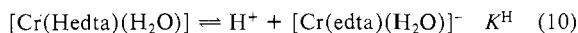
Materials. $[Cr(edtra)(H_2O)] \cdot H_2O$,² $[Cr(medtra)(H_2O)] \cdot 1.5H_2O$,² $[Cr(hedtra)(H_2O)] \cdot 1.5H_2O$,^{2,10} and $[Cr(Hedta)(H_2O)]$ ^{11,12} were prepared according to the literature. Sodium thiocyanate, sodium azide, and sodium nitrite were recrystallized from water.

Equilibrium and Kinetic Studies. The measurements were carried out at an ionic strength (I) of 1.0 M (NaClO₄) and at 25.0 ± 0.1 °C unless otherwise stated. The equilibrium studies were made with a Union-Giken SM-401 spectrophotometer. The equilibrium constants of eq 2 were determined as reported in the previous paper.²

The kinetic measurements were made under the pseudo-first-order condition; concentrations of X⁻ greatly exceeded those of $[CrY(H_2O)]^{(n-3)-}$. The rapid reactions were followed with a Union-Giken RA-401 stopped-flow spectrophotometer and the slow reactions with a Union-Giken SM-401 recording spectrophotometer by the conventional syringe technique. The plots of $\ln |A_t - A_\infty|$ vs. time were linear for at least 3 half-lives except for the reaction of $[Cr(edtra)(H_2O)]$ with thiocyanate ions, in which the plots were linear for 2 half-lives, where A_t and A_∞ represent the absorbancies at time t and infinity, respectively.

Adjustment of pH and the Determination of the Acid Dissociation Constant of $[Cr(Hedta)(H_2O)]$. The pH values were adjusted with HN₃-NaN₃ buffer solutions for the reactions containing azide ions as X⁻, with HNO₂-NaNO₂ buffer solutions for the reactions containing nitrite ions, and with perchloric acid for the other reactions. The measurements of pH were made with a Toa HM-20B digital pH meter, which was calibrated against standard perchloric acid solutions at $I = 1.0 M$ (NaClO₄).

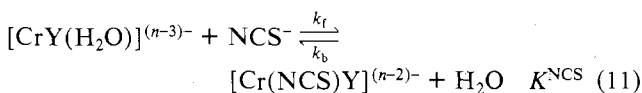
The acid dissociation constant of reaction 10 has been determined



at $I = 0.10$ and $0.15 M$.^{2,13} In this work, the K^H value at 25.0 °C and $I = 1.0 M$ (NaClO₄) was determined spectrophotometrically to be $(1.54 \pm 0.16) \times 10^{-2} M$.

Results

Reactions of $[Cr(hedtra)(H_2O)]$ and $[Cr(edtra)(H_2O)]$ with Thiocyanate Ions. The equilibrium constant of reaction 11,



K^{NCS} , was determined by using eq 12, where ϵ_1 and ϵ_2 are

$$\frac{1}{\bar{\epsilon} - \epsilon_1} = \frac{1}{\epsilon_2 - \epsilon_1} + \frac{1}{(\epsilon_2 - \epsilon_1)K^{NCS}[NCS^-]} \quad (12)$$

the molar absorptivities of $[CrY(H_2O)]^{(n-3)-}$ and $[Cr(NCS)Y]^{(n-2)-}$, respectively, and $\bar{\epsilon}$ denotes the apparent

molar absorptivity of the solution. When the values of the left-hand side of eq 12 were plotted against the reciprocals of thiocyanate concentrations, linear plots were obtained. The K^{NCS} values were found to be independent of the hydrogen ion concentrations within the acidity range studied. The determined values are shown in Table I.¹⁴

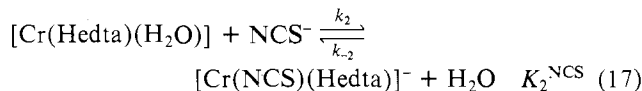
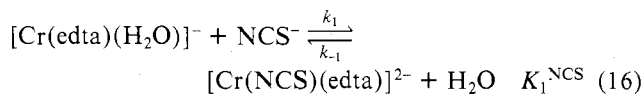
The observed pseudo-first-order rate constants of reaction 11, k_o , were found to be independent of the hydrogen ion concentrations (Tables II and III)¹⁴ and obeyed eq 13. The k_f and k_b values were calculated from the relations given in eq 14 and 15, respectively. The resolved rate constant values, k_f and k_b , are given in Tables IV and V, respectively.

$$k_o = k_f[NCS^-] + k_b \quad (13)$$

$$k_f = k_o K^{NCS} / (K^{NCS}[NCS^-] + 1) \quad (14)$$

$$k_b = k_o / (K^{NCS}[NCS^-] + 1) \quad (15)$$

Reaction of $[Cr(edta)(H_2O)]^-$ with Thiocyanate Ions. When eq 12 was applied to the system of the title reaction, linear plots were obtained. However, the observed equilibrium constants K_{obs}^{NCS} were found to increase with increase of the hydrogen ion concentrations as shown in Table VI. This acid dependency could be reasonably explained by the occurrence of reactions 16 and 17. Taking eq 16 and 17 into consid-



eration, the conditional equilibrium constant K_{obs}^{NCS} can be expressed as eq 18. The K_1^{NCS} and K_2^{NCS} values which were calculated from the relation of eq 18 are given in Table VII. The equilibrium constant of reaction 19 can be calculated by eq 20 to give $K_{Cr(NCS)Y}^H = (4.08 \pm 0.55) \times 10^{-4} M$.

$$K_{obs}^{NCS} = \frac{K_1^{NCS} K^H + K_2^{NCS} [H^+]}{K^H + [H^+]} \quad (18)$$



$$K_{Cr(NCS)Y}^H = (K_1^{NCS} / K_2^{NCS}) K^H \quad (20)$$

The pseudo-first-order rate constant, k_o , increased with the increase of the thiocyanate concentrations and decreased with the increase of hydrogen ion concentrations as shown in Table

Table V. Rate Constants of the Aquation Reactions (k_b , s^{-1}) of $[\text{CrX}(\text{H}_2\text{O})_5]^{2+}$, $[\text{CrX}(\text{NH}_3)_5]^{2+}$, and $[\text{CrXY}]^{(n-2)-}$ Complexes at 25 °C and $I = 1 \text{ M}$

complex	X^-					
	N_3^-	OAc^-	ONO^-	NCS^-	Cl^-	Br^-
$[\text{CrX}(\text{H}_2\text{O})_5]^{2+}$	$4.1 \times 10^{-8} \text{ }^a$	$4.1 \times 10^{-7} \text{ }^b$		$9.2 \times 10^{-9} \text{ }^c$	$2.8 \times 10^{-7} \text{ }^a$	$4.3 \times 10^{-6} \text{ }^a$
$[\text{CrX}(\text{NH}_3)_5]^{2+}$	$3.6 \times 10^{-8} \text{ }^{a,d}$			$8.7 \times 10^{-8} \text{ }^{a,e}$	$7.4 \times 10^{-6} \text{ }^a$	$8.1 \times 10^{-5} \text{ }^f$
$[\text{CrX}(\text{edtra})]^-$		$(1.63 \pm 0.13) \times 10^{-3} \text{ }^g$		$(2.40 \pm 0.17) \times 10^{-3} \text{ }^h$		
$[\text{CrX}(\text{medtra})]^-$		$(5.89 \pm 0.28) \times 10^{-5} \text{ }^g$	$(8 \pm 3) \times 10^{-4} \text{ }^h$			
$[\text{CrX}(\text{hedtra})]^-$	$0.189 \pm 0.012 \text{ }^{h,i}$	$0.450 \pm 0.030 \text{ }^g$	$6.24 \pm 0.32 \text{ }^h$	$0.244 \pm 0.019 \text{ }^h$	$0.697 \pm 0.044 \text{ }^{j,k}$	2.0 ^j
$[\text{CrX}(\text{aedtra})]^-$		$0.38 \pm 0.06 \text{ }^i$				
$[\text{CrX}(\text{Hedta})]^-$				$(3.17 \pm 0.33) \times 10^{-2} \text{ }^h$		
$[\text{CrX}(\text{edta})]^{2-}$	13.4 ^m	$5.4 \pm 0.6 \text{ }^g$		$26.8 \pm 1.9 \text{ }^h$		

^a J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, 11, 47 (1974). ^b E. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968). ^c C. Postmus and E. L. King, *J. Phys. Chem.*, 59, 1216 (1955). ^d $I = 0.2 \text{ M}$. ^e $I = 0.07 \text{ M}$. ^f T. Ramasami and A. G. Sykes, *Inorg. Chem.*, 15, 2885 (1976). ^g Reference 2. ^h This work. ⁱ $\Delta H^\ddagger = 60.4 \pm 1.2 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -55 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$. ^j Reference 9. ^k $\Delta H^\ddagger = 53.9 \pm 3.3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -68 \pm 11 \text{ J mol}^{-1} \text{ K}^{-1}$. ^l Reference 10. ^m Reference 6.

Table VI. Observed Equilibrium Constants ($K_{\text{obsd}}^{\text{NCS}}$) of the Reaction of $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ with Thiocyanate Ions

$[\text{H}^+]/\text{M}$	$K_{\text{obsd}}^{\text{NCS}}$	$[\text{H}^+]/\text{M}$	$K_{\text{obsd}}^{\text{NCS}}$
4.87×10^{-5}	0.618	9.33×10^{-2}	13.5
1.73×10^{-4}	0.753	1.40×10^{-1}	19.8
4.15×10^{-4}	1.17	1.87×10^{-1}	18.5
6.43×10^{-4}	1.34	2.33×10^{-1}	21.0
8.47×10^{-4}	1.55	2.80×10^{-1}	20.1
6.53×10^{-2}	16.2	3.73×10^{-1}	21.1

VIII. If the reaction proceeds through the paths given in eq 16 and 17, eq 21–23 can be derived. Equations 22 and 23

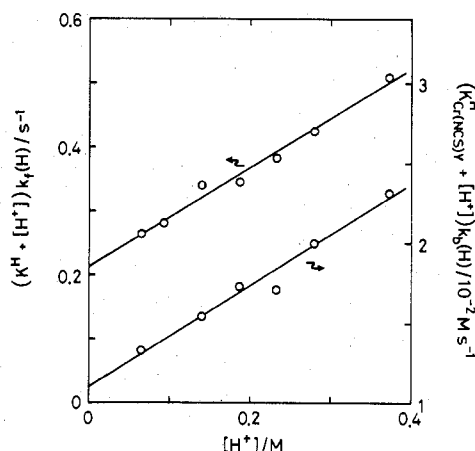
$$k_o = k_f(\text{H})[\text{NCS}^-] + k_b(\text{H}) \quad (21)$$

$$k_f(\text{H}) = \frac{K^{\text{H}}k_1 + k_2[\text{H}^+]}{K^{\text{H}} + [\text{H}^+]} \quad (22)$$

$$k_b(\text{H}) = \frac{k_{-1}K^{\text{H}}_{\text{Cr}(\text{NCS})\text{Y}} + k_{-2}[\text{H}^+]}{K^{\text{H}}_{\text{Cr}(\text{NCS})\text{Y}} + [\text{H}^+]} \quad (23)$$

indicate that the plots of $(K^{\text{H}} + [\text{H}^+])k_f(\text{H})$ vs. $[\text{H}^+]$ and $(K^{\text{H}}_{\text{Cr}(\text{NCS})\text{Y}} + [\text{H}^+])k_b(\text{H})$ vs. $[\text{H}^+]$ give linear relations. The data given in Table VIII were found to obey eq 21–23 satisfactorily. The individual rate constants, k_1 , k_2 , k_{-1} , and k_{-2} , were determined by the following procedures. The conditional constants $k_f(\text{H})$ and $k_b(\text{H})$ at the given hydrogen ion concentrations were calculated from the relations of eq 24 and 25. Then, the values of $(K^{\text{H}} + [\text{H}^+])k_f(\text{H})$ and $(K^{\text{H}}_{\text{Cr}(\text{NCS})\text{Y}} + [\text{H}^+])k_b(\text{H})$ were plotted against the hydrogen ion concentrations, respectively (Figure 1). As expected from eq 22 and 23, these plots give good linear relations. The individual rate constants were determined from the respective values of the intercepts and slopes. The rate constant values are summarized in Tables IV and V.

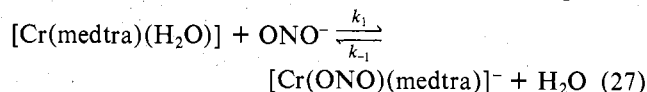
Reaction of $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]^-$ with Nitrite Ions. The equilibrium study of the title reaction was not attempted. The pseudo-first-order rate constant k_o was independent of the hydrogen ion concentrations and found to obey eq 9 (Table IX).¹⁴ The values of k_f and k_b were determined from the slope and intercept of the plots of k_o vs. $[\text{ONO}^-]$, respectively, and are given in Tables IV and V.

Figure 1. Plots of $(K^{\text{H}} + [\text{H}^+])k_f(\text{H})$ vs. $[\text{H}^+]$ and $(K^{\text{H}}_{\text{Cr}(\text{NCS})\text{Y}} + [\text{H}^+])k_b(\text{H})$ vs. $[\text{H}^+]$ for the reaction of $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ with thiocyanate ions.

Reaction of $[\text{Cr}(\text{medtra})(\text{H}_2\text{O})]^-$ with Nitrite Ions. The observed pseudo-first-order rate constants (k_o , s^{-1}) were dependent both on the concentrations of nitrite ions and on the concentration of nitrous acid as shown in Figure 2 and could be expressed as in eq 26. This kinetic behavior is compatible

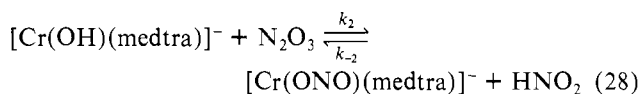
$$k_o = \{(1.7 \pm 0.9) \times 10^{-3} + (8.56 \pm 0.65) \times 10^{-1}[\text{HNO}_2]\}[\text{ONO}^-] + (8 \pm 3) \times 10^{-4} + (4.1 \pm 0.2) \times 10^{-1}[\text{HNO}_2] \quad (26)$$

with the occurrence of the two simultaneous reactions given in eq 27 and 28. On the basis of this mechanism, eq 29 can

**Table VII.** Equilibrium Constants (K , M^{-1}) of the Reactions of $[\text{CrY}(\text{H}_2\text{O})]^{(n-3)-}$ with Anions X^-

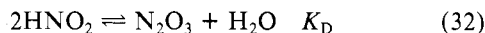
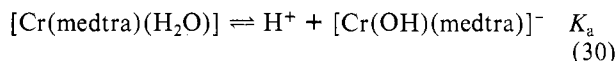
$[\text{CrY}(\text{H}_2\text{O})]^{(n-3)-}$	X^-					
	N_3^-	OAc^-	$\text{ONO}^- \text{ }^{a,b}$	$\text{NCS}^- \text{ }^a$	Cl^-	Br^-
$[\text{Cr}(\text{edtra})(\text{H}_2\text{O})]$		$17.7 \pm 0.9 \text{ }^c$		12.3 ± 1.0		
$[\text{Cr}(\text{medtra})(\text{H}_2\text{O})]$		$12.4 \pm 0.6 \text{ }^c$	2.1 ± 0.3			
$[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]$	$110 \pm 15 \text{ }^{a,d}$	$16.9 \pm 0.9 \text{ }^c$	1.9 ± 0.2	13.6 ± 1.2	$<0.1 \text{ }^e$	$<0.1 \text{ }^e$
$[\text{Cr}(\text{aedtra})(\text{H}_2\text{O})]$		$11.8 \pm 3.7 \text{ }^{b,f}$				
$[\text{Cr}(\text{Hedta})(\text{H}_2\text{O})]$				21.8 ± 0.4		
$[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$	$5.9 \pm 0.3 \text{ }^c$	$0.62 \pm 0.03 \text{ }^c$		0.57 ± 0.07		

^a This work. ^b The K value was calculated by the relation $K = k_f/k_b$. ^c Reference 2. ^d $\Delta H = -12.4 \pm 1.1 \text{ kJ mol}^{-1}$, $\Delta S = -3 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$. ^e Reference 9. ^f Reference 10.



be derived, where K_a , K_N^{H} , and K_D are the equilibrium constants of the reactions shown in eq 30–32. As the K_a value²

$$k_o = \frac{K_N^{\text{H}}k_1 + K_aK_Dk_2[\text{HNO}_2]}{K_N^{\text{H}}(K_a + [\text{H}^+]) + k_{-1} + k_{-2}[\text{HNO}_2]} [\text{H}^+][\text{ONO}^-] \quad (29)$$

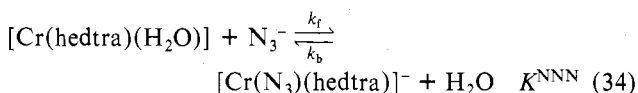


is much smaller than the hydrogen ion concentrations under the present experimental condition, eq 29 is simplified as eq 33. The data shown in Figure 2 were analyzed by use of eq

$$k_o = \left(k_1 + \frac{K_aK_D}{K_N^{\text{H}}} k_2[\text{HNO}_2] \right) [\text{ONO}^-] + k_{-1} + k_{-2}[\text{HNO}_2] \quad (33)$$

33 and the values of K_N^{H} ($=10^{-3.00}$ M)¹⁵ and K_D ($=10^{-0.80}$ M⁻¹).¹⁶ The rate constants of reactions 27 and 28 were determined to be $(1.7 \pm 0.9) \times 10^{-3}$ M⁻¹ s⁻¹ for k_1 , $(8 \pm 3) \times 10^{-4}$ s⁻¹ for k_{-1} , $(9.6 \pm 0.7) \times 10^3$ M⁻¹ s⁻¹ for k_2 , and 0.41 ± 0.02 M⁻¹ s⁻¹ for k_{-2} , respectively.

Reaction of [Cr(hedtra)(H₂O)] with Azide Ions. The equilibrium and kinetic measurements of reaction 34 were



made at various temperatures. The data were analyzed with a manner similar to that described for the reactions of [Cr(hedtra)(H₂O)] and [Cr(edtra)(H₂O)] with thiocyanate ions. The values of K^{NNN} (Table X)¹⁴ and the pseudo-first-order rate constants, k_o (Table XI),¹⁴ were found to be independent of the hydrogen ion concentrations ($[\text{H}^+] = 5.5 \times 10^{-6}$ – 4.3×10^{-5} M). The resolved rate constants, k_f and k_b , are shown in Tables IV and V. The kinetics of the reactions of [Cr(edtra)(H₂O)] and [Cr(medtra)(H₂O)] with azide ions showed anomalies: the pseudo-first-order plots did not show linear relations, but the reaction rate became slower with time than that expected for the first-order kinetics. Further investigations on these systems were not made.

Visible Absorption Spectra of Chromium(III) Complexes. The positions of the absorption maxima and the molar absorptivities of [CrXY]⁽ⁿ⁻²⁾⁻ were calculated by using the equilibrium constants of the reactions of [CrY(H₂O)]⁽ⁿ⁻³⁾⁻ with X⁻. Table XII summarizes the numerical data of the absorption spectra for the [CrY(H₂O)]⁽ⁿ⁻³⁾⁻ and [CrXY]⁽ⁿ⁻²⁾⁻ complexes.

Discussion

In Table VII, the equilibrium constants of the reactions of [CrY(H₂O)]⁽ⁿ⁻³⁾⁻ with X⁻ are summarized. The formation constants of [CrXY]⁽ⁿ⁻²⁾⁻ increase in the following order with the nature of the X⁻: Br⁻, Cl⁻ < ONO⁻ < NCS⁻ ~ OAc⁻ < N₃⁻. The order seems not to be related directly to that of the basicity of the X⁻.

Table XII shows that the absorption maxima of [Cr(NCS)Y]⁽ⁿ⁻²⁾⁻ are located at shorter wavelengths than those of [CrY(H₂O)]⁽ⁿ⁻³⁾⁻. This indicates that thiocyanate ion in [Cr(NCS)Y]⁽ⁿ⁻²⁾⁻ acts as the N-bonded ligand. It is notable that the molar absorptivities of the (aminopolycarboxylato)chromium(III) complexes given in Table XII are much

Table VIII. Pseudo-First-Order Rate Constants (k_o) of the Reaction of [Cr(edta)(H₂O)]⁻ with Thiocyanate Ions

[H ⁺]/M ^a	[NCS ⁻]/M	k_o/b s ⁻¹	[H ⁺]/M ^a	[NCS ⁻]/M	k_o/b s ⁻¹
6.53 × 10 ⁻²	0.107	0.563	1.87 × 10 ⁻¹ *	0.321	0.633
6.53 × 10 ⁻²	0.214	0.903	1.87 × 10 ⁻¹	0.482	0.926
6.53 × 10 ⁻²	0.321	1.22	1.87 × 10 ⁻¹	0.642	1.20
6.53 × 10 ⁻²	0.482	1.78	2.33 × 10 ⁻¹	0.107	0.243
6.53 × 10 ⁻²	0.642	2.32	2.33 × 10 ⁻¹	0.214	0.404
9.33 × 10 ⁻²	0.107	0.449	2.33 × 10 ⁻¹	0.321	0.559
9.33 × 10 ⁻²	0.214	0.712	2.33 × 10 ⁻¹	0.482	0.818
9.33 × 10 ⁻²	0.321	1.03	2.33 × 10 ⁻¹	0.642	1.06
9.33 × 10 ⁻²	0.482	1.48	2.80 × 10 ⁻¹	0.107	0.223
9.33 × 10 ⁻²	0.642	1.97	2.80 × 10 ⁻¹	0.214	0.371
1.40 × 10 ⁻¹	0.107	0.341	2.80 × 10 ⁻¹	0.321	0.531
1.40 × 10 ⁻¹	0.214	0.555	2.80 × 10 ⁻¹	0.482	0.780
1.40 × 10 ⁻¹	0.321	0.815	2.80 × 10 ⁻¹	0.642	1.00
1.40 × 10 ⁻¹	0.482	1.16	3.73 × 10 ⁻¹	0.107	0.197
1.40 × 10 ⁻¹	0.642	1.56	3.73 × 10 ⁻¹	0.214	0.320
1.87 × 10 ⁻¹	0.107	0.272	3.73 × 10 ⁻¹	0.321	0.491
1.87 × 10 ⁻¹	0.214	0.462	3.73 × 10 ⁻¹	0.482	0.636
1.87 × 10 ⁻¹	0.321	0.630	3.73 × 10 ⁻¹	0.535	0.811

^a Initial concentration of [Cr(edta)(H₂O)]⁻ is 3.04×10^{-3} M for all cases except for that marked with an asterisk in which it was 6.08×10^{-3} M. ^b Each value is the average of four determinations.

Table XII. Visible Absorption Maxima (λ) and Molar Absorptivity (ϵ) of the Amino(polycarboxylato)chromium(III) Complexes

complex	λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)	ref
[Cr(edtra)(H ₂ O)]	541 (133), 386 (107)	2
[Cr(medtra)(H ₂ O)]	539 (143), 386 (113)	2
[Cr(hedtra)(H ₂ O)]	545 (151), 385 (118)	2
[Cr(Hedta)(H ₂ O)]	544 (146), 384 (110)	this work
[Cr(edta)(H ₂ O)] ⁻	539 (228), 392 (115)	this work
[Cr(NCS)(edtra)] ⁻	534 (166), 392 (102)	this work
[Cr(NCS)(hedtra)] ⁻	535 (187), 392 (110)	this work
[Cr(NCS)(Hedta)] ⁻	539 (180), 394 (106)	this work
[Cr(NCS)(edta)] ²⁻	536 (208), 390 (120)	this work
[Cr(N ₃)(hedtra)] ⁻	552 (207), 407 (130)	this work
[Cr(N ₃)(edta)] ²⁻	551 (213), 407 (128)	2
[Cr(OAc)(edtra)] ⁻	546 (147), 393 (108)	2
[Cr(OAc)(medtra)] ⁻	549 (154), 394 (112)	2
[Cr(OAc)(hedtra)] ⁻	556 (162), 394 (113)	2
[Cr(OAc)(edta)] ²⁻	565 (147), 394 (119)	2
[CrCl(hedtra)] ⁻	565 (128), 397 (109)	9
[CrBr(hedtra)] ⁻	575 (127), 408 (145)	9

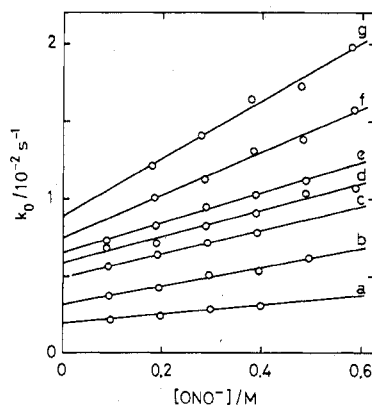


Figure 2. Plots of the pseudo-first-order rate constants (k_o) vs. $[\text{ONO}^-]$ for the reaction of [Cr(medtra)(H₂O)] with nitrite ions: $[\text{HNO}_2]/10^{-3}$ M = 3.26 (a), 6.53 (b), 9.79 (c), 11.7 (d), 13.1 (e), 16.3 (f), 21.0 (g).

larger than those of most other chromium(III) complexes.¹⁷ This may suggest that considerable strains are present in the complexes studied in this work. The rapid substitution reactions may be originated from the strains.

In Tables IV and V, the rate constants of reaction 2, k_f and k_b , are compared along with those of the corresponding reactions of pentaqua- and pentaamminechromium(III) complexes. Among the reactions studied in this work, the reactions of $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]$ with thiocyanate, nitrite, and azide ions and of $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ with thiocyanate were found to be so rapid that the stopped-flow technique was required. The k_f values which correspond to the rate constants of the anation reactions are not so sensitive to the change of the nature of the X^- . For the given anion, X^- , however, the change of the kind of chromium(III) complexes gives strikingly large changes of the rate constants. The order of the reactivities is $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} < [\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} \ll [\text{Cr}(\text{medtra})(\text{H}_2\text{O})] < [\text{Cr}(\text{edtra})(\text{H}_2\text{O})] \ll [\text{Cr}(\text{Hedta})(\text{H}_2\text{O})] < [\text{Cr}(\text{aedtra})(\text{H}_2\text{O})]$, $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]$, $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$.

The k_f value of the reaction of $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ with thiocyanate ions is 18 times larger than that of $[\text{Cr}(\text{Hedta})(\text{H}_2\text{O})]$ with thiocyanate ions; this is, $[\text{Cr}(\text{Hedta})(\text{H}_2\text{O})]$ is less reactive than $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$. This result will also help to clarify the mechanistic ambiguity of the $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^- \text{OAc}^-$ system (eq 4 and 5). If eq 4 is effective in the system, it must be concluded that the reaction of $[\text{Cr}(\text{Hedta})(\text{H}_2\text{O})]$ with OAc^- is 1.0×10^3 times faster than that of $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ with OAc^- . This would be unlikely, however, because it was shown in the $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^- \text{NCS}^-$ system that $[\text{Cr}(\text{Hedta})(\text{H}_2\text{O})]$ is less labile than $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$. On the other hand, the formulation of eq 5 gives a reasonable rate constant in magnitude, $k_f' = 5.5 \text{ M}^{-1} \text{ s}^{-1}$. This result suggests that eq 4 should be reformulated to eq 5.

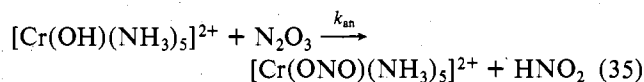
The k_f values of $[\text{Cr}(\text{edtra})(\text{H}_2\text{O})]$ and $[\text{Cr}(\text{medtra})(\text{H}_2\text{O})]$ complexes are much larger than those of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$. The result may support the explanation that coordination of Y^{n-} reduces the positive charge of the central chromium(III) ion and leads to loosening of the $\text{Cr}-\text{OH}_2$ bond.² The N substituent groups in the $[\text{Cr}(\text{edtra})(\text{H}_2\text{O})]$ and $[\text{Cr}(\text{medtra})(\text{H}_2\text{O})]$ complexes have no coordinating ability for the metal ions. On the other hand, when the N substituent groups of Y^{n-} have coordinating ability, such as CH_2COOH , $\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_2\text{CH}_2\text{OCOCH}_3$, or CH_2COO^- , the k_f values are much larger than those of the $[\text{Cr}(\text{edtra})(\text{H}_2\text{O})]$ and $[\text{Cr}(\text{medtra})(\text{H}_2\text{O})]$ complexes. This fact suggests strongly that the $\text{Cr}-\text{OH}_2$ bond rupture is accelerated by the transient coordination of these pendant groups to central chromium(III) ions.

The k_b values which correspond to the rate constants of the aquation reactions are also relatively insensitive to the change of the nature of the X^- . The order of the reactivities of the aquation reactions is very similar to that of the anation reactions. Therefore, a situation similar to that considered for the anation reactions may also exist for the aquation reactions.

The kinetic results obtained for the reversible nitrosation reaction of $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]$ may indicate that the reaction proceeds through the direct substitution of the aqua ligand by nitrite ion and vice versa. This provides additional support for the proposal that the free hydroxyethyl group in the complex coordinates to the chromium(III) ion and assists the elimination of the coordinated water molecule or X^- ion.

The nitrosation of $[\text{Cr}(\text{medtra})(\text{H}_2\text{O})]$ was found to occur via the two parallel reactions given in eq 27 and 28. Reaction 27 is considered to be the one which proceeds through the

cleavage of the chromium-oxygen bond as found for $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]$. On the other hand, reaction 28 is compatible with the nitrosation occurring without the cleavage of the chromium-oxygen bond, as found for $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$. In fact, the rate-constant value of reaction 28, k_2 , is reasonably quite similar to the rate constant value of reaction 35 ($k_{\text{an}} = 1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).



The substitution reactions of chromium(III) complexes have been investigated mainly for various acidopentaqua- and acidopentaamminechromium(III) complexes. As shown above, however, it should be noted that the features of the substitution reactions of the chromium(III) complexes containing aminopolycarboxylates are quite different from those of the acidopentaqua- and acidopentaamminechromium(III) complexes.¹⁸

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Registry No. $\text{Cr}(\text{edtra})(\text{H}_2\text{O})$, 55622-34-9; $\text{Cr}(\text{medtra})(\text{H}_2\text{O})$, 55622-36-1; $\text{Cr}(\text{hedtra})(\text{H}_2\text{O})$, 15955-78-9; $\text{Cr}(\text{Hedta})(\text{H}_2\text{O})$, 15955-81-4; $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$, 19610-17-4; $[\text{Cr}(\text{ONO})(\text{edtra})]^-$, 70864-85-6; $[\text{Cr}(\text{NCS})(\text{edtra})]^-$, 70864-86-7; $[\text{Cr}(\text{ONO})(\text{medtra})]^-$, 70864-87-8; $[\text{Cr}(\text{N}_3)(\text{hedtra})]^-$, 59184-04-2; $[\text{Cr}(\text{ONO})(\text{hedtra})]^-$, 70864-88-9; $[\text{Cr}(\text{NCS})(\text{hedtra})]^-$, 70864-89-0; $[\text{Cr}(\text{NCS})(\text{Hedta})]^-$, 70864-90-3; $[\text{Cr}(\text{NCS})(\text{edta})]^{2-}$, 70864-91-4; N_3^- , 14343-69-2; ONO^- , 14797-55-8; NCS^- , 302-04-5.

Supplementary Material Available: Table I (equilibrium data of the $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]^- \text{NCS}^-$ and $[\text{Cr}(\text{edtra})(\text{H}_2\text{O})]^- \text{NCS}^-$ systems), Table II (kinetic data of the $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]^- \text{NCS}^-$ system), Table III (kinetic data of the $[\text{Cr}(\text{edtra})(\text{H}_2\text{O})]^- \text{NCS}^-$ system), Table IX (kinetic data of the $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]^- \text{ONO}^-$ system), Table X (equilibrium data of the $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]^- \text{N}_3^-$ system), and Table XI (kinetic data of the $[\text{Cr}(\text{hedtra})(\text{H}_2\text{O})]^- \text{N}_3^-$ system) (5 pages). Ordering information is given on any current masthead page.

References and Notes

- Abbreviations used in this work: acetate = OAc^- , nitrilotriacetate = nta^{3-} , ethylenediamine-*N,N,N',N'*-tetraacetate = edta^{4-} , *N*-(hydroxyethyl)ethylenediamine-*N,N',N'*-triacetate = hedtra^{3-} , ethylenediamine-*N,N',N'*-triacetate = edtra^{3-} , *N*-methylthylenediamine-*N,N',N'*-triacetate = medtra^{3-} , *N*-(acetoxylethyl)ethylenediamine-*N,N',N'*-triacetate = aedtra^{3-} .
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- After the preparation of this manuscript, the following paper which is related to the present work appeared: J. Guardalabene, S. Gulnac, N. Keder, and R. E. Shepherd, *Inorg. Chem.*, **18**, 22 (1979).