

Monoalkylchromium(III) Complexes of a Tetradentate N<sub>4</sub> Macrocyclic

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Chromium(II) chloride in mixed aqueous solvents forms a strongly reducing complex with the macrocyclic ligand [15]aneN<sub>4</sub>. Reactions of this complex with organic halides produce the monoalkyl complexes RCr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup> which have been characterized and shown to have a trans configuration. The kinetics of these reactions have been studied, with the result that the reaction follows a second-order rate law. Rate constants have been evaluated for a range of organic halides. These results, together with the stoichiometry, the variation of rate with the constitution of RX, and related tests, suggest the following mechanism. The chromium(II) complex reacts with alkyl halides in two steps, rate-limiting halogen atom abstraction to generate a carbon-centered free radical followed by rapid coupling of the latter with a second chromium(II) complex.

## Introduction

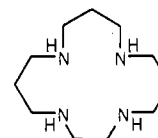
There are now known a number of different types of organometallic compounds or complexes of chromium. In conjunction with mechanistic studies relating to organic derivatives of cobalt(III), such as the monoalkylcobaloximes and -cobalamins, we have undertaken a number of studies of the reactions of related Cr(III) complexes. The organochromium complexes on which our previous efforts have focused have been members of the family of pentaquo chromium(III) cations (H<sub>2</sub>O)<sub>5</sub>CrR<sup>2+</sup>, of which a considerable number are now known.<sup>2-8</sup>

Until the present time, the pentaquo series has been the only one for which a general preparation of a substantial number of monoalkyl derivatives has been available. Kochi and co-workers<sup>9</sup> have prepared monoorganochromium complexes containing ethylenediamine, but these have not been well characterized as to exact composition and structure.

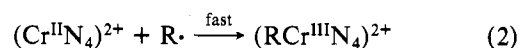
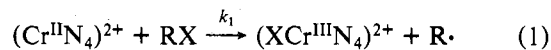
The only broad class of monoalkylchromium complexes which also contain a macrocyclic, tetradentate ligand (and are therefore more closely analogous to the cobalt complexes) are the perfluoroalkyls of [*N,N'*-ethylenebis(salicylaldimino)]chromium(III) pyridine, R<sub>F</sub>Cr(salen)py.<sup>10</sup> These complexes were formed by a two-step process, first reaction of CrCl<sub>2</sub>·2NCCH<sub>3</sub> with R<sub>F</sub>I to form an organochromium(III) complex followed by incorporation of the salen macrocycle. The latter involves substitution at the d<sup>3</sup> Cr(III) complex, a hindered reaction expected to be suitable for only the most kinetically stable of organochromium derivatives such as these perfluoroalkyls.

The second general method which might be devised to prepare the desired RCr<sup>III</sup>(N<sub>4</sub>chel)B compounds involves prior formation of the chromium(II) chelate, followed by formation of the carbon-chromium σ bond, now under mild reaction conditions. We are not aware that this method has been used before, and it is the approach we have taken. We recognize that the reducing strength of the Cr<sup>II</sup>N<sub>4</sub> complex is much enhanced compared to that of Cr<sup>2+</sup>(aq). On the one hand this very likely precludes the use of unsaturated N<sub>4</sub> macrocycles which would be susceptible to reduction by Cr(II). On the other hand, it opens the possibility that, as with the "Cr<sup>II</sup>-en" system<sup>9</sup> and CrSO<sub>4</sub> in aqueous DMF,<sup>11</sup> but unlike the case of Cr<sup>2+</sup>(aq), direct reactions between Cr<sup>II</sup>(N<sub>4</sub>chel) and RX may occur. This might afford a higher yield route to these compounds, as opposed to the indirect and lower yield methods based on peroxides<sup>6,8</sup> employed for the alkyls (H<sub>2</sub>O)<sub>5</sub>CrR<sup>2+</sup>. It must be recalled that alkyl halides do not react with Cr<sup>2+</sup>(aq), although "activated" halides such as C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>X and CHCl<sub>3</sub> do.<sup>3,4,11</sup>

With these points in mind, we undertook a study of the possibilities using the water-soluble, 15-membered macrocycle<sup>12</sup> [15]aneN<sub>4</sub>. This 15-membered ligand was chosen for the chromium complexes, rather than the 14-membered rings often used in organocobalt complexes.<sup>13</sup> A

[15]aneN<sub>4</sub>

structure of this size better accommodates the larger chromium atom especially in the chromium(II) complex;<sup>14</sup> also the water solubility of this ligand, in contrast to the water-insoluble [14]aneN<sub>4</sub> analogue, facilitates preparation of its chromium complexes. Considering such processes as the reactions of Cr<sup>2+</sup>(aq) with benzyl halides,<sup>15</sup> a radical mechanism such as that in eq 1 and 2 seems likely, leading to the net reaction shown in eq 3 (the macrocyclic ligand is abbreviated simply



as N<sub>4</sub> in these equations; in many instances water molecule(s) completing the coordination sphere may not be shown although six-coordination has been demonstrated).

This paper reports results on the preparation and characterization of the organochromium(III) cations RCr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup> and on the mechanism of their formation from the chromium(II) chelate by reaction with alkyl halides. Evidence is presented that the complexes have a trans structure.

## Experimental Section

**Materials.** The chromium(II) complex Cr([15]aneN<sub>4</sub>)<sup>2+</sup> was prepared in solution from CrCl<sub>2</sub>·4H<sub>2</sub>O(s)<sup>16</sup> and the macrocyclic amine;<sup>17</sup> zinc-reduced chromium(II) must be avoided because of competing complexation of Zn<sup>2+</sup>, and a low[H<sup>+</sup>], <5 × 10<sup>-4</sup> M, is essential for complete reaction. Formation of (Cr<sup>II</sup>N<sub>4</sub>)<sup>2+</sup> requires a few minutes for completion as judged by the instant color change from the blue of Cr<sup>2+</sup>(aq) to brown and then slowly to the deep royal purple of the chromium(II) chelate complex. Solutions of (Cr<sup>II</sup>N<sub>4</sub>)<sup>2+</sup> were prepared in this manner by using the solvents water (especially for product isolation), 85% aqueous THF, 99% aqueous CH<sub>3</sub>OH, and (for the bulk of the kinetic determinations) 1:1 v/v *tert*-butyl alcohol-water. When necessary, the Cr(II) solutions were analyzed by reaction with a 10–30% excess of (NH<sub>3</sub>)<sub>2</sub>CoCl<sup>2+</sup>, after which the Co<sup>2+</sup> produced was determined spectrophotometrically as Co(NCS)<sub>4</sub><sup>2-</sup> in 50% aqueous acetone, λ 632 nm (ε 1843 M<sup>-1</sup> cm<sup>-1</sup>). The Cr(II) solutions are extremely sensitive to oxygen, considerably more so than Cr<sup>2+</sup>(aq), and must be handled with great care. Syringe techniques using vessels stopped with rubber septa proved satisfactory, although minimal handling of the solutions was required for quantitative work.

The organic halides were commercially available. Each was appropriately distilled before use; 1-adamantyl bromide was recrystallized twice from methanol.

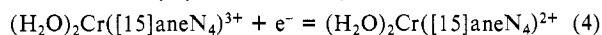
**Separations and Analyses.** Chromium(III) complexes of the ligand [15]aneN<sub>4</sub> were separated on columns of Sephadex C-25, a strong

acid ion-exchange resin. The column of resin was often kept cold by circulation of water at 0 °C through its jacket. Chromium concentrations were determined spectrophotometrically as chromate,  $\lambda$  372 nm ( $\epsilon$  4830 M<sup>-1</sup> cm<sup>-1</sup>), after oxidation with peroxide in basic solution.

Some organochromium complexes were characterized by reaction with mercury(II) ion or with aqueous bromine. The resulting R<sub>2</sub>Hg<sup>+</sup> in the former, precipitated as the chloride, was identified mass spectrometrically,<sup>18</sup> as was the organic bromide from the latter reaction. Organic products resulting from reaction of Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup> and BrCH<sub>2</sub>Cl and BrCCl<sub>3</sub> were determined similarly. The origins of particular ion peaks were verified by a determination of their appearance potentials.

Both 1-hexene and methylcyclopentane are produced by thermolysis of the RCr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup> products resulting from reaction of 6-bromo-1-hexene with Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup>. Their ratio was determined by gas chromatography<sup>19</sup> with a Tracor 550 instrument at ambient temperature equipped with a 2 m × 4 mm column packed with 10% SE 30 on Chromosorb W at a flow rate of 4.8 cm s<sup>-1</sup>. Samples from the reaction mixture were injected directly onto the GC column, and the retention times and peak areas were compared with values obtained for known samples.

The reduction potential corresponding to the half-reaction in eq 4 was determined<sup>20</sup> by cyclic voltammetry with instrumentation from



Princeton Applied Research—a Model 173 potentiostat/galvanostat and a Model 175 universal programmer. Solutions of the Cr(III) complex were prepared by base hydrolysis of ICr([15]ane)H<sub>2</sub>O<sup>2+</sup> followed by reacidification and ion-exchange chromatography. The measurements were made at 0.40 M H<sup>+</sup> (25 °C) in aqueous solution. The reference electrode was isolated by a Teflon-fritted tube filled with 0.4 M HClO<sub>4</sub> separated by a KNO<sub>3</sub> salt bridge. The counterelectrode was isolated by a ground-glass frit. The value of  $E_{1/2}$ ,  $-0.82 \pm 0.01$  V vs. SCE or  $-0.58 \pm 0.01$  V vs. NHE, was determined from the peak separation and did not vary with scan rate (200 mV/s to 1 V/s).

The reaction of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br with Cr([15]aneN<sub>4</sub>)<sup>2+</sup> was sufficiently rapid to permit convenient study of its stoichiometry by spectrophotometric titration using solutions of the Cr(II) complex which had been carefully analyzed. Qualitative evidence of the stoichiometry was obtained in other reactions by noting the production of roughly comparable quantities of the two Cr(III) products shown in eq 3 as they were being separated on the Sephadex column.

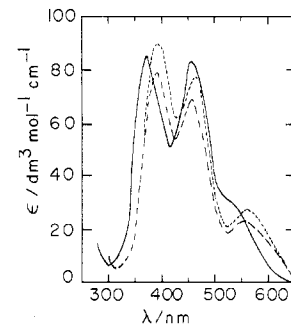
**Kinetics.** Reaction rates were determined spectrophotometrically, usually at or near an absorption maximum of the organochromium complex, often  $\sim 390$  nm. Reactions with  $t_{1/2} > 10$  s were followed with a Cary Model 14 spectrophotometer and faster reactions with a Durrum stopped-flow instrument.

Many kinetic runs were conducted under pseudo-first-order conditions, often with a large and known excess of the organic bromide. (This is advantageous in that any partial oxidation of the chromium(II) complex during transfer is immaterial.) Reactions under these conditions followed pseudo-first-order kinetics, and the data were analyzed by a plot of  $\log(D_\infty - D_t)$  vs. time ( $D$  = absorbance). Much of the stopped-flow data was analyzed by the same expression by using least-squares refinement of the data by a PDP-15 computer interfaced to the instrument.

## Results

**Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup>.** Chromium(II) complexes with ammine ligands have not been extensively characterized, perhaps because of their exceptional sensitivity to oxygen. Several bis- and tris(ethylenediamine) complexes are known.<sup>21a</sup> More directly related to the present work are the macrocyclic amine complexes characterized by Dei and Mani.<sup>21b</sup> They include X<sub>2</sub>Cr(Me<sub>2</sub>[14]aneN<sub>4</sub>) (X = Cl, Br) and X<sub>2</sub>Cr(Me<sub>6</sub>[14]aneN<sub>4</sub>) (X = Cl, Br, I) and are directly analogous to the solution species used in this work, (H<sub>2</sub>O)<sub>2</sub>Cr([15]aneN<sub>4</sub>)<sup>2+</sup>. The slowness of its formation from Cr<sup>2+</sup>(aq) and the macrocyclic ligand might arise from a cis-to-trans isomerization,<sup>21b</sup> although slowness at one stage of stepwise coordination of the tetradentate ligand cannot be ruled out.

This chromium(II) complex is characterized by a greater reducing strength than Cr<sup>2+</sup>(aq),  $E^\circ = -0.58$  V (where  $E^\circ$



**Figure 1.** Absorption spectra of inorganic chromium(III) complexes of [15]aneN<sub>4</sub>: [(H<sub>2</sub>O)<sub>2</sub>Cr([15]aneN<sub>4</sub>)]<sup>3+</sup> (solid line), [BrCr([15]aneN<sub>4</sub>)(H<sub>2</sub>O)]<sup>2+</sup> (dashed line), and [ICr([15]aneN<sub>4</sub>)(H<sub>2</sub>O)]<sup>2+</sup> (dotted line).

**Table I.** UV-Visible Spectra of Cr(III) Complexes LCr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup>

L	$\lambda_{max}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )		
I <sup>a</sup>	394 (90)	462 (75)	562 (26)
Br	393 (78)	460 (68)	560 (23)
Cl	393 (76)	462 (62)	564 (22)
H <sub>2</sub> O <sup>b</sup>	377 (88)	454 (87)	540 (28, sh)
CH <sub>3</sub>	258 (3300, sh)	375 (227)	468 (69)
C <sub>2</sub> H <sub>5</sub>	264 (3100)	383 (387)	467 (66)
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	265 (3440)	383 (465)	468 (71)
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	268 (3300)	383 (459)	468 (69)
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	287 (3280)	396 (550)	510 (69, sh)
<i>c</i> -C <sub>6</sub> H <sub>11</sub> <sup>a</sup>	298 (3070)	400 (422)	500 (67, sh)
1-adamantyl	268 (3070)	383 (347)	463 (88)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -	273 (7920)	297 (7470)	353 (2170)

<sup>a</sup> Estimated; complex thermally unstable. <sup>b</sup> Charge 3+.

is approximated by  $E_{1/2}$ ) compared to  $E^\circ = -0.41$  V, and by a visible absorption spectrum in 1:1 aqueous *tert*-butyl alcohol with a maximum at shorter wavelength,  $\lambda$  540 nm ( $\epsilon$  28.7  $\pm$  1.0 M<sup>-1</sup> cm<sup>-1</sup>) compared to  $\lambda$  713 nm ( $\epsilon$  5.0 M<sup>-1</sup> cm<sup>-1</sup>). The spectrum of (H<sub>2</sub>O)<sub>2</sub>Cr([15]aneN<sub>4</sub>)<sup>2+</sup> is quite similar to that of (H<sub>2</sub>O)<sub>2</sub>Cr(en)<sub>2</sub><sup>2+</sup>,<sup>9b</sup>  $\lambda$  550 nm ( $\epsilon$  25 M<sup>-1</sup> cm<sup>-1</sup>).

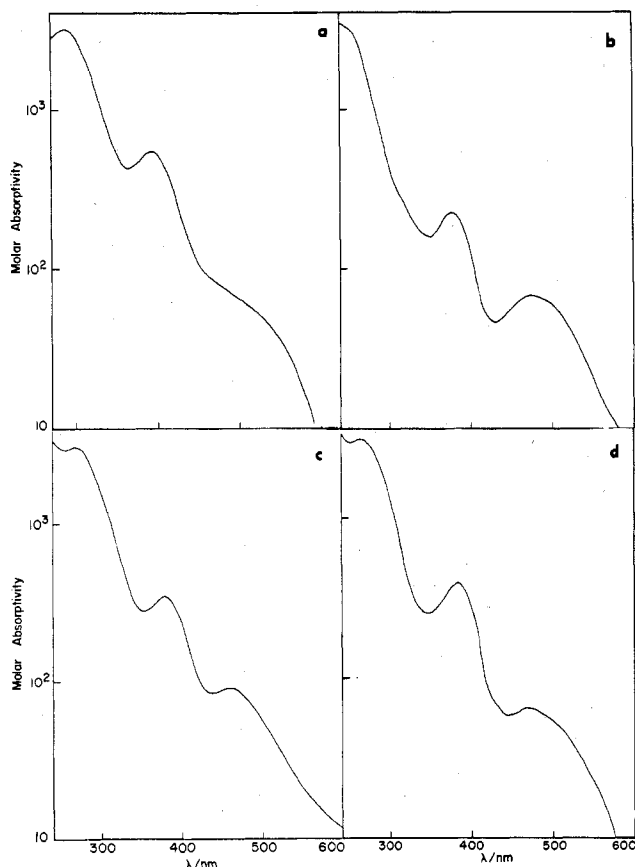
Implicit in the preceding discussion has been the assignment of a trans structure to (H<sub>2</sub>O)<sub>2</sub>Cr([15]aneN<sub>4</sub>)<sup>2+</sup>. This is substantiated, as amplified later, by comparison of electronic spectra of selected Cr(III) products with comparison of tetraamminechromium(III) complexes of known stereochemistry and by a structure determination.<sup>22</sup>

**Reaction with Organic Halides.** The Cr(II) complex reacts with all organic halides tried other than halobenzenes. The purple of the Cr(II) solution turns to yellow through reddish brown, depending on the halide used.

When the product solution is placed on a column of Sephadex C-25 ion-exchange resin (Na<sup>+</sup> form) and slowly eluted with 0.2 M sodium perchlorate (pH  $\sim$  4.5), the following characteristic pattern emerges. The first band off the column, judged to be a monocation by its elution behavior, is dull red and turns greenish brown instantaneously upon acidification to pH < 3. The column species is believed to be XCr([15]aneN<sub>4</sub>)OH<sup>+</sup>, and addition of H<sup>+</sup> affords rapid conversion to the haloquo complex. These assignments are amplified below.

The second band varies in color from yellow to orange or red-orange and is the desired organochromium cation RCr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup>. The third and last band, often quite variable in yield, is the aquohydroxo complex (H<sub>2</sub>O)Cr([15]aneN<sub>4</sub>)(OH)<sup>2+</sup>, readily converted by acidification<sup>23</sup> to the diaquo species (H<sub>2</sub>O)<sub>2</sub>Cr([15]aneN<sub>4</sub>)<sup>3+</sup>.

These products are formulated as stated above on the basis of the following information. The absorption spectra of the inorganic complexes, shown in Figure 1 and Table I, correspond closely to the spectra of analogous species of known



**Figure 2.** Absorption spectra of organochromium(III) complexes  $[\text{RCr}(\text{[15]aneN}_4)\text{H}_2\text{O}]^{2+}$ : R = *i*-C<sub>3</sub>H<sub>7</sub>, a; CH<sub>3</sub>, b; 1-adamantyl, c; C<sub>2</sub>H<sub>5</sub>, d.

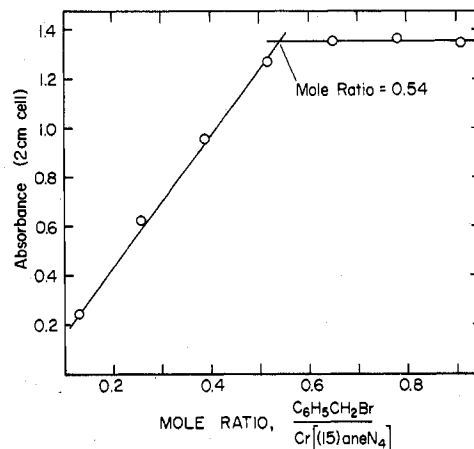
stereochemistry, namely, *trans*-[Cr<sup>III</sup>(NH<sub>3</sub>)<sub>4</sub>AB]<sup>n+</sup><sup>24</sup> and *trans*-X<sub>2</sub>Cr<sup>III</sup>([14]-aneN<sub>4</sub>)<sup>+</sup><sup>25</sup> although the present species have somewhat higher molar absorptivities. The spectra support the assignment of a *trans* structure, *cis*-tetraamines having characteristically different spectra.

Addition of Hg<sup>2+</sup> to any of the haloquo complexes results in their conversion to (H<sub>2</sub>O)<sub>2</sub>Cr([15]aneN<sub>4</sub>)<sup>3+</sup>, as does base hydrolysis and subsequent reacidification. The latter complex is also produced by reaction of hydrogen peroxide with the Cr(II) complex.

Various methods were used to characterize the organochromium complexes. Their elution pattern from the Sephadex resin suggests a 2+ charge. These complexes react with aqueous bromine and with Hg<sup>2+</sup> to cleave the chromium-carbon bond and produce *trans*-(H<sub>2</sub>O)<sub>2</sub>Cr([15]aneN<sub>4</sub>)<sup>3+</sup>. Such reactions are characteristic of organochromium complexes and are well-characterized processes for members of the (H<sub>2</sub>O)<sub>5</sub>CrR<sup>2+</sup> series.

These reactions were further studied to characterize the products formed. Reaction of aqueous bromine with C<sub>2</sub>H<sub>5</sub>Cr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup>, prepared from ethyl iodide and isolated chromatographically, was carried out in a closed vessel attached to a mass spectrometer. The only volatile organic detected mass spectrometrically was ethyl bromide, present in a copious amount.<sup>18</sup> The ethyl and *n*-butyl complexes were prepared from their bromides and reacted (without chromatographic separation) with mercury(II) perchlorate. Addition of chloride caused precipitation of RHgCl along with some RHgBr. These solids had mass spectra in agreement with the mixed halides, including proper isotopic splitting patterns for the many isotopes of Cl, Br, and Hg.

The complex C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup> was prepared from benzyl chloride. Reaction with mercury(II) ion and



**Figure 3.** Spectrophotometric titration of a solution of (H<sub>2</sub>O)<sub>2</sub>Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup> with benzyl bromide at λ 390 nm.

addition of sodium chloride produced a precipitate of benzylmercury chloride, identified by its melting point of 103–104 °C (lit.<sup>27</sup> mp 104 °C) and by its mass spectrum.

The alkylchromium complexes have similar absorption spectra, the most prominent feature being a maximum at 375–400 nm ( $\epsilon$  230–550 M<sup>-1</sup> cm<sup>-1</sup>). The benzyl complex has a spectrum very similar to that of (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>Ph<sup>2+</sup>. Representative spectra are shown in Figure 2, and a tabulation of spectral characteristics is given in Table I.

Isolation of the organometallic complexes as solid derivatives is not easily achieved. Tetraphenylborates can be precipitated, although they are not necessarily pure; they do redissolve, however, in acetonitrile giving solutions which show the characteristic spectra of RCr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup>. Two perchlorate salts were precipitated in low yield. (1) [*trans*-*n*-PrCr([15]aneN<sub>4</sub>)H<sub>2</sub>O](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. Anal. Calcd for CrC<sub>14</sub>H<sub>37</sub>N<sub>4</sub>O<sub>10</sub>Cl<sub>2</sub>: C, 30.89; H, 6.85; N, 10.29. Found: C, 30.72; H, 6.32; N, 10.00. (2) [*trans*-EtCr([15]aneN<sub>4</sub>)-NCS]ClO<sub>4</sub>. Anal. Calcd for CrC<sub>14</sub>H<sub>31</sub>N<sub>5</sub>O<sub>4</sub>S: C, 37.12; H, 6.90; N, 15.46. Found: C, 36.48; H, 6.78; N, 15.54.

**Stoichiometry and Kinetics.** The radical mechanism suggested in eq 1 and 2 leads to an overall stoichiometry of 2:1 (Cr<sup>II</sup>N<sub>4</sub>)<sup>2+</sup>:RX. Evidence confirming this comes from a spectrophotometric titration of Cr([15]aneN<sub>4</sub>)<sup>2+</sup> with benzyl bromide. As shown in Figure 3, the interpolated equivalence point occurs at a Cr(II):RX ratio of 1.85:1. The slowness of other reactions together with the difficulty of maintaining the Cr(II) complex over longer periods of time precluded similar tests for the alkyl halides, and production of comparable concentrations of the two chromium complexes shown in eq 3 was taken as sufficient evidence in these cases.

Most kinetic runs employed a large excess of the organic halide, with [RX]<sub>0</sub> ≥ 10[Cr<sup>II</sup>]<sub>0</sub>. The data were fit by a pseudo-first-order expression and gave rise to values of *k*<sub>obsd</sub> defined by eq 5. Division of *k*<sub>obsd</sub> by [RX]<sub>0</sub> affords values

$$-d[\text{Cr}(\text{[15]aneN}_4)^{2+}]/dt = k_{\text{obsd}}[\text{Cr}(\text{[15]aneN}_4)^{2+}] \quad (5)$$

for *k*<sub>2</sub>, a second-order rate constant defined by eq 6.

$$\frac{2d[\text{RX}]}{dt} = \frac{-d[(\text{Cr}^{\text{II}})^{2+}]}{dt} = k_{\text{RX}}[(\text{Cr}^{\text{II}})^{2+}][\text{RX}] \quad (6)$$

The constancy of *k*<sub>RX</sub> over the range of [RX] studied was used to verify the validity of eq 6 for most reactions, although in a few instances in which a single concentration was used it was necessary to assume this form was valid.

The data for primary halides are given in Table II, for secondary and tertiary halides in Table III, and for benzyl halides in Table IV. The latter data include runs in which the chromium(II) complex is present in substantial excess over

**Table II.** Kinetic Data<sup>a</sup> for the Reactions of Various Primary Organic Halides with *trans*-(H<sub>2</sub>O)<sub>2</sub>Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup>

halide	10 <sup>2</sup> [RX] <sub>0</sub> , M	k <sub>RX</sub> , M <sup>-1</sup> s <sup>-1</sup>	halide	10 <sup>2</sup> [RX] <sub>0</sub> , M	k <sub>RX</sub> , M <sup>-1</sup> s <sup>-1</sup>
CH <sub>3</sub> I	11.7	0.047	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br	2.02	0.176
	11.7	0.045		2.04	0.172
C <sub>2</sub> H <sub>5</sub> Br	7.29	av 0.046 ± 0.01	6.03	0.166	
		0.169	6.03	0.184	
	7.29	0.179	6.03	0.150	
	7.38	0.150	10.0	0.161	
	7.38	0.169	10.0	0.174	
	7.38	0.156	av 0.169 ± 0.011		
	7.38	0.161			
	7.38	0.195	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	1.71	0.150
	7.63	0.147		2.90	0.148
	12.10	0.168	4.27	0.138	
	12.10	0.174	5.96	0.127	
C <sub>2</sub> H <sub>5</sub> I	2.30	av 0.164 ± 0.016	6.80	0.128	
		0.409	7.64	0.142	
	2.30	0.414	8.49	0.134	
	2.30	0.447	av 0.138 ± 0.009		
	6.80	0.432			
	6.80	0.404	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> Br	2.30	0.122
	6.80	0.399		3.08	0.153
	6.80	0.411	3.83	0.124	
	6.80	0.414	5.37	0.102	
	6.88	0.446	6.89	0.086	
	6.88	0.423	7.62	0.089	
10.9	0.379	9.88	0.088		
10.9	0.390	av 0.11 ± 0.02 <sup>b</sup>			
10.9	0.399				
CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> Br	av 0.413 ± 0.020		2.50	0.153	
			3.78	0.156	
			4.42	0.162	
			6.32	0.154	
			av 0.156 ± 0.004		

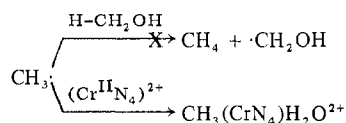
<sup>a</sup> At 25.0 °C and  $\mu = 0.20$  M in 1:1 v/v *t*-BuOH/H<sub>2</sub>O except as noted. <sup>b</sup> The plot of  $k_{\text{obsd}}$  vs. [(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>Br] is linear but extrapolates to a nonzero intercept. A better representation of the true second-order rate constant may be the slope of this plot (=0.067).

benzyl bromide. A constant value of  $k_{\text{RX}}$  is obtained if, according to eq 6, a factor of 2 is included in the calculation. This constitutes a "kinetic determination of stoichiometry" and stands as independent evidence on this point.

Kinetic studies were carried out at different temperatures to evaluate activation parameters for three different reactions, those of ethyl bromide, ethyl iodide, and benzyl chloride. These data are given in Table V.

The ready solvolysis of *t*-BuBr in 50% aqueous *tert*-butyl alcohol required a change to a different solvent. The halide solutions were made up in dry THF, and reaction was initiated by mixing with a solution of the Cr(II) complex in aqueous THF to give a solvent finally containing 85% aqueous THF. For purposes of rate comparisons, calibration experiments were done with C<sub>2</sub>H<sub>5</sub>Br in this solvent; it reacts 1.4 times slower than in 50% aqueous *tert*-butyl alcohol. Similarly, the low solubility of 1-adamantyl bromide required the use of methanol. The kinetic data (Table III) were obtained in 1% aqueous methanol, and, again, runs with *n*-C<sub>3</sub>H<sub>7</sub>Br were carried out to show the effect of the solvent change, which in this case was a 20-fold acceleration.

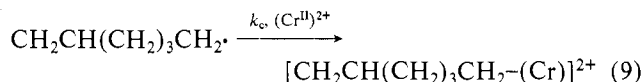
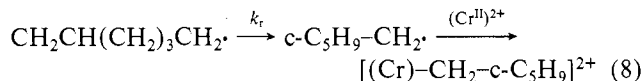
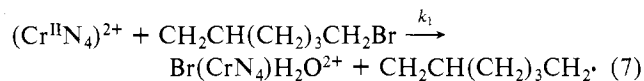
Experiments were done to show that the reaction of CH<sub>3</sub>I and the Cr(II) complex produces the methylchromium complex in each of the solvent mixtures. This was demonstrated<sup>1</sup> by showing that the products reacted identically with CH<sub>3</sub>Hg<sup>+</sup>, which would not be the case were other organochromium complexes formed. That is to say, the methyl radical preferentially combines with the Cr(II) complex rather than abstracting hydrogen from solvent:



A second stage of reaction was seen during the reaction of *t*-BuBr. This is thought to be the decomposition of the corresponding organochromium complex. The secondary complexes and the neopentyl complex also show considerably

less stability toward decomposition than the primary complexes or the ion (1-adamantyl)Cr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup> although the rates of decomposition were not determined.

**Rate of Radical Capture.** Evidence for a mechanism in which a carbon-centered free radical occurs as an intermediate was obtained, as done by Kochi and Powers<sup>9b</sup> for the reaction of the "Cr<sup>II</sup>-en" complex, by reaction of Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup> with 6-bromo-1-hexene. The 5-hexenyl radical derived therefrom is known<sup>28</sup> to cyclize to the cyclopentylmethyl radical. Consequently, the relative amounts of two organochromium products not only provide confirmation of the mechanism but also provide a value for the rate constant for the radical capture reaction of R· with the Cr(II) complex (eq 7-9). The organochromium(III) products are decomposed



by base to the corresponding hydrocarbons for GC analysis. The expression for  $k_c$  for a run with a large excess of chromium(II) is given as eq 10. On the basis of the known value<sup>28</sup>

$$k_c = k_r \frac{[1\text{-hexene}]}{[\text{methylcyclopentane}]} \Big/ [(\text{Cr}^{\text{II}})^{2+}]_{\text{av}} \quad (10)$$

for  $k_r = 1 \times 10^5$  s<sup>-1</sup>, the results summarized in Table VI give the average value of  $k_c = (0.9 \pm 0.2) \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>.

**Reactions of Geminal Halides.** Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup> reacts readily with BrCH<sub>2</sub>Cl ( $k_{\text{RX}} = 42$  M<sup>-1</sup> s<sup>-1</sup>) and ClCH<sub>2</sub>CN ( $k_{\text{RX}} = 314$  M<sup>-1</sup> s<sup>-1</sup>), but no organochromium product was detected by spectral means or by ion-exchange separation. In contrast Cr<sup>2+</sup>(aq) reacts with the former to produce CrCH<sub>2</sub>Cl<sup>2+</sup>. The products in the Cr([15]aneN<sub>4</sub>)<sup>2+</sup> reactions consist of the

Table III. Kinetic Data<sup>a</sup> for Reactions of Secondary and Tertiary Organic Halides with *trans*-(H<sub>2</sub>O)<sub>2</sub>Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup>

halide	10 <sup>2</sup> [RX] <sub>0</sub> , M	k <sub>RX</sub> , M <sup>-1</sup> s <sup>-1</sup>	halide	10 <sup>2</sup> [RX] <sub>0</sub> , M	k <sub>RX</sub> , M <sup>-1</sup> s <sup>-1</sup>	
<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br	1.95	1.96	<i>c</i> -C <sub>6</sub> H <sub>11</sub> Br	1.43	0.853	
	1.95	2.03		1.83	0.886	
	4.80	1.85		2.92	0.771	
	4.80	2.02		3.73	0.824	
	4.80	1.88		4.40	0.823	
	6.80	1.95		5.18	0.859	
	6.80	1.97			av 0.836 ± 0.040	
	6.80	1.82		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Br <sup>b</sup>	4.46	6.6
	7.76	1.88			5.85	6.1
	7.76	1.71				av 6.3 ± 0.4
<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	5.0	4.96	(1-adamantyl)Br <sup>d</sup>	3.63	cor 9.0 <sup>c</sup>	
	5.0	4.90		3.63	19.9	
		av 4.93 ± 0.04		3.63	18.7	
<i>c</i> -C <sub>5</sub> H <sub>9</sub> Br	1.95	5.12		3.63	19.3	
	4.75	4.69			av 19.4 ± 0.5	
	4.75	4.67		cor 0.98 <sup>e</sup>		
	9.45	4.59				
		av 4.77 ± 0.24				

<sup>a</sup> At 25.0 °C, μ = 0.20 M, in 1:1 *t*-BuOH/H<sub>2</sub>O, except as noted. <sup>b</sup> In 15:85 H<sub>2</sub>O/THF. <sup>c</sup> k<sub>RX</sub> × 1.4, corrected to 1:1 *t*-BuOH/H<sub>2</sub>O based on the rates of C<sub>2</sub>H<sub>5</sub>Br in both solvents. <sup>d</sup> In 1:99 H<sub>2</sub>O/CH<sub>3</sub>OH. <sup>e</sup> k<sub>RX</sub>/19.9, corrected to 1:1 *t*-BuOH/H<sub>2</sub>O based on the rates of *n*-C<sub>3</sub>H<sub>7</sub>Br in both solvents.

Table IV. Kinetic Data<sup>a</sup> for Reactions of Benzyl Halides with Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup>

10 <sup>2</sup> [(Cr <sup>II</sup> ) <sup>2+</sup> ] <sub>0</sub> , M	10 <sup>2</sup> [RX] <sub>0</sub> , M	k <sub>RX</sub> , M <sup>-1</sup> s <sup>-1</sup> (no. of detns)
	A. C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	
0.022	0.130	3.59 × 10 <sup>2</sup>
0.022	0.205	(3.54 ± 0.03) × 10 <sup>2</sup> (3)
0.022	0.304	(3.21 ± 0.03) × 10 <sup>2</sup> (2)
0.022	0.569	(3.24 ± 0.02) × 10 <sup>2</sup> (2)
0.022	0.869	(3.32 ± 0.02) × 10 <sup>2</sup> (3)
		av (3.23 ± 0.05) × 10 <sup>2</sup>
	B. C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	
0.316	0.017	(2.06 ± 0.08) × 10 <sup>4</sup> (4) <sup>b</sup>
0.167	0.017	(1.94 ± 0.07) × 10 <sup>4</sup> (3) <sup>b</sup>
0.011	0.042	(1.98 ± 0.20) × 10 <sup>4</sup> (4)
0.011	0.127	(1.60 ± 0.14) × 10 <sup>4</sup> (6)
0.011	0.212	(2.04 ± 0.16) × 10 <sup>4</sup> (6)
0.011	0.294	(1.94 ± 0.16) × 10 <sup>4</sup> (7)
0.011	0.356	(1.93 ± 0.08) × 10 <sup>4</sup> (6)
0.011	0.420	(1.86 ± 0.06) × 10 <sup>4</sup> (3)
		av (1.91 ± 0.06) × 10 <sup>4</sup>

<sup>a</sup> At 25.0 °C and μ = 0.20 M in 1:1 H<sub>2</sub>O/*t*-BuOH. <sup>b</sup> With excess (Cr<sup>II</sup>)<sup>2+</sup>; owing to the stoichiometric factor, these values have been multiplied by 2 for consistency with the remaining values (see text).

complexes X(Cr<sup>III</sup>N<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup> (X = Br, Cl) and of (H<sub>2</sub>O)<sub>2</sub>(Cr<sup>III</sup>N<sub>4</sub>)<sup>3+</sup>. The organic products from BrCH<sub>2</sub>Cl are C<sub>2</sub>H<sub>4</sub>, CO<sub>2</sub>, and CH<sub>4</sub> in ratios of >10<sup>3</sup>:30:1. Cr([15]aneN<sub>4</sub>)<sup>2+</sup> reacts with BrCCl<sub>3</sub>, apparently in several stages, to form CO (largely), CH<sub>4</sub>, and possibly CO<sub>2</sub>.

### Interpretation and Discussion

In the paragraphs that follow we summarize the mechanistic evidence and conclude that the two-step radical mechanism (eq 1-3) is generally applicable. If this is the case, a comparison of the kinetic relationship of eq 6 with this mechanism gives values of *k*<sub>1</sub> as 2*k*<sub>RX</sub>.

The following points are summarized in support of the mechanism of eq 1-3 as applied to the present reactions: (1)

the reaction occurs with a 2:1 stoichiometry of (Cr<sup>II</sup>):RX; (2) approximately equimolar quantities of organo- and halochromium(III) complexes are produced; (3) the reaction rate shows a first-order dependence on each reactant concentration; (4) alkyl halides react in the order tertiary > secondary > primary in accord with the stabilities of the free radical produced (this comparison requires calibration of rate effects in different solvents as explained previously); (5) for a given group R, the halides react in the order iodide > bromide > chloride; (6) products from the reaction of 6-bromo-1-hexene indicate the intermediate production of carbon-centered free radicals; (7) the derived rate constant for combination of Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup> with R• (=cyclopentylmethyl radical) is *k*<sub>c</sub> = 0.9 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>, a value comparable to that for the "Cr<sup>II</sup>-en" reagent (4 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>) but some 5-10 times slower than directly measured values<sup>7</sup> for Cr<sup>2+</sup>(aq) + R• combinations.

Comparisons between the present reaction and certain related processes provide further support for the assigned mechanism. On the one hand Cr<sup>2+</sup>(aq) fails to react with simple alkyl halides, even iodides. Complexation by nitrogen donor ligands affects the reaction, whether the "Cr-en" reagent, CrSO<sub>4</sub> in aqueous Me<sub>2</sub>SO, or the present Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup> complex is used. Presumably the effects are due to the much greater reducing strengths of these Cr(II) complexes as compared to the hydrated cation. The rate acceleration for Cr([15]aneN<sub>4</sub>)<sup>2+</sup> compared to that for Cr<sup>2+</sup>(aq),<sup>9b</sup> toward benzyl bromide, is 5 × 10<sup>4</sup> ((2 × 10<sup>4</sup>)/0.4). This effect lies outside that expected were the acceleration to be attributed solely to the change in E<sup>0</sup>. Were this the case, the difference of 0.17 V might be expected, on the basis of a Marcus theory correlation, to produce an increase in rate of (10<sup>0.17/0.059</sup>)<sup>1/2</sup> ≈ 30. That the effect is larger than this might be attributed to a self-exchange rate constant between X(Cr<sup>III</sup>)H<sub>2</sub>O<sup>2+</sup> and (H<sub>2</sub>O)<sub>2</sub>(Cr<sup>II</sup>)<sup>2+</sup> much larger than that for (H<sub>2</sub>O)<sub>5</sub>CrX<sup>2+</sup> and Cr(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, but no independent evidence on this point is available.

Table V. Activation Parameters for Reactions of Selected Organic Bromides with *trans*-(H<sub>2</sub>O)<sub>2</sub>Cr([15]aneN<sub>4</sub>)<sup>2+</sup>

	k <sub>RX</sub> , M <sup>-1</sup> s <sup>-1</sup>				ΔH <sup>‡</sup> , kJ mol <sup>-1</sup>	ΔS <sup>‡</sup> , J mol <sup>-1</sup> K <sup>-1</sup>
	11.0 °C	18.0 °C	25.0 °C	35.0 °C		
C <sub>2</sub> H <sub>5</sub> Br	0.0662	0.0954	0.164	0.300	44.2 ± 1.0	-112 ± 4
C <sub>2</sub> H <sub>5</sub> I	0.157	0.253	0.414	0.695	44.1 ± 1.3	-104 ± 4
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	242 <sup>a</sup>	323 <sup>b</sup>	384 <sup>c</sup>	411 <sup>d</sup>	30.6 ± 1.6	-94 ± 5

<sup>a</sup> 18.5 °C. <sup>b</sup> 25.0 °C. <sup>c</sup> 27.4 °C. <sup>d</sup> 30.3 °C.

Table VI. Rate of Radical Capture

$10^3[\text{Cr}^{\text{II}}\text{[15]aneN}_4^{2+}]_{\text{av}}$	$10^3[\text{BrCH}_2\text{-(CH}_2\text{)}_3\text{-CHCH}_2]_0, \text{M}$	$R^a$	$10^{-6}k_c, \text{M}^{-1} \text{s}^{-1}$
22.1	2.87	1.60	7.2
44.6	4.84	4.88	10.9
			av 9.1 ± 1.8

<sup>a</sup> [1-hexene]/[methylcyclopentane]; determined by GC analysis.<sup>b</sup> From eq 10.Table VII. Values of  $k_{\text{RX}}$  ( $\text{M}^{-1} \text{s}^{-1}$ ) for Three Halogen-Abstracting M(II) Complexes

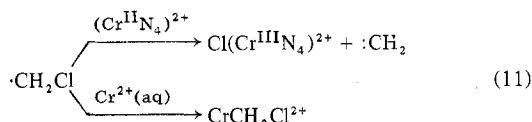
halide	$(\text{Cr}^{\text{II}}\text{[15]aneN}_4^{2+})^{2+}$	"Cr <sup>II</sup> -en" reagent	$\text{Co}(\text{CN})_5^{3-}$
RBr <sup>a</sup>	0.16	0.2	
RBr <sup>b</sup>	1.8	2	
RI <sup>a</sup>	0.41		0.086
RI <sup>b</sup>	4.9	$10^2$	2.4
RBr <sup>c</sup>	10	10	
PhCH <sub>2</sub> Cl	$3.2 \times 10^2$		$1 \times 10^{-3}$
PhCH <sub>2</sub> Br	$1.9 \times 10^4$		4.6

<sup>a</sup> Primary. <sup>b</sup> Secondary. <sup>c</sup> Tertiary.

Consider the rates of the present family of reactions and of the "Cr<sup>II</sup>-en" reagent and of  $\text{Co}(\text{CN})_5^{3-}$  with various RX's. The available data, summarized in Table VII, are sketchy, although, aside from the unusually low reactivity of  $\text{Co}(\text{CN})_5^{3-}$  with benzyl halides, other rates are comparable in actual as well as relative magnitude. This, too, supports a similarity between the mechanisms.

Values of  $\Delta H^\ddagger$  are, as expected, much below the bond dissociation energies of a carbon-halogen bond. They appear quite consistent with the atom-abstraction process being rate limiting as shown in eq 1. The relatively large, negative values of  $\Delta S^\ddagger$  are consistent with a highly ordered transition state and with values found for related reactions.<sup>29</sup>

The dihalides may react to produce carbene- or carbenoid-type intermediates.<sup>11c</sup> The major product, CO, from  $\text{BrCCl}_3$ , may arise from reaction between dichlorocarbene and water.<sup>30</sup> Methylene carbene may be responsible for ethylene formation in the reaction of  $\text{BrCH}_2\text{Cl}$  with  $\text{Cr}^{\text{II}}\text{[15]aneN}_4^{2+}$ , although it is difficult to reconcile lack of organochromium product in this case, considering a nearly quantitative yield of  $\text{CrCH}_2\text{Cl}^{2+}$  upon reaction of  $\text{BrCH}_2\text{Cl}^{2+}$  and  $\text{Cr}^{2+}(\text{aq})$ . This must surely reflect the stronger reducing strength of the  $(\text{Cr}^{\text{II}}\text{N}_4)^{2+}$  species, such that halogen abstraction (either from the carbene as depicted or from a transient (chloromethyl)-chromium complex) occurs in preference to coupling of Cr(II) and the radical



**Registry No.**  $\text{ICr}(\text{[15]aneN}_4)\text{H}_2\text{O}^{2+}$ , 70832-92-7;  $\text{BrCr}(\text{[15]aneN}_4)\text{H}_2\text{O}^{2+}$ , 70832-93-8;  $\text{ClCr}(\text{[15]aneN}_4)\text{H}_2\text{O}^{2+}$ , 70832-94-9;  $(\text{H}_2\text{O})_2\text{Cr}(\text{[15]aneN}_4)^{3+}$ , 70832-95-0;  $\text{CH}_3\text{Cr}(\text{[15]aneN}_4)\text{H}_2\text{O}^{2+}$ , 70832-96-1;  $\text{C}_2\text{H}_5\text{Cr}(\text{[15]aneN}_4)\text{H}_2\text{O}^{2+}$ , 70832-97-2;  $n\text{-C}_3\text{H}_7\text{Cr}(\text{[15]aneN}_4)\text{H}_2\text{O}^{2+}$ , 70832-98-3;  $n\text{-C}_4\text{H}_9\text{Cr}(\text{[15]aneN}_4)\text{H}_2\text{O}^{2+}$ , 70832-99-4;  $i\text{-C}_3\text{H}_7\text{Cr}(\text{[15]aneN}_4)\text{H}_2\text{O}^{2+}$ , 70833-00-0;  $c\text{-C}_6\text{H}_{11}\text{Cr}(\text{[15]aneN}_4)\text{H}_2\text{O}^{2+}$ , 70833-01-1; (1-adamantyl)Cr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup>, 70833-02-2; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cr([15]aneN<sub>4</sub>)H<sub>2</sub>O<sup>2+</sup>, 70833-03-3; *trans*-(H<sub>2</sub>O)<sub>2</sub>Cr<sup>II</sup>([15]aneN<sub>4</sub>)<sup>2+</sup>, 70833-04-4; CH<sub>3</sub>I, 74-88-4; C<sub>2</sub>H<sub>5</sub>Br,

74-96-4; C<sub>2</sub>H<sub>5</sub>I, 75-03-6; *n*-C<sub>3</sub>H<sub>7</sub>Br, 106-94-5; *n*-C<sub>4</sub>H<sub>9</sub>Br, 109-65-9; (CH<sub>3</sub>)<sub>2</sub>CCH<sub>2</sub>Br, 630-17-1; CH<sub>2</sub>=CH(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>Br, 2695-47-8; *i*-C<sub>3</sub>H<sub>7</sub>Br, 75-26-3; *i*-C<sub>3</sub>H<sub>7</sub>I, 75-30-9; *c*-C<sub>3</sub>H<sub>7</sub>Br, 137-43-9; *c*-C<sub>6</sub>H<sub>11</sub>Br, 108-85-0; *i*-C<sub>4</sub>H<sub>9</sub>Br, 507-19-7; (1-adamantyl)Br, 768-90-1; C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>Cl, 100-44-7; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br, 100-39-0; Cr(en)<sub>2</sub><sup>2+</sup>, 15525-39-0; Co(CN)<sub>5</sub><sup>3-</sup>, 14971-18-7; [*trans*-*n*-PrCr([15]aneN<sub>4</sub>)H<sub>2</sub>O](ClO<sub>4</sub>)<sub>2</sub>, 70879-09-3; [*trans*-EtCr([15]aneN<sub>4</sub>)NCS]ClO<sub>4</sub>, 70833-06-6.

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- (18) We are grateful to Mr. G. D. Flesch for the mass spectrometric determinations.
- (19) We gratefully acknowledge Mr. Larry D. Kissinger and Mr. Terry Marshall for assistance in these measurements.
- (20) The assistance of Mr. Garry Kirker with the electrochemical determination is gratefully acknowledged.
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- (22) The crystallographic data will be published separately. These results show that the compound [ClCr([15]aneN<sub>4</sub>)H<sub>2</sub>O](I)<sub>2</sub>·2H<sub>2</sub>O has *trans* structures with a nitrogen conformation agreeing with that predicted by strain-energy calculations<sup>14b</sup> for this chelate system.
- (23) The formulation of the first and third bands, the inorganic Cr(III) complexes, as monohydroxo species in solutions of pH ~ 5 is consistent with their charges as judged from elution behavior and with their fast conversion to the aquo complexes upon acidification; compare (H<sub>2</sub>O)<sub>2</sub>Cr(en)<sub>2</sub><sup>3+</sup>, pK<sub>a</sub> = 4.1, and (H<sub>2</sub>O)<sub>2</sub>Cr(en)(NCS)<sub>2</sub><sup>2+</sup>, pK<sub>a</sub> = 6 (Garner, C. S.; House, D. A. *Transition Met. Chem.* **1970**, *6*, 177).
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