Table V. Comparison of Observed Fragment Ion Intensity Ratios with Those Predicted for Random Fragmentation[a] of $^{*}B^{10}B_3H_{10}$

Species	Ion intensity ratios: Random	Obsd
$^{10}B_3/^{10}B_2{}^{11}B$	2.4	≥ 2.9
$^{10}B_3/^{10}B^{11}B_2$	18	$\simeq 49$
$^{10}B_2/^{10}B^{11}B$	3.7	≤ 3.4
$^{10}B_2/^{11}B_2$	54	$\simeq 100$
$^{10}B/^{11}B$	7.3	5.2 to 6.4

[a] *Cf.* Table IVb.[24*]

It was found, however, that the best fits were obtained using the significantly different stripping ratios shown in the last column.

It appears that $B_3H_x{}^+$, $B_2H_x{}^+$, and $BH_x{}^+$ ions result, in part, from dissociation and/or ionization processes in which the ion fragments are lost in a specific fashion and which bear a structural relationship to the original tetraborane molecules. Therefore, $B_3H_x{}^+$ ions are formed by the loss of a monoboron species from the 2 or 4 positions of tetraborane. Since the two-boron fragments contain considerably more ^{11}B than would be expected if they arose exclusively from $B_3H_x{}^+$ ions, it appears that direct formation of $B_2H_x{}^+$ ions from tetraborane is a significant process; and, since the $^{10}B/^{11}B$ ratios of the one-boron fragment ions are consistently lower than 7.3 : 1.0, preferential loss of $BH_x{}^+$ ions from the 2 or 4 positions of tetraborane must occur. It must be emphasized, however, that at an ionizing voltage of 70 ev contributions to the spectrum from random dissociation processes, dissociations of partially scrambled molecules, and ions resulting from direct cleavage of tetraborane molecules upon electron impact must be considered.

The metastable transitions observed in the zero source contact spectra of $^{10}B_4H_{10}$ and $^{10}B_4D_{10}$ in part substantiate the previously reported[2] stepwise dissociation process leading to the formation of $B_4H_x{}^+$ ions; however, the data obtained from the specifically labeled sample, μ-$^{10}B_4H_9D$, provides no evidence for an energetically favored process involving loss of hydrogen or deuterium from specific positions in the molecules, since the spectrum of the scrambled material is unchanged (within the limits of experimental error) from that of the labeled material. Earlier work on μ-$^{n}B_4D_9H$ has shown that the label atom drifts nonpreferentially to all positions of the molecule upon scrambling;[29] therefore, it is necessary to conclude that at an ionizing voltage of 70 ev, hydrogen atoms are lost by random processes or that the deuterium and hydrogen atoms of the labeled sample become isotopically scrambled prior to dissociation.

It had been concluded previously[2] that H and D are lost from specific positions during dissociation of $B_4H_x{}^+$ ions on the basis of a mass spectral analysis of a mixture of partially deuterated tetraboranes assumed to contain a greater-than-statistical concentration of 1,3-dideuteriotetraborane molecules.[3] The results of the $^{n}B_2D_6$–$^{n}B_4H_{10}$ experiment (Figure 4, Table IV) do not indicate that a preferential exchange process involving only the 1(3) positions of tetraborane exists. Also, as expected from earlier work,[9–11] considerable tetraborane decomposition and deuterated pentaborane-11 formation took place during the exchange. It seems possible that a reinterpretation of the previous $^{n}B_2D_6$–$^{n}B_4H_{10}$ exchange data, considering tetraborane decomposition, and B_2D_6 exchange processes with both pentaborane and tetraborane might lead to a simpler explanation for the observed kinetic exchange data.

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(29) A. D. Norman and R. Schaeffer, unpublished work.

Transition Metal Complexes of Triethylenetetramine. III. *cis*-α-Diacidotriethylenetetraminechromium(III) Complexes[1]

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Abstract: The synthesis, characterization, properties, and infrared and visible absorption spectra of *cis*-α-[Cr(trien)Cl_2]Z (Z = Cl, ClO_4, NCS, NO_3), *cis*-α-[Cr(trien)$(NCS)_2$]Z (Z = Cl, NCS, NO_3), *cis*-α-[Cr(trien)$(N_3)_2$]Br, and α-[Cr(trien)ox]Z (Z = Br, ClO_4, NCS) are described.

Previous papers in this series[2,3] have described some nickel(II) and copper(II) complexes containing triethylenetetramine ligand (N,N′-bis(2-aminoethyl)-ethylenediamine, $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, abbreviated trien). In the present paper we report the synthesis, characterization, properties, and infrared and visible absorption spectra of some diacido-

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(1) This work was partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University of California.

(2) D. A. House and N. F. Curtis, *J. Chem. Soc.*, 3149 (1963).

(3) N. F. Curtis and D. A. House, *ibid.*, 6194 (1965).

triethylenetetramine complexes of chromium(III) and compare them with similar complexes of cobalt(III)[4–14] and rhodium(III).[8,13,15,16] The only trien complex of chromium(III) previously reported[17] is *cis*-[Cr(trien)Cl$_2$]Cl·H$_2$O, which has been assigned an α configuration[13] (see Figure 2).

Results

Properties of ***cis*-α-Cr(trien)Cl$_2^+$.** Originally *cis*-α-[Cr(trien)Cl$_2$]Cl·H$_2$O was prepared by reacting anhydrous chromium(III) chloride and trien together under anhydrous conditions in the absence of a solvent.[17] We have developed a simpler procedure, using zinc powder as a reducing catalyst[18] and anhydrous methanol as solvent. Infrared and visible absorption spectra show that the compounds formed by the two different methods are identical. We have also isolated the same product by reacting anhydrous chromium(III) chloride and trien together in ethylene glycol at 130–140°.

These methods differ substantially from those used previously to make the cobalt(III) and rhodium(III) analogs. The former were prepared either by air oxidation of cobalt(II) chloride in aqueous trien solution (followed by treatment with concentrated hydrochloric acid)[4] or by chloride anation of the *cis*-α isomer of the chloroaquo,[8] diaquo,[8] or dinitro[14] complexes. The latter were made by prolonged treatment of sodium hexachlororhodate(III) in aqueous trien solution[8] or from rhodium(III) chloride 3-hydrate and trien 4-hydrochloride in aqueous solution, with gradual neutralization of the hydrochloric acid by potassium hydroxide.[15] Attempts to prepare *cis*-α-Rh(trien)Cl$_2^+$ by direct reaction of either rhodium(III) chloride 3-hydrate or potassium pentachloroaquorhodate(III) with free trien leads to the formation of very insoluble yellow substances.[15]

The water of crystallization is lost from *cis*-α-[Cr(trien)Cl$_2$]Cl·H$_2$O on heating the solid at 110° for 16 hr as evidenced by the required weight loss and disappearance of the OH stretching and bending vibrations at 3550 and 1620 cm^{-1} in the infrared spectrum. The salt is readily soluble in water and also in concentrated hydrochloric acid, from which it can be precipitated by addition of absolute ethanol. In aqueous solution at 25° *cis*-α-Cr(trien)Cl$_2^+$ appears to aquate extensively in 0.5–2 hr. This aquation behavior parallels that of the cobalt(III) analog, for which the half-time for aquation of the first chloro ligand in 0.1 *F* nitric acid or 0.01 *F* perchloric acid is 80 min. at 25°,[5,9,11] whereas the rhodium(III) analog aquates extremely slowly.[8]

The perchlorate, nitrate, and thiocyanate 1-hydrate are all isolated from cold aqueous solutions of the chloride 1-hydrate by addition of the sodium salt of the appropriate anion, and all are less soluble in water than the parent. All four salts are insoluble in acetone, ethanol, and 2-propanol at 25°.

The chloro ligands in *cis*-α-Cr(trien)Cl$_2^+$ are readily replaced by thiocyanate, azide, and oxalate ions to form the corresponding *cis*-α-Cr(trien)(NCS)$_2^+$, *cis*-α-Cr(trien)(N$_3$)$_2^+$, and α-Cr(trien)ox$^+$ ions (ox = oxalate ion). Presumably this ease of replacement of the chloro ligand would apply to the cobalt(III) analog, where it has been observed[8,14] for oxalate ion. Nucleophilic displacement of the chloro ligands of the rhodium(III) analog are exceedingly slow except in the presence of sodium borohydride.[8]

Attempts to isomerize *cis*-α-Cr(trien)Cl$_2^+$ to the *trans* configuration by reaction with mercury(II) bromide in concentrated hydrobromic acid (a method used[19] to convert *cis*-[Cr(en)$_2$Cl$_2$]Cl (en = ethylenediamine) to *trans*-[Cr(en)$_2$Br$_2$]HgBr$_3$) led to decomposition, and heating of the moist chloride 1-hydrate salt at 180° for 15 min (the method used[8] to isomerize *cis*-[Co(trien)Cl$_2$]Cl quantitatively and rapidly to the *trans* form) gave only the unchanged anhydrous starting material. Heating of the moist chloride 1-hydrate salt for 48 hr gave a solid which had an infrared spectrum essentially like that of the starting material, but a visible absorption spectrum suggesting that some aquation may have occurred. An unsuccessful attempt was also made to isomerize *cis*-α-Cr(trien)Cl$_2^+$ to the *cis*-β form by treatment with sodium hydroxide solution, followed by addition of excess concentrated hydrochloric acid and storage overnight in a refrigerator, a procedure which converts the *cis*-α cobalt(III) analog to the *cis*-β form quantitatively.[13]

Properties of ***cis*-α-Cr(trien)(NCS)$_2^+$.** The chloro ligands in *cis*-α-Cr(trien)Cl$_2^+$ are slowly displaced by thiocyanate ion at 25°, and in the presence of excess thiocyanate the sparingly water-soluble *cis*-α-[Cr(trien)(NCS)$_2$]NCS is precipitated from the aqueous solution. This salt is readily soluble, however, in acetone and methanol, and from an acetone solution the corresponding nitrate 1-acetone and chloride can be precipitated by addition of 8 *F* nitric acid or 6 *F* hydrochloric acid, respectively. The latter two salts are readily soluble at 25° in water but insoluble in acetone and methanol.

The acetone in the crystal lattice of *cis*-α-[Cr(trien)(NCS)$_2$]NO$_3$·(CH$_3$)$_2$CO is retained very strongly and is not lost on heating the solid for 16 hr at 120°; it is removed, however, by heating for 16 hr at 160°.

Treatment of any of these three salts in concentrated hydrochloric acid with chlorine gas at 0° yields a violet solution with a visible absorption spectrum corresponding to that of *cis*-α-Cr(trien)Cl$_2^+$.

The cobalt(III) and rhodium(III) analogs have apparently not been made.

Properties of ***cis*-α-Cr(trien)(N$_3$)$_2^+$.** The bromide is prepared by heating an aqueous solution of *cis*-α-[Cr(trien)Cl$_2$]Cl·H$_2$O in the presence of excess sodium azide and then adding excess potassium bromide. The

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(4) F. Basolo, *J. Am. Chem. Soc.*, 70, 2634 (1948).

(5) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

(6) B. Das Sarma and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 77, 5480 (1955).

(7) J. Selbin and J. C. Bailar, Jr., *ibid.*, 82, 1524 (1960).

(8) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3193 (1963).

(9) A. M. Sargeson and G. H. Searle, *Nature*, **200**, 356 (1963).

(10) A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964).

(11) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

(12) D. Dollimore, R. D. Gillard, and E. D. McKenzie, *J. Chem. Soc.*, 4479 (1965).

(13) D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

(14) E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **87**, 4458 (1965).

(15) S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).

(16) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3594 (1963).

(17) O. Kling and H. L. Schläfer, *Z. Anorg. Allgem. Chem.*, **313**, 187 (1961).

(18) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, pp 86, 87.

(19) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

Table I. Frequencies[a] (cm^{-1}) of α-[Cr(trien)ox]Br · $2H_2O$ and of *cis*-α Isomers of [Cr(trien)Cl_2]Cl · H_2O, [Cr(trien)$(NCS)_2$]Cl, and [Cr(trien)$(N_3)_2$]Br (KBr Disk)

-ox	-$(N_3)_2$	-$(NCS)_2$	-Cl_2	-ox	-$(N_3)_2$	-$(NCS)_2$	-Cl_2
3550 m				1255 w			
3430 m	3400 w br	3430 w br	3420 m br	1245 m sh	1247 w	1245 w	1240 w
3360 m				1234 s			
				1216 w	1216 w	1212 w	1220 w
3280 s	3215 s	3200 s	3245 s				
3220 s	3180 s	3165 s	3210 s	1182 m sh	1188 m	1188 m sp	1187 w
3135 s	3140 s	3100 s sh	3180 s	1172 s		1166 m	1140 m } sp
3085 s	3100 s	3080 s	3100 s br	1154 m br	1150 m sp	1158 m	1135 m }
				1109 m	1112 m sp	1118 w	1118 w
2960 m	2950 m sp	2970 m				1100 m sp	1100 w
2940 m	2930 m	2950 m	2945 m br				
2910 m				1097 w	1090 w		1087 w
2880 m	2880 m sp	2880 m sp	2880 m	1083 m sh			
2865 m			2860 m	1070 s			
1695 vs br	2090 vs	2065 vs br		1049 m } sp	1052 s br	1050 s br	1058 s } sp
1680 vs	2055 vs			1044 m }			1044 s }
1660 vs			1615 m br				
				1030 s	1033 m }	1035 m } sp	
1587 s	1587 m br	1587 m br	1572 m br		1023 s } sp	1018 s br }	1018 s br
1565 s sp					1010 m }		
				997 s } sp	997 s } sp	998 s } sp	997 s sp
1482 w	1477 m } sp		1482 m	988 m }	988 m }	985 w }	985 w
1470 sh	1472 m }	1472 m sp	1471 m				
1454 s sp	1454 m br	1450 m	1452 m sp		962 m		975 w
1447 sh	1445 m	1442 m	1449 m		949 m		
1438 sh	1436 m	1432 m sp	1430 s sp	898 m br	888 w	892 m	886 m
		1410 w		865 w } sp	857 m br	860 m sp	860 m
				859 w }			
1381 s } sp	1390 w	1390 w	1392 w	825 w			
1375 s }	1379 w	1376 m	1378 w	800 s	810 w	810 w	812 w
		1365 w	1368 w		788 m	786 s	785 m
1325 w	1356 m	1348 w			761 m	760 s	762 m
1320 w	1332 m	1330 m sp	1330 m			728 s	730 m br
1310 w	1317 m	1312 m	1212 m br		711 s	713 s	702 w br
				690 m	680 w	692 w	
1295 w	1290 w	1290 w	1291 w	660 m	640 m	655 w	653 w
1280 m	1272 m	1274 m	1273 w	610 w	606 m	618 m	609 m
1265 w		1265 w	1265 w		591 m		

[a] Intensities estimated as follows: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder; sp, split.

compound is soluble in water but insoluble in methanol, ethanol, and acetone. The cobalt(III) analog has been reported,[13] although the method of its synthesis has not been given. The rhodium(III) analog has not been reported.

Properties of α-Cr(trien)ox$^+$. The orange-red α-Cr(trien)ox$^+$ can be obtained either from *cis*-α-Cr(trien)Cl_2^+ by reaction with ammonium oxalate 1-hydrate or by treating potassium trioxalatochromate(III) 3-hydrate with trien in aqueous solution. The product can be isolated as the bromide 2-hydrate salt using either of these two methods, and the infrared spectra show the products to be identical. The bromide 2-hydrate salt is readily soluble in water, and the sparingly water-soluble perchlorate 1-hydrate or thiocyanate salts can be obtained by metathesis.

The cobalt(III) analog has been synthesized from *cis*-α-[Co(trien)Cl_2]Cl by reaction with oxalate ion,[8,14] as well as by the action of oxalic acid on the carbonato complex.[4] Attempts[8] to prepare the Rh(trien)ox$^+$ ion by treating *cis*-α-Rh(trien)Cl_2^+ with oxalate ion in solution, under the same conditions which work for the cobalt(III) analog, failed.

Spectra. The visible absorption spectra of these chromium trien complexes in 0.1 *F* hydrochloric acid at *ca.* 22° are shown in Figure 1. The infrared frequencies of the chloride or bromide salts are given in Table I; the measured frequencies of certain bands of the perchlorate and nitrate salts exhibit some variations from those of analogous bands of the halide salts, presumably because of cation–anion interactions in the crystal some of which may arise from hydrogen bonding involving oxygen atoms of the perchlorate and nitrate anions.

The infrared spectrum of *cis*-α-[Cr(trien)Cl_2]NCS · H_2O has a single intense band at 2050 cm.$^{-1}$ due to the C≡N stretching frequency in the anionic thiocyanate and single medium-intensity bands at 3525 and 1619 cm^{-1} due to the OH stretching and bending modes of the water of crystallization.

The spectrum of *cis*-α-[Cr(trien)$(NCS)_2$]NO_3 · $(CH_3)_2$CO shows an intense band at 2065 cm^{-1} due to the coordinated NCS group (C≡N stretch) and also an intense band at 1700 cm^{-1} assigned to the carbonyl stretching frequency of the lattice-bonded acetone.

The oxalatotriethylenetetramine compounds exhibit three bands at 1658, 1675, and 1694 cm^{-1} due to the carbonyl stretching frequencies of the coordinated oxalate.

Discussion

There are three possible geometric isomers of Cr(trien)X_2^+ (Figure 2). The *cis*-α and *cis*-β isomers are theoretically capable of existing in optically active forms, which have been resolved[9] for Co(trien)Cl_2^+.

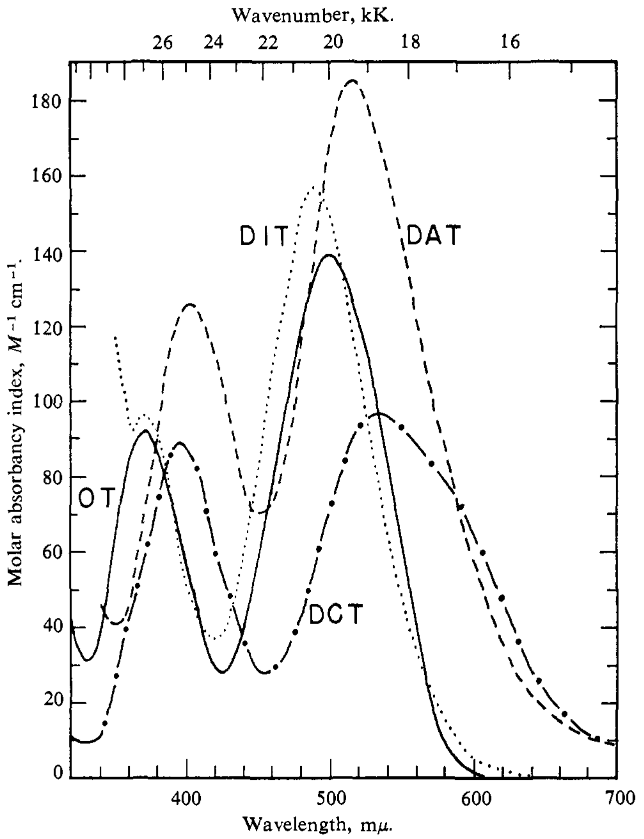
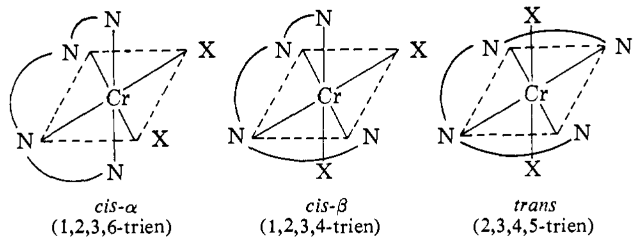


Figure 1. Visible absorption spectra of chromium(III) trien complexes in 0.1 *F* HCl at *ca.* 22°: DCT, *cis*-α-$Cr(trien)Cl_2^+$; DIT, *cis*-α-$Cr(trien)(NCS)_2^+$; DAT, *cis*-α-$Cr(trien)(N_3)_2^+$; OT, α-$Cr(trien)ox^+$.

We have not been able to prepare any chromium(III) trien complexes with the *trans* configuration, although at least some of the analogous chromium(III) bis(ethylenediamine) complexes are known in both *cis* and *trans* configurations, and *trans*-$Co(trien)Cl_2^+$ is known.[8–10,12] In the trien complexes the near-planarity of the nitrogen atoms of the trien ligand results in appreciable strain, presumably leading to thermodynamically less stable complexes.

In the cobalt(III) trien system the *cis*-α and *cis*-β isomers have been well characterized and established by several different methods, namely, detection of aquation products,[9] use of rotatory dispersion and circular dichroism curves,[11] and infrared spectra.[13] The first method uses the fact that in the absence of isomerization there will be two different primary aquation products from the *cis*-β isomer (namely, with the H_2O ligand *trans* to a primary and secondary nitrogen, respectively) and a third different primary aquation product from the *cis*-α isomer.

Buckingham and Jones[13] have used infrared frequencies to make configuration assignments for a number of diacidotriethylenetetraminecobalt(III) complexes, as well as for $[Cr(trien)Cl_2]Cl \cdot H_2O$ prepared by the method of Kling and Schlafer.[17] We have found that this compound, to which Buckingham and Jones assign a *cis*-α configuration, has an infrared spectrum identical with that of the compound prepared by our methods. The diisothiocyanato, diazido, and oxalato complexes have been prepared from the *cis*-α dichloro complex by displacement of the chloro ligands and would be expected to have the *cis*-α configuration assuming no rearrangement of the trien ligand. This assumption is supported by the infrared spectra of these complexes (Table I).



cis-α (1,2,3,6-trien)
cis-β (1,2,3,4-trien)
trans (2,3,4,5-trien)

Figure 2. Possible geometric isomers of $Cr(trien)X_2^+$.

The absorption bands of $Co(trien)Cl_2^+$ salts and of several other diacidotriethylenetetraminecobalt(III) compounds in the region of 1560–1600 cm^{-1} have been assigned to the antisymmetric NH_2 bending vibration. In this region the *cis*-α salts have a single strong absorption showing splitting, the *cis*-β salts have two strong-to-medium absorptions with splitting of one band, and *trans*-$[Co(trien)Cl_2]ClO_4$ (the only *trans* complex studied) has only one strong and narrow absorption, showing no observable splitting.[13] Table I shows that the chromium(III) dichloro, diazido, and diisothiocyanato complexes give only one strong-to-medium band in this region, a broad and asymmetrical one indicative of splitting, and thus favoring a *cis*-α assignment. The oxalato complexes, $[Cr(trien)ox]ClO_4 \cdot H_2O$ and $[Cr(trien)ox]NCS$, also exhibit only one band in this region, in agreement with an α configuration (the bidentate oxalato ligand occupies coordination positions which must be *cis* to each other). The presence of two bands for $[Cr(trien)ox]Br \cdot 2H_2O$ is apparently associated with lattice interactions, possibly involving the two waters of crystallization or a different crystal structure. Two facts directly support this conclusion: (1) all of these oxalato complexes have identical visible absorption spectra in aqueous solution; and (2) the two bands are exhibited by $[Cr(trien)ox]Br \cdot 2H_2O$ even when it is prepared from α-$[Cr(trien)ox]ClO_4 \cdot H_2O$ (which has only one band) by rapid metathesis with potassium bromide. Moreover, $[Cr(trien)ox]Br \cdot 2H_2O$ has the same infrared spectrum whether it is synthesized directly from trioxalatochromate(III) anion and trien or from *cis*-α-$[Cr(trien)Cl_2]Cl \cdot H_2O$. In connection with the latter, we note that Kyuno, Boucher, and Bailar[14] report having obtained α-$[Co(trien)ox]Cl$ similarly from *cis*-α-$[Co(trien)Cl_2]Cl$. Since the infrared spectra of all our chromium(III) trien compounds and their cobalt(III) analogs of the same configuration are very similar (absorption bands of the former often being displaced to smaller wavenumbers by *ca.* 15–50 cm^{-1}), further indirect support for our assignment of the α configuration to all our $Cr(trien)ox^+$ compounds comes from a comparison of their infrared spectra with that of β-$[Co(trien)ox]Cl$.[20] The latter has one more band than the $Cr(trien)ox^+$ salts in the 980–1100-cm^{-1} region (see below), from which we infer that these $Cr(trien)ox^+$ compounds are not of the β type (infrared spectra on α-$Co(trien)ox^+$ salts are not available, so a direct comparison cannot be made at this time). Dissolution of $[Cr(trien)ox]Br \cdot 2H_2O$ in 0.1 *F* HCl, followed by ad-

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(20) D. A. Buckingham, private communication.

Table II. Absorption Maxima and Minima in the 320–700-mμ Range for Some Cr(III)–bis(en) and M(III)–trien (M = Co or Cr) Complexes at *ca.* 25°[a]

Complex	λ_{min}, mμ	λ_{max}, mμ	λ_{min}, mμ	λ_{max}, mμ	λ_{min}, mμ	λ_{max}, mμ
cis-α-$Cr(trien)Cl_2^+$ [b,c]		396 (86.7)	455 (28.5)	535 (95.5)		580 (79) sh
cis-$Cr(en)_2Cl_2^+$ [d]		402 (68.5)	456 (20.7)	528 (70.6)		
trans-$Cr(en)_2Cl_2^+$ [e]		396 (34.0)	439 (22.3)	453 (22.8)	514 (8.1)	578 (24.5)
cis-α-$Co(trien)Cl_2^+$ [f]		381 (132) sh	∼463 (45)	539 (132)		∼600 (115) sh
cis-β-$Co(trien)Cl_2^+$ [f]		392 (118) sh	∼460 (47)	531 (131)		
trans-$Co(trien)Cl_2^+$ [g]		∼360 (62)		∼455 (137)	∼545 (17)	∼630 (50)
cis-α-$Cr(trien)(NCS)_2^+$ [b]	363 (82.0)	372 (86.7)	420 (36.9)	488 (157)		
cis-$Cr(en)_2(NCS)_2^+$ [h]	360 (87)	370 (91)	417 (40)	490 (148)		
trans-$Cr(en)_2(NCS)_2^+$ [i]		365 (67) sh	416 (31)	486 (95)		
cis-α-$Cr(trien)(N_3)_2^+$ [b]	352 (41.1)	402 (126)	452 (70.0)	518 (185)		
cis-$Cr(en)_2(N_3)_2^+$ [j]	352 (37.5)	398 (148)	447 (68.5)	515 (224)		
α-$Cr(trien)ox^+$ [b]	332 (32.0)	372 (96.5)	425 (28.0)	500 (139)		
$Cr(en)_2ox^+$ [k]	325 (25)	370 (87)	416 (23)	495 (97)		
α?-$Co(trien)ox^+$ [l]		352 (200)		501 (132)		

[a] Values inside parentheses are molar absorbancy indices a_M (extinction coefficients ϵ) in M^{-1} cm^{-1}, defined by the relation $A = a_Mcd$, where A = absorbancy = $\log (I_0/I)$, c = molarity of absorbing complex, d = optical path in cm; sh = shoulder. [b] This research; 0.1 *F* HCl. [c] The spectrum of ref 17, in an aqueous solution, is the same except that the 535-mμ peak is given as 526 mμ ($a_M = 96$). [d] D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4152 (1961); 0.1 *F* HCl. [e] Same as footnote *d*, except 0.1 *F* HNO_3. [f] A. M Sargeson, personal communication (data for absorption minimum read off curve in ref 11); spectrum of "*cis*"-$Co(trien)Cl_2^+$ reported in ref 8 is similar except for much larger a_M values. [g] From curve in ref 10; 0.1 *F* $HClO_4$. [h] K. G. Poulsen and C. S. Garner, unpublished research; 0.1 *F* $HClO_4$. [i] J. M. Veigel, Ph.D. Dissertation, UCLA, Jan 1965, p 59; 0.1 *F* $HClO_4$. [j] M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **271**, 131 (1953); solvent not repōrted. [k] A. Mead, *Trans. Faraday Soc.*, **30**, 1052 (1934); 15°, solvent not reported. [l] Ref 8; H_2O solution of what is labeled simply as the *cis* form.

sorption on a H^+ Dowex AG50W-X8 (100–200 mesh) column at 0° and elution with 200 ml of 0.5 *F* HCl, showed that 98% of the complex appeared in the effluent, suggesting further that the compound is not a mixture of isomers.

In the N–H stretching region (3000–3300 cm^{-1}), the *cis*-α-diacidotriethylenetetraminecobalt(III) salts show three strong-to-medium bands and usually a fourth band or shoulder, the *cis*-β salts seem generally to give five or six strong-to-medium absorptions, some of which may show splitting, and the *trans* salt gives four strong-to-medium bands.[13] Here the distinction between isomers is harder to draw, and the 3000–3300-cm^{-1} region for the chromium complexes (Table I) shows bands compatible with either a *cis*-α or a *trans* configuration.

The CH_2 rocking region (860–940 cm^{-1}) is more useful for configuration assignment. The above cobalt compounds show two medium bands in this region for the *cis*-α salts, four such bands for the *cis*-β salts, and four or five medium-to-weak bands for the *trans* salt.[13] The spectra of the chromium complexes in this region (Table I) strongly support a *cis*-α configuration in each case.

In the 980–1100-cm^{-1} region (where some of the frequencies are tentatively assigned to CH_2 or NH_2 twisting modes), the cobalt compounds exhibit two to three strong bands for the *cis*-α salts, four or five for the *cis*-β salts, and three for the *trans* compound.[13] For each of the chromium compounds of Table I there are three strong bands in this region, consistent with either a *cis*-α or *trans* assignment.

Further support for the *cis*-α configuration is provided by the visible absorption spectrum of our $Cr(trien)Cl_2^+$ salts. Figure 1 shows a marked shoulder at *ca.* 580 mμ on the main visible absorption peak; a similar shoulder (at *ca.* 600 mμ) occurs on the main visible absorption peak in the spectrum of *cis*-α-$Co(trien)Cl_2^+$ ion[8,11] which is absent in the spectra of the *cis*-β[11] and *trans*[10] isomers. No corresponding shoulder is reported[8] for the visible absorption spectrum of the Co(trien)ox^+ ion (configuration not certain), nor is one shown in Figure 1 for $Cr(trien)ox^+$ prepared by any of our methods, nor for *cis*-α-$Cr(trien)(NCS)_2^+$ and *cis*-α-$Cr(trien)(N_3)_2^+$. No cobalt(III) diisothiocyanatotriethylenetetramine complexes have been reported, and no visible spectra given for either the *cis*-α or *cis*-β isomer of $Co(trien)(N_3)_2^+$.

Although the infrared spectra of the $Cr(trien)(NCS)_2^+$ salts indicate a *cis*-α configuration, the possibility of a *trans* configuration should be further considered because of the fact that *trans*-$[Cr(AA)_2(NCS_2)]NCS$ compounds (AA = en,[21] pn = propylenediamine,[22] and ibn = isobutylenediamine[22]) are readily obtained with thiocyanate reactant. However, oxidative removal of the thiocyanate ligands of our $Cr(trien)(NCS)_2^+$ complexes with chlorine or hydrogen peroxide in concentrated hydrochloric acid produces *cis*-α-$Cr(trien)Cl_2^+$. Moreover, a method similar to ours for the synthesis of the diisothiocyanato complexes with *cis*-$[Cr(en)_2Cl_2]Cl$[23] or *cis*-$[Cr(NH_3)_4(OH_2)Cl]Cl_2$[24] yields the *cis*-diisothiocyanato complexes on reaction with thiocyanate ion. Finally, a *trans* isomer of $Cr(trien)(NCS)_2^+$ would be expected to have less intense visible absorption bands than observed (Figure 1). Accordingly, the *cis*-α configuration seems well established for the diisothiocyanato complex, as well as for the other complexes.

The visible and near-ultraviolet absorption spectra of the *cis*-α-$Cr(trien)X_2^+$ complexes are of interest not only for their support of our assignment of the *cis*-α configuration, but also for comparison purposes with the chromium(III) bis(ethylenediamine) and cobalt(III) trien analogs. The comparison is given in Table II. In general, the Cr trien complexes have their absorption maxima at nearly the same wavelength as for their bis(ethylenediamine) analogs, the greatest shift being 7

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(21) C. L. Rollinson and J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 200 (1946).

(22) K. G. Poulsen and C. S. Garner, *J. Am. Chem. Soc.*, **81**, 2615 (1959).

(23) P. Pfeiffer, *Ber.*, **37**, 4255 (1904).

(24) G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., Inc., New York, N. Y., 1962, p 225.

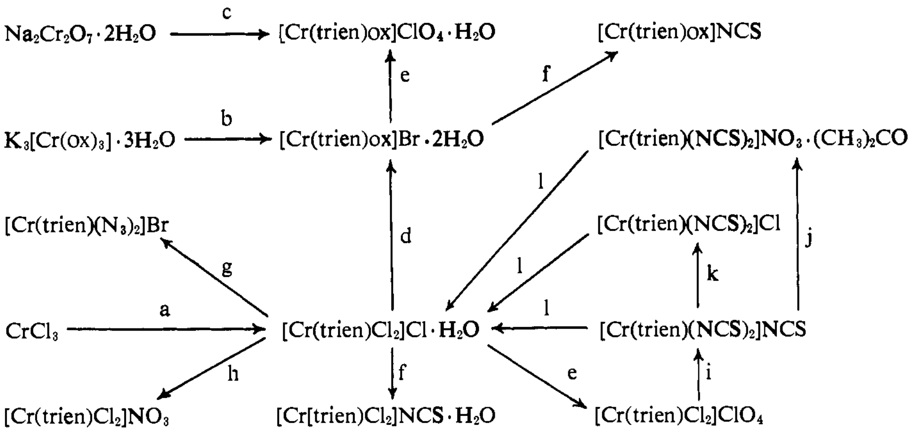

Figure 3. Interconversions in the *cis*-α-chromium(III) trien system. Reagents: a = Zn + trien + CH_3OH; b = H_2O + trien + KBr; c = H_2O + $H_2ox \cdot 2H_2O$ + trien + $NaClO_4 \cdot H_2O$; d = H_2O + $(NH_4)_2ox \cdot H_2O$ + KBr; e = H_2O + $NaClO_4 \cdot H_2O$; f = H_2O + KSCN; g = H_2O + NaN_3 + KBr; h = H_2O + $NaNO_3$; i = H_2O + NH_4SCN; j = $(CH_3)_2CO$ + HNO_3; k = $(CH_3)_2CO$ + HCl; l = HCl + Cl_2.

mμ; the molar absorbancy indices of the corresponding absorption peaks vary by as much as a factor of 1.4. This general similarity between the visible absorption spectra of the *cis*-α-Cr trien and *cis*-Cr bis(ethylenediamine) analogs is to be expected since these complexes are identical except for a bridging CH_2CH_2 group (between two secondary nitrogens in the trien ligand, each of which nitrogens would be a primary nitrogen in separate ethylenediamine ligands in the bis(ethylenediamine) complexes). In both the above cases all the coordinated nitrogens can assume a strain-free tetrahedral arrangement while in the *cis*-β isomer one secondary nitrogen is strained out of a tetrahedral arrangement, and in the *trans* isomer both secondary nitrogens are so strained.

The spectrum of *cis*-α-$Cr(trien)Cl_2^+$ shows a shoulder in the 580-mμ region, as does *cis*-α-$Co(trien)Cl_2^+$ (*ca.* 600 mμ), whereas *cis*-$Cr(en)_2Cl_2^+$ has no such shoulder. In other respects *cis*-α-$Cr(trien)Cl_2^+$ and α-$Cr(trien)ox^+$ have visible absorption spectra much like their cobalt(III) analogs, except that the band intensities are generally much smaller.

The interconversions and reactions involving the *cis*-α-$Cr(trien)X_2^+$ complexes synthesized in this investigation are summarized in Figure 3. In every case these complexes (including the oxalato complex) are very similar in properties, spectra, and reactions to the analogous *cis*-$Cr(en)_2X_2^+$ compounds.

The kinetics of aquation of some of these trien complexes are being investigated for comparison with their bis(ethylenediamine) and cobalt(III) trien analogs.

Experimental Section

Anhydrous $CrCl_3$ (Diamond Alkali Co., finely-powdered commercial grade) and trien (Eastman Kodak Co. technical grade) were used without purification. All other commercially available chemicals were reagent grade.

***cis*-α-Dichlorotriethylenetetraminechromium(III) Chloride and Its 1-Hydrate.** Anhydrous $CrCl_3$ (10 g) and Zn powder (10 mg) were stirred together in a 500-ml beaker. A solution of trien (11 ml) in anhydrous methanol (150 ml) was added, the mixture was stirred once or twice, and the solids were allowed to settle. Spontaneous reaction occurred within 0.5 min, resulting in vigorous boiling. As the boiling started to subside, it was continued by heating for 5 min; then the purple solution was allowed to cool to *ca* 25° and placed in ice. The crude chloride salt (12 g) precipitated from solution and was collected by filtration, along with a little unreacted $CrCl_3$. The crude chloride was purified by dissolving it in 20 ml of cold concentrated HCl, filtering out the undissolved $CrCl_3$, and collecting the filtrate in 250 ml of ice-cold absolute ethanol. A flocculent lilac precipitate formed which converted to a denser purple product after 10–12 hr at 5°. This was collected by filtration, washed with absolute ethanol and then with methanol, and air-dried; yield 10 g (50%).

Anal. Calcd for $[Cr(trien)Cl_2]Cl \cdot H_2O$: Cr, 16.11; C, 22.52; H, 6.25; N, 17.36; C, 32.9; H_2O, 5.58. Found: Cr, 15.95; C, 22.50; H, 6.05; N, 17.24; Cl, 32.7; H_2O, 5.55.

The hydrate can be converted to the anhydrous salt by heating for 16 hr at 110°. The visible absorption spectrum of the latter salt is identical with that of the hydrated salt.

Anal. Calcd for $[Cr(trien)Cl_2]Cl$: Cr, 17.0; C, 23.6; H, 5.95; Cl, 34.9. Found: Cr, 17.0; C, 23.5; H, 6.00; Cl, 35.2.

The preparation can be scaled up at least twofold, and addition of 10 g of $NaClO_4 \cdot H_2O$ to the methanolic mother liquor from a synthesis starting with 20 g of $CrCl_3$ gave some 2–3 g of the less soluble perchlorate salt (see below).

***cis*-α-Dichlorotriethylenetetraminechromium(III) Perchlorate.** Three grams of *cis*-α-$[Cr(trien)Cl_2]Cl \cdot H_2O$ was dissolved in 70 ml of water at *ca.* 25° and quickly filtered into a solution of 10 g of $NaClO_4 \cdot H_2O$ in 30 ml of water at *ca.* 5°. Fine blue-violet crystals were precipitated, collected by filtration, and washed with acetone and air-dried; yield 2.5 g (70%).

Anal. Calcd for $[Cr(trien)Cl_2]ClO_4$: Cr, 14.10; ligand Cl, 19.23. Found: Cr, 13.75; ligand Cl, 19.35.

There was no visible evidence of change on heating the compound to 300° (5°/min).

***cis*-α-Dichlorotriethylenetetraminechromium(III) Thiocyanate 1-Hydrate.** Similar conditions and methods were used as for the perchlorate salt, except that the $NaClO_4 \cdot H_2O$ was replaced by 20 g of KSCN. The solid product is violet in color; yield 2 g (62%).

Anal. Calcd for $[Cr(trien)Cl_2]NCS \cdot H_2O$: Cr, 15.1; C, 24.35; H, 5.84; Ag^+ precipitate, 37.3; H_2O, 5.22. Found: Cr, 15.0; C, 24.47; H, 5.84; Ag^+ precipitate, 36.7; H_2O, 5.14.

***cis*-α-Dichlorotriethylenetetraminechromium(III) Nitrate.** The nitrate salt was prepared in a manner similar to that used for the perchlorate salt, except that the $NaClO_4 \cdot H_2O$ was replaced by 15 g of $NaNO_3$. The product is blue; yield 1.5 g (50%).

Anal. Calcd for $[Cr(trien)Cl_2]NO_3$: Cr, 15.7; C, 21.78; H, 5.48; Cl, 21.4. Found: Cr, 15.4; C, 21.73; H, 5.57; Cl, 21.6.

No visual evidence of change was noted on heating (5°/min) the compound to 300°.

***cis*-α-Diisothiocyanatotriethylenetetraminechromium(III) Thiocyanate.** Five grams of *cis*-α-$[Cr(trien)Cl_2]ClO_4$ was dissolved in 200 ml of water and a solution of 25 g of NH_4SCN in 50 ml of water was added. When the solution was left at *ca.* 25° for 5–6 days, fine orange crystals were deposited on the walls of the flask. The crystals were collected, washed once with *ca.* 5–7 ml of water, and dried over silica gel; yield 3 g (62%).

Anal. Calcd for $[Cr(trien)(NCS)_2]NCS$: Cr, 13.9; C, 29.0; H, 4.9; N, 26.32; NCS, 46.8. Found: Cr, 13.6; C, 28.8; H, 5.1; N, 26.93; NCS, 47.0.

If the mother liquor from this procedure is warmed at 50° for about 1 day, red crystals of unknown composition are precipitated.

***cis*-α-Diisothiocyanatotriethylenetetraminechromium(III) Nitrate 1-Acetone.** Two grams of *cis*-α-[Cr(trien)$(NCS)_2$]NCS was partially dissolved in 100 ml of acetone, and 50 ml of 50° 8 *F* HNO_3 was added. All the solid dissolved and on cooling, orange crystals of the nitrate salt were precipitated. The orange product was washed with acetone and air-dried; yield, almost quantitative.

Anal. Calcd for [Cr(trien)$(NCS)_2$]$NO_3\cdot(CH_3)_2CO$: Cr, 11.96; C, 30.41; H, 5.57; NCS, 26.7; $(CH_3)_2CO$, 13.4. Found: Cr, 11.88, C, 30.36; H, 5.57; NCS, 26.8; $(CH_3)_2CO$, 13.0.

***cis*-α-Diisothiocyanatotriethylenetetraminechromium(III) Chloride.** Similar conditions and amounts were used as for the nitrate salt except that the 8 *F* HNO_3 was replaced by 6 *F* HCl. The yellow-orange product was washed with acetone and air-dried; yield 80–90%.

Anal. Calcd for [Cr(trien)$(NCS)_2$]Cl: Cr, 14.8; C, 27.46; H, 5.18; Ag^+ precipitate, 43.4. Found: Cr, 14.4; C, 27.27; H, 5.38; Ag^+ precipitate, 43.5.

***cis*-α-Diazidotriethylenetetraminechromium(III) Bromide.** Two grams of *cis*-α-[Cr(trien)Cl_2]$Cl\cdot H_2O$ and 5 g of NaN_3 were dissolved in 20 ml of water and warmed at 75–80° on a water bath until the solution was rose red (20 min). Five grams of KBr was then added; on cooling, brick-red crystals were formed. The crystals were washed with methanol and then air-dried by suction; yield 1.5 g (67%).

Anal. Calcd for [Cr(trien)$(N_3)_2$]Br: Cr, 14.3; C, 19.91; H, 5.01; N, 38.67; Br, 22.0. Found: Cr, 14.1; C, 19.82; H, 5.4; N, 38.76; Br, 22.1.

On heating (5°/min) the compound to 300° a nonviolent decomposition occurred. Storage of the compound in laboratory light for a month leads to a change in color to violet.

α-Oxalatotriethylenetetraminechromium(III) Bromide 2-Hydrate. When a solution of 20 g of $K_3[Cr(ox)_3]\cdot 3H_2O$, prepared by the method of Bailar and Jones,[25] and 8 ml of trien in 200 ml of water was heated on a water bath at 80–85° for 2 hr, the color slowly changed to red. Solid KBr (25 g) was added to the hot solution. When this had dissolved, the reaction mixture was allowed to cool to *ca.* 25° and then placed in ice for 3 hr. The orange-red product that crystallized was collected by filtration and washed with 95% ethanol; yield 10 g (75%).

Anal. Calcd for [Cr(trien)ox]$Br\cdot 2H_2O$: Cr, 12.93; C, 24.0; H, 5.51; N, 13.9; Br, 19.7; H_2O, 8.96. Found: Cr, 12.85; C, 24.2; H, 5.48; N, 13.8; Br, 20.0; H_2O, 8.82.

This complex was also prepared by heating a solution of 3 g of *cis*-α-[Cr(trien)Cl_2]$Cl\cdot H_2O$ and 2 g of $(NH_4)_2ox\cdot H_2O$ in 50 ml of water at 80° for 30 min and then adding 7 g of KBr and cooling in ice. The precipitate was washed with 95% ethanol; yield 1.5 g (40%).

Anal. Found: Cr, 13.0.

This compound has infrared and visible absorption spectra identical with those of the compound prepared from $K_3[Cr(ox)_3]\cdot 3H_2O$.

α-Oxalatotriethylenetetraminechromium(III) Perchlorate 1-Hydrate. Oxalic acid 2-hydrate (110 g, 0.87 mole) was suspended in 200 ml of water and solid $Na_2Cr_2O_7\cdot 2H_2O$ (37 g, 0.125 moles) cautiously added. A vigorous reaction occurred, with heat and CO_2 evolution. When all the dichromate was added, the solution was heated at 80° on a water bath until the CO_2 evolution ceased (*ca.* 10 min); then trien (40 ml, 0.25 mole) was added and heating continued until the solution developed an orange-red color (30 min). A solution of 100 g of $NaClO_4\cdot H_2O$ in 60 ml of water at 50–60° was then added, and the product soon commenced to crystallize from the hot solution. After cooling to *ca.* 25° and then in ice, the pink product was collected by filtration, washed with 95% ethanol, then methanol, and finally air-dried; yield 83 g (83%).

Anal. Calcd for [Cr(trien)ox]$ClO_4\cdot H_2O$: Cr, 12.88. Found: Cr, 12.82.

This complex was also obtained by addition of 7 g of $NaClO_4\cdot H_2O$ in 10 ml of water to a 50° solution of 2 g of α-[Cr(trien)ox]-$Br\cdot 2H_2O$ in 30 ml of water. The pink product was washed and dried as above. The yield was almost quantitative. The visible absorption spectrum was identical with that obtained for the salt prepared by the other method above.

Anal. Found: Cr, 12.85.

Heating the compound at 5°/min to 300° resulted in a barely perceptible color change, perhaps due to dehydration.

α-Oxalatotriethylenetetraminechromium(III) Thiocyanate. Two grams of α-[Cr(trien)ox]$Br\cdot 2H_2O$ was dissolved in 30 ml of water at 50°, and a solution of 4 g of KSCN in 15 ml of water was added. The reddish pink product crystallized immediately, and after cooling in ice the solid was filtered, washed with 95% ethanol, and air-dried; yield, almost quantitative.

Anal. Calcd for [Cr(trien)ox]NCS: Cr, 15.1; C, 31.39; H, 5.27; N, 20.34. Found: Cr, 15.0; C, 31.53; H, 5.16; N, 20.63.

Chemical Analyses. Chromium was determined by spectrophotometric analysis of chromate at 372 mμ after decomposition and oxidation with hot alkaline peroxide. Halides and thiocyanate were determined gravimetrically as the silver salts, the complexes being decomposed with boiling 2 *F* HNO_3 for the halides and with hot 1 *F* NaOH for thiocyanate. Bromide was determined in the diazido compound by dissolving it in 1 *F* HNO_3, heating to 85° for 15 min with KNO_2 to destroy N_3^-, adding excess $AgNO_3$, coagulating at 85° for 15 min, cooling, filtering off the AgBr, and weighing it. Standard microanalytical procedures were used to determine C, H, and N.

Spectrophotometry. Visible absorption spectra were measured at *ca.* 22° with a Cary Model 15 recording spectrophotometer, using matched 10.00-cm quartz cells, with the reference cell filled with water. A Beckman DU spectrophotometer was used for the chromium analyses. The infrared spectra were determined both in Nujol mulls and in KBr disks using a Perkin-Elmer Model 421 spectrophotometer; only very minor differences in spectrum were found for the two methods.

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(25) J. C. Bailar, Jr., and E. M. Jones, *Inorg. Syn.*, **1**, 35 (1939).