

had the *L-uns-cis* geometry as evidenced by ORD spectra. It is interesting to note that the *L-uns-cis*-Co(trien)Cl₂⁺ does *not* hydrolyze or rearrange under any conditions to give the *D-s-cis* isomer.⁵

In an attempt to effect and observe a similar phenomenon with the cobalt(III) complexes of eee, the base hydrolysis of *D*- and *L-s-cis*-[Co(eee)Cl₂]Cl was studied using both ORD and CD techniques. From these studies, several contrasting features were obvious. Addition of excess sodium hydroxide to a solution containing optically pure *D*- or *L-s-cis*-[Co(eee)Cl₂]Cl immediately produces the dihydroxo species with the characteristic ORD and CD spectra as illustrated in Figures 6 and 8, respectively. The dihydroxo complex loses optical activity only very slowly, a 5% decrease in optical activity being observed over a period of several hours at pH 8 as evidenced by both ORD and CD curves. At pH 10, a slow loss of optical activity is detectable and is accompanied by the development of a brown coloration and rank odor characteristic of decomposition. This reaction was followed by ORD

and CD spectra for approximately 5 hr without any indication of change in the absolute configuration. In addition, samples of the dihydroxo complex were periodically converted to the corresponding carbonato complex and the ORD and CD spectra were compared with the spectrum of the optically pure *D-s-cis*-Co(eee)CO₃⁺ ion. Again at pH 8, no significant changes were observed in the signs, intensities, or energies of the ORD and CD Cotton effects, thus substantiating retention of configuration, and the absence of any isomerization of *D-s-cis* to *L-uns-cis*. Numerous other attempts to produce chemically such an isomerization have been unsuccessful with the *s-cis*-Co(eee)L₂ⁿ⁺ ions.¹

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The Preparation and Spectral Properties of Bis(halogenoacetato)(β,β',β'' -triaminotriethylamine)cobalt(III) Complexes

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Bis(halogenoacetato)(triaminotriethylamine)cobalt(III) complexes, [Co(halac)₂(tren)]ClO₄ (halac = CF₃CO₂⁻, CH₂ClCO₂⁻, CHCl₂CO₂⁻, CCl₃CO₂⁻, CH₂BrCO₂⁻, CHBr₂CO₂⁻, and CBr₃CO₂⁻), have been prepared from carbonato(triaminotriethylamine)cobalt(III) perchlorate, and their infrared and electronic absorption spectra have been examined. Assignments of the bands arising from the amino groups have been made by a comparison of the spectra with those of the deuterated complexes, [Co(tren-*d*₆)Cl₂]Cl·0.5H₂O and [Co(tren-*d*₆)Br₂]Br. Comparison of the visible spectra of these tren complexes with the spectra of the corresponding tetraammine, bis(ethylenediamine), and triethylenetetramine (trien) complexes suggests that the ligand field strength of tren ligand is between that of ethylenediamine and ammonia.

Introduction

Kuroda and Gentile² have described the preparation and the physical and chemical properties of a large series of halogenoacetatopentaamminecobalt(III) complexes. Both *cis*- and *trans*-bis(halogenoacetato) complexes of tetraamminecobalt(III), bis(ethylenediamine)cobalt(III), and triethylenetetraminecobalt(III) were also reported. From the visible spectra of these complexes it was found that, regardless of the amine ligand, those halogenoacetato anions with the lowest basicity were highest in the spectrochemical series. However, for any given halogenoacetato ligand in the *cis* complexes, the frequencies of the visible and ultra-

violet absorption maxima were not identical, but always increased in the order

$$\nu(\text{NH}_3)_4 > \nu(\text{en})_2 > \nu(\text{trien})$$

It was also found that the absorption intensities increased in the same order.

Previous work has shown that the triaminotriethylaminecobalt(III) complexes which had been reported were found to be the *cis* isomers.^{3,4} Since the bis(halogenoacetato)(triaminotriethylamine)cobalt(III) complexes have not been reported in the literature, we have now synthesized these new complexes and have investigated their spectral properties in order to see how they compare with those of the other amine analogs.

(1) Author to whom inquiries should be addressed.

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TABLE I
 ANALYTICAL DATA FOR THE TRIAMINOTRIETHYLAMINE-COBALT(III) COMPLEXES

Compound	% carbon		% hydrogen		% nitrogen		% perchlorate	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[Co(tren)CO ₃]ClO ₄ ·H ₂ O	21.95	22.53	5.23	5.45	14.62	14.40	26.00	26.10
[Co(tren)Br ₂]Br	16.15	16.22	4.05	4.28	12.60	12.38
[Co(tren)(CH ₃ CO ₂) ₂]ClO ₄	28.41	28.74	5.67	5.95	13.25	13.19	23.58	23.08
[Co(tren)(CF ₃ CO ₂) ₂]ClO ₄	22.62	22.93	3.40	3.24	10.56	10.61	18.70	18.50
[Co(tren)(CH ₂ ClCO ₂) ₂]ClO ₄	24.43	24.42	4.51	4.60	11.40	11.60	20.20	20.20
[Co(tren)(CHCl ₂ CO ₂) ₂]ClO ₄	21.43	21.42	3.60	3.56	10.00	10.21	17.71	17.70
[Co(tren)(CCl ₃ CO ₂) ₂]ClO ₄	19.08	19.29	2.88	3.24	8.90	9.10	15.80	16.00
[Co(tren)(CH ₂ BrCO ₂) ₂]ClO ₄	20.69	21.01	3.82	3.45	9.65	9.55	17.15	16.65
[Co(tren)(CHBr ₂ CO ₂) ₂]ClO ₄	16.27	17.05	2.73	2.98	7.95	7.54	13.50	13.30
[Co(tren)(CBr ₃ CO ₂) ₂]ClO ₄	13.40	13.54	2.10	2.47	6.25	6.45	11.10	11.25

Experimental Section

Materials.—Acetic acid, monochloroacetic acid, dichloroacetic acid, and trichloroacetic acid (Fisher Scientific Co.), monobromoacetic acid and trifluoroacetic acid (Eastman Organic Chemicals), dibromoacetic acid (K & K Laboratories Inc.), and all the other reagent grade chemicals were used without further purification.

Infrared Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 521 recording spectrophotometer. Solid samples in Nujol mulls were examined between potassium bromide plates from 4000 to 600 cm⁻¹. Measurements in the 600–250-cm⁻¹ region were performed with cesium bromide plates.

Electronic Absorption Spectra.—The visible and ultraviolet absorption spectra were obtained with a Cary Model 14M recording spectrophotometer, using a pair of 1-cm quartz cells. The concentration of the complexes was 2.5 × 10⁻³ M for the measurement in the visible and near-ultraviolet regions. A water-ethanol mixture (1:1) was used as the solvent. In order to detect a possible aquation, the spectra of some complexes were also measured in 2 × 10⁻² M free halogenoacetato acid solution, and it was found that the addition of the acid does not influence the spectra.

Analyses.—The perchlorate ion was analyzed by precipitation with nitron.⁵ All carbon, nitrogen, and hydrogen analyses were performed by Weiler and Strauss, Microanalytical Laboratory, Oxford, England. Analytical data are given in Table I.

Preparation of Compounds. (1) *β,β',β''*-Triaminotriethylamine Trihydrochloride.—This compound was prepared by the method of Paoletti, Ciampolini, and Sacconi.⁶

(2) Carbonato(triaminotriethylamine)cobalt(III) Perchlorate Monohydrate.—The method of G. M. Harris (to be submitted for publication) was used for the preparation of this complex.

(3) Dichloro(triaminotriethylamine)cobalt(III) Chloride Hemihydrate.—This preparation was described in an earlier paper.^{5a}

(4) Dibromo(triaminotriethylamine)cobalt(III) Bromide.—Although this compound can be prepared by the method of Madan and Peone,^{5b} we synthesized the complex by adding an excess amount of concentrated hydrobromic acid to carbonato(triaminotriethylamine)cobalt(III) perchlorate. The HBr solution was concentrated on a steam bath, and after cooling in an ice bath [Co(tren)Br₂]Br was obtained as dark green crystals.

(5) Deuterated Complexes.—Deuterated complexes, [Co(tren-*d*₆)Cl₂]Cl·0.5H₂O and [Co(tren-*d*₆)Br₂]Br [(tren-*d*₆) = N(CH₂CH₂ND₂)₃], were prepared by a method similar to that reported for *cis*-[Co(tren-*d*₆)Cl₂]Cl·H₂O.⁷ The lattice water in [Co(tren-*d*₆)Cl₂]Cl·0.5H₂O can only be deuterated by repeated recrystallization from D₂O. The purity of the deuterated complexes has been indicated by the complete disappearance of N-H bands in the infrared spectrum.

(6) Bis(acetato)(triaminotriethylamine)cobalt(III) Perchlorate.

rate.—A mixture of the carbonato complex and a slight excess amount of acetic acid was heated on a steam bath to dryness. The oily red solid was mixed with ethanol, and the resulting product was washed with ethanol and then ether and dried *in vacuo*.

(7) Bis(trifluoroacetato)(triaminotriethylamine)cobalt(III) Perchlorate.—A mixture of the carbonato complex (0.5 g), trifluoroacetic acid (0.4 g), and water (2 ml) was evaporated to dryness at 65–70°. The product was mixed with 2 ml of 20% sodium perchlorate solution, and the resulting material was washed with a small amount of cold water followed by 1-propanol and ether. The red solid was dried *in vacuo*. No further purification has been made.

(8) Bis(chloroacetato)(triaminotriethylamine)cobalt(III) Perchlorate.—These complexes were prepared by procedures similar to those for the trifluoroacetato complex. The amount of each chloroacetic acid used was slightly in excess of the theoretical amount needed.

(9) Bis(bromoacetato)(triaminotriethylamine)cobalt(III) Perchlorate.—These complexes were prepared by procedures similar to those for trifluoroacetato and chloroacetato complexes.

Results and Discussion

Infrared Spectra.—The infrared spectral data for all of the bis(halogenoacetato)(triaminotriethylamine)cobalt(III) complexes have been obtained and are shown in Table II. Some band assignments have been made by a comparison of the spectral data with those of dichloro(triaminotriethylamine)cobalt(III), dibromo(triaminotriethylamine)cobalt(III), and several cobalt(III) complexes of other amines. These assignments as well as their implications are discussed below.

In general, lattice water with hydrogen bonding absorbs at 3200–3550 cm⁻¹ due to antisymmetric and symmetric O-H stretching modes and at 1620–1650 cm⁻¹ due to the H-O-H bending mode.^{8,9} The absorption at 3540, 3480, 3370, 3278, and 1630 cm⁻¹ for the *cis*-[Co(tren)Cl₂]Cl·0.5H₂O may be attributed to the antisymmetric and symmetric O-H stretching modes and the symmetric H-O-H bending mode of the lattice-bound water. These bands are not affected on deuteration and disappeared after the compound was dried for 2 days at 120°. The observation that the lattice water is not deuterated may be a result of the lower lability of the water protons due to hydrogen bonding. Analytical evidence indicates the presence of 0.5 mol of water in this compound and the absorptions remain following deuteration of [Co(tren-*d*₆)Cl₂]Cl·0.5H₂O. There are no such absorptions in these regions

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TABLE II^a
 INFRARED SPECTRA OF COBALT(III) COMPLEXES OF β, β', β'' -TRIAMINOTRIETHYLAMINE

Band assignment	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
O-H str (lattice H ₂ O)	3540 m 3480 m 3370 m 3278 sh	3540 m 3480 m 3370 m 3278 m										
H-O-H bend (lattice H ₂ O)	1630 m	1630 m										
N-H str and N-D str	3330 s 3310 w	2480 s 2475 w	3310 s 3239 s	2475 m 2430 s	3330 s 3295 s	3330 s 3308 s	3310 s 3260 s	3320 m 3280 s	3305 s 3290 s	3310 s 3260 s	3321 s 3310 s	3320 s 3280 sh
	3241 s 3180 s, b 3078 s	2430 s 2378 s 2281 s	3140 sh 3098 s 3065 s	2380 sh 2300 s 2275 s	3238 sh 3145 s 3050 m	3278 sh 3145 s 3080 m	3205 m 3140 s 3078 m	3240 m 3180 m ?	3210 sh 3130 m 3050 m	3210 m 3150 m 3080 m	3270 s 3130 m, b ?	3160 m 3140 m ?
N-H (N-D) antisym bend	1605 m 1590 m	1182 m 1178 sh	1602 s 1578 s	1175 sh 1165 m	1610 m	1610 m	1605 sh	1610 sh	1615 m	1620 m
N-H (N-D) sym bend	1315 m 1295 sh	1065 (?) ?	1310 m 1290 sh	? ?	1320 sh 1295 sh	1320 m 1300 sh	1318 m 1297 sh	? ?	1330 sh 1305 sh	1320 sh 1300 sh	? ?	1328 w 1315 w 1310 w
NH ₂ (ND ₂) rock	790 m	570 m	790 m	565 m (?)	790 m	790 m	790 m	?	790 m	795 m	810 m	790 s
N-H (N-D) wag	1168 m 1151 m	958 m 945 m	1140 s 1138 s	958 s 940 m
NH ₂ (ND ₂) twist	1035 m 1008 s 830 m	870 m 840 m 830 m	1022 m 999 s 980 m	861 m 834 m 820 m	...	1035 s 998 m 995 m	1033 s 1005 m 995 m	1035 sh 990 m 979 m	1038 s 1000 m 985 m	1035 s 1005 m 995 m	1038 sh 990 m 980 m	1035 s 1005 m 989 m
CH ₂ rock	900 m {865 m 858 m		892 m 852 m		900 m {870 m 860 w	900 m {865 m 858 m	900 m {870 m 860 m	900 m	900 m 870 m	900 m {870 m 863 m	900 m {870 m 863 m	900 m
C-O str ClO ₄ ⁻					1593 s, b 1030-	1650 s, b 1050-	1670 s, b 1040-	1680 s, b 1050-	1630 s, b 1050-	1656 s, b 1050-	1675 s, b 1060-	1685 s, b 1070-
ν_3					1130	1135	1130	1130	1130	1130	1130	1160
ν_1					935 m	935 m	935 m	935 m	935 m	935 m	935 m	935 m
ν_4					625 s	625 s	625 s	625 s	625 s	625 s	625 s	625 s

^a Intensities are estimated as follows: s, strong; m, medium; w, weak; b, broad; sh, shoulder. Compounds: I, *cis*-[Co(tren)Cl₂]Cl·0.5H₂O; II, *cis*-[Co(tren-*d*₆)Cl₂]Cl·0.5H₂O; III, *cis*-[Co(tren)Br₂]Br; IV, *cis*-[Co(tren-*d*₈)Br₂]Br; V, *cis*-[Co(tren)(CH₃CO₂)₂]ClO₄; VI, *cis*-[Co(tren)(CH₂ClCO₂)₂]ClO₄; VII, *cis*-[Co(tren)(CHCl₂CO₂)₂]ClO₄; VIII, *cis*-[Co(tren)(CCl₃CO₂)₂]ClO₄; IX, *cis*-[Co(tren)(CH₂BrCO₂)₂]ClO₄; X, *cis*-[Co(tren)(CHBr₂CO₂)₂]ClO₄; XI, *cis*-[Co(tren)(CBr₃CO₂)₂]ClO₄; XII, *cis*-[Co(tren)(CF₃CO₂)₂]ClO₄.

for any of the halogenoacetato complexes, thus confirming the analytical results which show that all of these complexes are anhydrous.

In metal-amine complexes the four principal regions of absorption are ~ 3300 , ~ 1600 , ~ 3000 , and 800 cm^{-1} . These absorptions have been assigned to N-H stretching modes,¹⁰ antisymmetric stretching,¹¹ symmetric deformation, and NH rocking modes,¹² respectively. In [Co(tren)Cl₂]Cl·0.5H₂O and [Co(tren)Br₂]Br, the absorptions in the regions 3000–3300, 1550–1620, 1290–1330, 1130–1170, 1040, 1000, and 790 cm^{-1} showed isotopic shifts upon deuteration, and, therefore, can be assigned to the vibrations of the NH₂ group.

The bands in the N-H stretching region 3000–3330 cm^{-1} shift on deuteration to 2280–2480 cm^{-1} with an NH:ND ratio of 1.34, a value which is close to the theoretical value (by assuming a similar force constant) of 1.37. Only two strong absorptions have been observed in this region for *cis*-[Co(en)₂Cl₂]Cl and *cis*- α -[Co(tren)Cl₂]Cl, both of which have only two different

kinds of coordinated nitrogens. All of these nitrogens assume a strain-free tetrahedral arrangement.⁷ In the *cis*- β -[Co(tren)Cl₂]Cl complex, however, five strong absorptions are observed in this region, since one of the secondary nitrogens is strained into an intermediate planar-tetrahedral conformation and all four nitrogens are nonequivalent.⁷ In the case of tren complex, the tertiary nitrogen is obviously different from the other three, and one of the primary nitrogens is different from the other two, since it is *trans* to an acetato group. Furthermore, an X-ray study of the bis(thiocyanato)-(triaminotriethylamine)nickel(II) complex¹³ has shown that the two primary nitrogens which are *trans* to each other are also nonequivalent, owing to distortion of the complex. Since distortion is also present in the Co(III)-tren complexes,^{8,4} it is not unreasonable to assume that all four nitrogens are nonequivalent. This may well account for the presence of five N-H stretching bands in the infrared spectra, as in the case of *cis*- β -tren-Co(III) complexes. The bands at $\sim 1600\text{ cm}^{-1}$, which is known to be the region of antisymmetric NH₂ bending vibrations for metal-amine complexes, shift to $\sim 1180\text{ cm}^{-1}$ on deuteration. The NH:ND ratio (1.34) is in good agreement with that found for

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TABLE III
 VISIBLE AND NEAR-ULTRAVIOLET SPECTRA OF BIS(HALOGENOACETATO)(AMINE)COBALT(III) COMPLEXES

Halogeno- acetato ligand	1st band (visible)								2nd band (near-uv)							
	(NH ₃) ₄ ^a		(en) ₂ ^a		trien ^b		tren ^{c,d}		(NH ₃) ₄ ^a		(en) ₂ ^a		trien ^b		tren ^{c,d}	
	10 ³ ν, cm ⁻¹	ε ^e	10 ³ ν, cm ⁻¹	ε	10 ³ ν, cm ⁻¹	ε	10 ³ ν, cm ⁻¹	ε	10 ³ ν, cm ⁻¹	ε	10 ³ ν, cm ⁻¹	ε	10 ³ ν, cm ⁻¹	ε	10 ³ ν, cm ⁻¹	ε
CH ₃ CO ₂	19.08	112	19.76	150	19.60	191	27.40	64.3	27.62	95.5	27.40	114
CH ₂ ClCO ₂	19.12	108	19.92	136	20.20	190	19.70	189	27.40	62.2	27.66	90.2	27.67	120	27.40	112
CH ₂ Cl ₂ CO ₂	19.31	96.5	20.06	123	20.24	185	19.80	184	27.62	61.9	27.70	86.1	27.70	118	27.50	106
CCl ₃ CO ₂	19.46	85	20.09	126	20.27	178	19.85	170	27.70	59.6	27.70	88	27.70	117	27.55	100
CH ₂ BrCO ₂	19.16	104.5	20.18	187	19.70	191	27.55	63.5	27.67	121	27.50	120
CHBr ₂ CO ₂	19.27	108	20.06	140.5	20.24	186.9	19.75	186	27.59	65.2	27.70	96.5	27.67	120.5	27.50	109
CBr ₃ CO ₂	19.75	192	27.60	123
CF ₃ CO ₂	19.49	78.4	20.20	115	20.35	172	19.90	168	27.86	51.5	27.78	80	27.78	110	27.65	100

^a Reference 2a. ^b Reference 2b. ^c This work. ^d A 1:1 H₂O-C₂H₅OH mixture was used as the solvent; concentration 2.5 × 10⁻² M. ^e ε is the molar absorptancy in l. mol⁻¹ cm⁻¹.

deformation modes in [Co(en)₂Cl₂]Cl¹⁴⁻¹⁶ and [Co(trien)Cl₂]Cl.⁷ It can be seen in Table II that most of the tren complexes have two main absorptions in this region. However, the acetato, monochloroacetato, and monobromoacetato complexes have the CO stretching and NH₂ deformation frequencies overlapped so that the NH₂ deformation bands are partially hidden by the more intense ν_{CO} band.

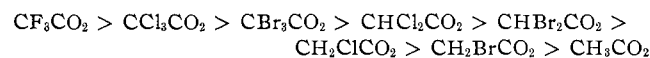
The bands in the region 1290-1335 cm⁻¹ are medium to weak and absent in the deuterated complexes. Further, the peaks in this region are not altered by variation in the anion and by substitution in the coordination sphere. Therefore, they can still be assigned to the symmetric NH₂ deformation. In addition, some medium and weak bands at ~1130-1170, 980-1040, and 790 cm⁻¹ show isotopic shifts upon deuteration. Because of the complicated nature of the spectra in these regions, however, the exact assignment of these bands¹⁴ is difficult. Baldwin¹⁵ and Morris and Bush¹⁴ have attempted to assign these bands in other systems to wagging, twisting, or rocking modes of the NH₂ groups. Two other bands were also observed in the 850-900-cm⁻¹ region and were assigned to CH₂ rocking modes. These bands have also been found in all the other amine complexes with a *cis* configuration.

In the spectra of all of the perchlorates a very broad single band at 1050-1170 cm⁻¹, a medium band at 935 cm⁻¹, and a strong-intensity single band at 630 cm⁻¹ were observed. These bands can be assigned to the ν₃, ν₁, and ν₄ vibrations of the perchlorate ion, respectively.¹⁷

A final point of interest in the infrared spectra of these bis(halogenoacetato)(triaminotriethylamine)cobalt(III) complexes is the ν_{CO} band. It is known that saturated carboxylic acids have strong absorption between 1700 and 1725 cm⁻¹, and the absorptions are shifted to higher frequencies by the successive halogen substitution at the α carbon.^{18,19}

It is also known that the CO stretching frequency of a free acid is shifted to a lower frequency when it is oxygen coordinated to a metal.^{20,21}

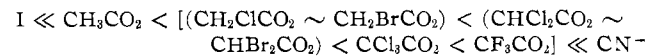
As we examine the CO stretching frequencies of the bis(halogenoacetato)(triaminotriethylamine)cobalt(III) complexes (Table II), we can see that these generalities are completely maintained, *i.e.*, the order of CO stretching frequencies is



and the frequencies are lower than those of corresponding free acids by 80-125 cm⁻¹. This effect was also observed for the other halogenoacetatoamine complexes.²

Visible and Ultraviolet Spectra.—The visible and near-uv spectral data of the *cis*-bis(halogenoacetato)-(triaminotriethylamine)cobalt(III) complexes are given in Table III and are compared with the corresponding data for the tetraammine, bis(ethylenediamine), and trien complexes. Apart from small shifts in the absorption maxima, there is a close similarity between the character and the shape of the spectra of the tren complexes and those of the *cis* isomers of other amine complexes. In the spectra of all of these complexes, there is no observable split in the longest wavelength band, which is, however, found for their *trans* isomers.^{2b,f}

The relative positions of the halogenoacetato ligands in the spectrochemical series have been reported as²



Our data indicate that this order is maintained in the present study; *i.e.*, as the basicity of the ligand decreases, its position in the spectrochemical series shifts to a higher wave number, as shown in Table III. The ligand CBr₃CO₂, which has not been used to prepare other tetramine complexes, has its position in the spectrochemical series as predicted by Kurodo and Gentile.^{2a}

As one compares the frequency of the absorption maxima of the visible bands of tren complexes with

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those of the other *cis* compounds, for a given halogenoacetato ligand, the following order is found

$$\nu_{\text{trien}} > \nu_{(\text{en})_2} > \nu_{\text{tren}} > \nu_{(\text{NH}_3)_4}$$

This is believed to indicate that the ligand field strength of the tren ligand is between that of en and NH_3 and less than that of trien. This trend is not surprising since the less flexible branched structure of tren gives rise to a somewhat distorted octahedral complex. Furthermore, tren has a tertiary nitrogen atom, which is a weaker electron donor than either a secondary or a primary nitrogen atom.

Theory²² suggests that the intensity of a d-d transition should be enhanced by increasing the asymmetry of the ligand field, and this proposition has been supported by experiments.²³ It seems reasonable, then, that the rise in the ϵ value accompanying the more rigid tetramine ligands is caused by increased distortion of the octahedral field. On this basis, one would expect that the absorption intensity of the tren complexes should have a higher value than that of the trien complexes, since trien is more flexible than branched tren. Comparing the visible spectra of a series of amine complexes

(22) F. A. Cotton, "Chemical Application of Group Theory," Interscience Publishers, Inc., New York, N. Y., 1963, p 231.

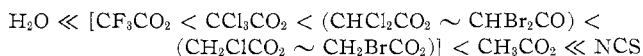
(23) R. L. Belford and W. A. Yeranov, *Mol. Phys.*, **6**, 121 (1963); P. W. Schneider and H. Brintzinger, *Helv. Chim. Acta*, **47**, 1717 (1964).

for a given halogenoacetato ligand, the absorption intensities are in the order

$$\epsilon_{\text{tren}} \sim \epsilon_{\text{trien}} > \epsilon_{(\text{en})_2} > \epsilon_{(\text{NH}_3)_4}$$

Collman and Schneider²⁴ found that the ϵ values of dichlorocobalt(III)-trien and -tren complexes are about the same (130 and 125). However, for the complexes with a larger central atom such as *cis*-dichlororhodium(III)-trien and -tren complexes, the ϵ values differ by a factor of 3 (101 and 300). Therefore, it appears that the increase of the distortion from trien to tren complex is minimal for the relatively smaller Co(III) central atom.

We have also observed that when one compares the electronic absorption spectra of the different halogenoacetato complexes for a given amine ligand, the intensity of the absorption maxima increase in the order



This trend suggests that the intensity of the absorption maxima is related to the inductive effect of the halogenoacetato ligands.

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The Isomerization of *cis*-Diacetatobis(ethylenediamine)cobalt(III) Perchlorate in Acetic Acid

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The kinetics of the isomerization of *cis*-[Co(en)₂(OAc)₂]ClO₄ were studied as a function of added sodium acetate in acetic acid in the range 68.8–84.5° by observing the absorbance decrease at 20.00 kK. It was found that sodium acetate retarded the rate of isomerization and the first-order rate constant appeared to have an acetate dependence of the form

$$k_{\text{obsd}} = \frac{k_a + k_b K K_1^{1/2} [\text{NaOAc}]^{1/2}}{1 + K K_1^{1/2} [\text{NaOAc}]^{1/2}} \quad (k_a > k_b)$$

where K_1 is the ionization constant for sodium acetate in acetic acid. The decreased rate is attributed to formation of an acetate ion pair that is less reactive than the perchlorate ion pair initially present. It is proposed that the isomerization within the ion pairs involves a solvent-assisted dissociation.

The isomerization, racemization, and substitution reactions of disubstituted bis(ethylenediamine)cobalt(III) complexes in nonaqueous media have been fairly extensively studied and reviewed.^{1,2} Kinetic studies of *cis-trans* isomerization in nonaqueous media have centered on the dichloro compound $\text{Co}(\text{en})_2\text{Cl}_2^+$, which has been studied in methanol^{3,4} and other alcohols,⁵

2-methoxyethanol,⁶ dimethyl sulfoxide,⁷ dimethylformamide and dimethylacetamide,⁸ and sulfolane.⁹ The ions $\text{Co}(\text{en})_2\text{Br}_2^+$ and $\text{Co}(\text{en})_2\text{BrCl}^+$ have also been studied in a variety of aprotic solvents.^{10,11} In addition, the *cis-trans* isomerizations of diaquobis(ethylene-

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