CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, METCALF RESEARCH
LABORATORIES, BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND 02912

Infrared Spectra of Cobalt(III) Triethylenetetramine Complexes

BY DAVID A. BUCKINGHAM AND D. JONES

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The infrared absorption spectra of the two *cis* isomers of a number of diacido and chelate triethylenetetraminecobalt(III) complexes and of *trans*-dichlorotriethylenetetraminecobalt(III) perchlorate have been measured in the region 400–4000 cm.$^{-1}$. Assignments of the bands arising from vibrations of the amino groups have been made by observing shifts resulting on deuteration. A study in the regions 3000–3300 and 990–1100 cm.$^{-1}$ provides a method for differentiating between the *cis*-triethylenetetramine isomers. By this means the configurations of the analogous Rh(III) and Cr(III) complexes have been deduced.

Introduction

Recent work by Sargeson and Searle[1] has shown that all three geometrical isomers of dichlorotriethylenetetraminecobalt(III) chloride, $[Co(trien)Cl_2]Cl$[2] (Figure 1), may be obtained by carefully controlling the experimental conditions.

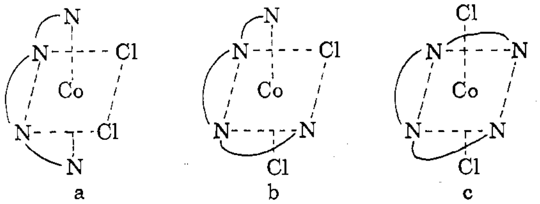

Figure 1.—Possible geometrical isomers of the complex cation $[Co(trien)Cl_2]^+$: a, *cis*-α; b, *cis*-β; and c, *trans* configurations.

The two *cis* forms were resolved into their optically active antipodes, and from a study of the rates of complete aquation of the optically active ions it was possible to predict the configuration of each *cis* isomer. Aquation rates for *cis*-α-(+)-$[Co(trien)Cl(H_2O)]^{2+}$ could be described by a simple first-order rate law, while two competing first-order paths were required for the *cis*-β isomer. From an examination of Figure 1 it is immediately obvious that the *cis*-α compound has two identically positioned Cl atoms, while in the *cis*-β form they are differently disposed with respect to the rest of the molecule.

Several other methods have been applied with varying degrees of success to the problem of differentiating between *cis* and *trans* isomers of hexacovalent cobalt(III) complexes. X-Ray diffraction and resolution into optically active antipodes of compounds of the types $[M(AA)_2a_2]$, $[M(AA)ab]$, and $[M(AA)a_2b_2]$ (where AA represents a bidentate ligand) can give a definite proof of structure.[3] A study of the visible absorption spectra has also been used in some cases, but the interpretation of such results is open to question. Another method which has been used for the distinction of *cis* and *trans* configurations in ammine- and amine–cobalt(III) complexes is infrared absorption spectroscopy.

Faust and Quagliano[4] applied infrared spectral techniques to a study of the *cis*- and *trans*-dinitrotetraamminecobalt(III) complexes, $[Co(NH_3)_4(NO_2)_2]Cl$. A significant spectral difference was noted at about 1300 cm.$^{-1}$, the *cis* isomer having an absorption which was split while the *trans* form showed no observable splitting. This was interpreted on the basis of the lower symmetry of the *cis* isomer. Morris and Busch,[5] in a study of *cis*- and *trans*-$[Co(en)_2(NO_2)_2]X$ ($X = NO_2$, NO_3) and *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$, gave evidence for splitting in the *cis* isomer of the degenerate antisymmetric NH_2 deformation mode at about 1600 cm.$^{-1}$, whereas in the *trans* form no split was in general observed. Merritt and Wiberley,[6] however, list no splitting in this region for either isomer. More recently Baldwin[7] has carried out an extensive spectral examination of *cis*- and *trans*-$[Co(en)_2Cl_2]X$ (X = Cl, Br, I, SCN, ClO_4, $^1/_2S_2O_6$) compounds, and he concludes that significant differences occur only in the 850–900 cm.$^{-1}$ region.

The present investigation was undertaken in order to discover whether infrared spectral studies could be used to distinguish between the two *cis* and one *trans* arrangements of the tetradentate chelate ring of triethylenetetramine (trien) and the extent to which substitution in the coordination sphere, variation of the central metal(III) ion, and ionic interactions affect the interpretation of such spectra. A large number of triethylenetetramine complexes of cobalt(III) have been studied in the solid state using Nujol mull and KBr disk techniques.

Results and Discussion

In the solid state the vibrational modes of metal–amine chelate rings are affected by (i) the orientation of the chelating ligand about the central metal atom, (ii) the spatial configuration of the individual chelate rings and the nonbonded interactions between them, and (iii)

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[1] A. M. Sargeson and G. H. Searle, *Nature*, **200**, 356 (1963); G. H. Searle, Ph.D. Thesis, Australian National University, Canberra, A.C.T., Australia, 1963.

[2] The following abbreviations are used in this article; trien for triethylenetetramine; en for ethylenediamine; acac for acetylacetonate anion; gly for glycinate anion; ala for alanine anion, and pyox for pyruvic acid oxime anion.

[3] R. G. Wilkins and M. J. G. Williams, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, pp. 193, 197.

[4] J. P. Faust and J. V. Quagliano, *J. Am. Chem. Soc.*, **76**, 5346 (1954).

[5] M. L. Morris and D. H. Busch, *ibid.*, **82**, 1521 (1960).

[6] P. E. Merritt and S. E. Wiberley, *J. Phys. Chem.*, **59**, 55 (1955).

[7] M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).

TABLE I

NH STRETCHING AND ANTISYMMETRIC DEFORMATION FREQUENCIES[a] (CM.$^{-1}$) FOR THE COMPOUNDS *cis*-α-[Co(trien)Cl_2]X AND *cis*-β-[Co(trien)Cl_2]X, WHERE X = Cl, Br, I, N_3, ClO_4, NO_2, NO_3, SCN, $^1/_2C_2O_4$, HSO_4 (NUJOL MULLS)

cis-α-[Co(trien)Cl_2]X, X =								*cis*-β-[Co(trien)Cl_2]X, X =								
Cl	Br	I	N_3	ClO_4	NO_2	NO_3	$^1/_2C_2O_4$	Cl	Br	I	N_3	SCN	ClO_4	NO_2	NO_3	HSO_4
								NH Stretching								
3262 s	3270 s	3280 m	3271 s	3280 s	3270 m	3287 s	3270 s	3235 sh	3265 sh	3285 m	3272 m	3271 m	3315 m	3310 w	3330 m	3312 m
3188 sh	3205 s	3250 s	3215 s	3228 s	3225 s	3235 s	3210 s	3215 m	3250 m	3230 m	3228 s	3221 m	3290 sh	3288 m	3289 m	3250 s
3095 s	3112 s	3105 s	3165 s	3155 s	3149 s	3210 sh	3100 s	3155 s	3185 s	3202 s	3185 m	3195 s	3272 s	3220 s	3228 s	3238 sh
3055 m		3130 s	3110 sh		3060 sh	3160 m		3080 m	3198 s	3152 s	3147 s	3155 s	3210 s	3160 sh	3160 sh	3208 s
								3060 m	3059 m	3118 s	3080 s	3120 sh	3130 m	3108 s	3140 s	3150 sh
								3000 m		3002 m	2985 m	3000 sh		3060 sh	3100 sh	3000 sh
								NH Deformation								
1570 s	1575 s	1590 s	1587 s	1592 s	1585 s	1600 s	1578 s	1590 m	1585 m	1590 sh	1600 m	1588 sh	1598 m	1600 m	1598 m	1601 m
								1560 s	1560 s	1580 s	1570 s	1579 s	1580 s	1580 s	1575 s	1588 s

[a] Intensities are estimated as follows: s, strong; m, medium; w, weak; b, broad; sh, shoulder.

ionic interaction or hydrogen bonding between the cation, anion, and lattice-bound water. The measured frequencies of the absorption bands of compounds of the type *cis*-α- and *cis*-β-[Co(trien)Cl_2]X show only minor variations with varying anion X.[8] This is to be expected since, in the solid state, interactions between cation and anion would be essentially electrostatic in nature and occur over rather large distances. Relatively major frequency variations occur only in the N–H stretch region (3300–3000 cm.$^{-1}$). Table I shows a regular decrease in frequency in the *cis*-α series, where the order is in general $NO_3 > ClO_4 \sim I > N_3 \sim NO_2 > C_2O_4 \sim Br > Cl$ and in the *cis*-β series $ClO_4 \sim NO_3 \sim HSO_4 > NO_2 > I \sim SCN \sim N_3 \sim Br > Cl$. Similar, although less pronounced frequency fluctuations occur in the N–H deformation region (1570–1600 cm.$^{-1}$). A less extensive series has previously been found for salts of the $[Co(NH_3)_6]^{3+}$ ion.[9] It is likely that the above shifts involve terminal NH_2 groups since it has been shown that secondary amine hydrogens are only very slightly affected by hydrogen bonding.[10]

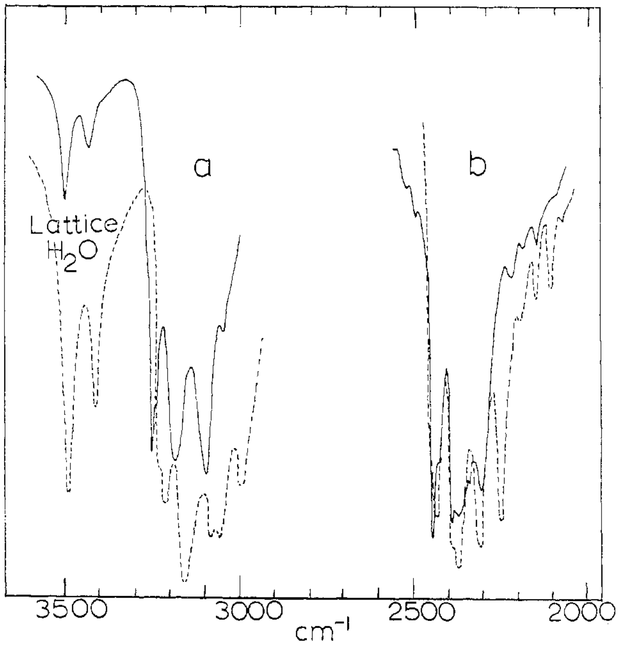

Figure 2.—Effect of deuteration on the N–H stretching modes of *cis*-α- and *cis*-β-[Co(trien)Cl_2]Cl: (a) undeuterated, (b) deuterated; ——, *cis*-α; - - -, *cis*-β.

Assignment of Absorption Bands. (a) Lattice-Bound Water.[8]—The two absorption bands at about 3500 and 3400 cm.$^{-1}$ (Figure 2) may be attributed to the antisymmetric and symmetric O–H stretching modes of lattice-bound water. Analytical evidence supports the

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(8) A tabulation of infrared absorption frequencies for these compounds has been deposited as Document No. 8455 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(9) A. Nakahara, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **25**, 231 (1952); J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Am. Chem. Soc.*, **78**, 3295 (1956).

(10) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 1955); 2712 (1956).

TABLE II

FREQUENCIES[a] (CM.$^{-1}$) OF THE NH_2 AND ND_2 VIBRATIONS IN UNDEUTERATED AND DEUTERATED COMPLEXES (KBr DISK)

cis-α-$[Co(trien)Cl_2]Cl \cdot H_2O$			*cis*-α-$[Rh(trien)Cl_2]Cl \cdot H_2O$			*cis*-β-$[Co(trien)Cl_2]Cl \cdot H_2O$			
NH_2	ND_2	NH/ND	NH_2	ND_2	NH/ND	NH_2	ND_2	NH/ND	Designation
3262 s	2440 s	1.34	3251 s	2440 s	1.33	3235 sh	2450 sh	1.32	NH str.
3188 s, b	2382 s, b	1.34	3205 s, b	2385 s	1.34	3215 s	2440 s	1.32	
3095 s	2308 s	1.34	3105 s	2370 sh			2387 sh		
3055 sh	2280 w	1.34	3045 m	2302 m	1.35	3155 s, b	2370 s	1.33	
				2220 m	1.37	3080 s	2315 s	1.33	
						3060 s	2298 sh	1.33	
						3000 s	2250 s	1.33	
1570 s	1160 s	1.34	1590 sh	1174 s	1.35	1590 s	1170 s	1.35	Antisym. bend.
			1582 vs	1163 sh	1.36	1560 vs	1156 s	1.35	
1333 m	1040 m	1.28	1332 m	1042 m	1.28	1329 w			Sym. bend.
1304 m	1018 m	1.28	1310 m	1023 m	1.28	1319 w			
1290 sh			1300 sh	1018 sh	1.28	1300 m			
						1295 sh			
1167 m	970 m	1.20	1171 s	970 s	1.21	1150 s	968 s	1.19	Wagging
1110 m	927 m	1.20	1114 s	927 s	1.20	1101 s	926 s	1.19	
1038 s	820 s	1.27	1036 s	818 s	1.27	1048 s	826 s	1.27	Twisting
1005 m	796 m	1.27	1013 m	801 m	1.27	1027 s	807 s	1.27	
981 m	760 m	1.29	976 m	760 m	1.28	994 s	772 s	1.29	
800 m	615 m	1.30	789 m	607 m	1.30	825 m	635 m	1.31	Rocking

[a] See footnote to Table I.

presence of water in these compounds and the absorptions remain following deuteration in both *cis*-α-$[Rh(trienD_6)Cl_2]Cl \cdot H_2O$ and *cis*-β-$[Co(trienD_6)Cl_2]Cl \cdot H_2O$. The shift to lower frequencies of these stretching modes and the shift to higher frequencies of the accompanying OH bending modes (1620–1650 cm.$^{-1}$) may be attributed to hydrogen bonding in these compounds.[11,12]

That the absorption at 1620–1650 cm.$^{-1}$ is observed in deuterated *cis*-α-$[Rh(trienD_6)Cl_2]Cl \cdot H_2O$ and *cis*-β-$[Co(trienD_6)Cl_2]Cl \cdot H_2O$ indicates that the absorption at about 1630 cm.$^{-1}$ in the *cis*-$[Co(en)_2X_2]^+$ (X = Cl, NO_2) ions is due to the symmetric OH deformation mode rather than the previously attributed NH_2 antisymmetric deformation mode.[5] This was confirmed by examination of *cis*-$[Co(enD_4)_2Cl_2]Cl \cdot H_2O$ and *cis*-$[Co(enD_4)_2(NO_2)_2]NO_2 \cdot H_2O$.

(b) **Vibrations of the NH_2 and NH Groups.**—The principal modes of vibration of the NH_2 group are symmetrical stretching, antisymmetrical stretching, bending, wagging, twisting, and rocking. An assignment of the bands arising from these vibrations has been made by observing the resultant shifts on deuteration of *cis*-α-$[Co(trien)Cl_2]Cl$, *cis*-β-$[Co(trien)Cl_2]Cl$, and *cis*-α-$[Rh(trien)Cl_2]Cl$ (*cf.* Table II). Bands in the regions 3000–3300, 1570–1600, 1290–1330, 1160, 1110, 980, 1070, and 790–835 cm.$^{-1}$ showed isotopic shifts and may therefore be assigned to vibrations of the NH_2 or NH groups.

In metal–ammine compounds the four principal regions of absorption are ~3300, ~1600, ~1300, and ~800 cm.$^{-1}$. These have been assigned to NH stretching modes,[10] antisymmetric deformation,[13] symmetric deformation, and NH_3 rocking,[13,14] respectively. In all triethylenetetramine complexes investigated (Tables I and III and text) the N–H stretching region occurs in the ranges 3055–3287 cm.$^{-1}$ for the *cis*-α compounds and 2985–3330 cm.$^{-1}$ in the *cis*-β series. These bands shift on deuteration to 2220–2450 cm.$^{-1}$ with NH/ND ratios close to the theoretical value (assuming similar force constants) of 1.37 (Figure 2).

The bands at about 1600 cm.$^{-1}$ may be assigned to the antisymmetric NH_2 bending vibration derived from the similar degenerate mode in metal–ammine complexes. These shift on deuteration to 1160–1175 cm.$^{-1}$, in good agreement with shifts found for NH_2 deformation modes in $[Co(en)_2Cl_2]Cl$.[5,7,15] The deformation modes for the secondary amine groups are probably too weak to be observed.[16] It can be seen (Table IV) that the *cis*-α and *trans* salts have only one main absorption in this region, whereas *cis*-β salts give in general two. Closer examination indicates that the *cis*-α absorption and the lower-frequency *cis*-β absorption are in fact composite (Figure 3), this being most obvious in the halogen salts (X = Cl, Br, I) rather than when X = ClO_4 (where it still is observed, however). The band at 1580 cm.$^{-1}$ in *trans*-$[Co(trien)Cl_2]ClO_4$ shows no observable splitting.

Medium to weak absorptions in the region 1290–1335 cm.$^{-1}$ occur in both *cis*-α and *cis*-β compounds, but are absent in the deuterated compounds. In the deuterated *cis*-α spectra it is possible to identify new weak absorptions at 1020–1040 cm.$^{-1}$, but due to the complex nature of the spectrum in this region in both deuterated and undeuterated *cis*-β-$[Co(trien)Cl_2]Cl \cdot H_2O$ no confident assignments can be made for this latter compound. However, the grouping of peaks in the 1290–1335 cm.$^{-1}$ region is not altered by variation in the anion (Table I) nor by substitution in the coordi-

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(11) P. J. Lucchesi and W. A. Glasson, *J. Am. Chem. Soc.*, **78**, 1347 (1956).

(12) A. Murata and K. Kawai, *J. Chem. Phys.*, **28**, 516 (1958).

(13) S. I. Mizushima, I. Nakagawa, and J. V. Quagliano, *ibid.*, **23**, 1367 (1955).

(14) G. M. Barrow, R. H. Kreuger, and F. Basolo, *J. Inorg. Nucl. Chem.*, **2**, 340 (1956); N. Sheppard and D. B. Powell, *J. Chem. Soc.*, 4495, 3108 (1956).

(15) S. I. Mizushima, I. Nakagawa, I. Ichishima, and J. V. Quagliano, *J. Phys. Chem.*, **59**, 293 (1955); T. J. Lane, D. N. Sen, and J. V. Quagliano, *J. Chem. Phys.*, **22**, 1855 (1954).

(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 256.

TABLE III

FREQUENCIES (CM.$^{-1}$) OF *cis*-α- AND *cis*-β-[Co(trien)X_2]X COMPOUNDS (X = Cl, Br) AND OF *trans*-[Co(trien)Cl_2]ClO_4 (KBr DISK)

cis-α		*cis*-β		*trans*
Cl	Br	Cl	Br	Cl
3262 s	3252 s	3234 sh	3262 s	3365 m
3188 s	3170 s	3215 m	3190 s	3310 s
3095 s	3105 s	3155 s	3145 m	3270 s
3055 m	3055 sh	3089 m	3125 m	3150 m
		3060 m	3078 s	
		3000 m		
1570 s	1580 s	1590 m	1585 s	1580 s
		1560 m	1562 s	
1491 w	1487 s	1481 m	1482 m	1491 m
1480 m	1482 s	1451 s	1452 s	1476 sh
1452 sh	1455 m	1431 sh	1433 w	1460 s
1440 s	1449 s			1430 sh
1431 s	1431 s			
1390 w	1399 w	1390 w	1394 w	1381 w
1374 m	1376 m	1374 w	1378 w	1376 w
1362 m	1362 m	1364 w	1368 m	1362 w
		1354 m	1355 m	
1333 sh	1334 m	1329 w	1326 w	1321 w
1327 m	1322 m	1319 w	1314 m	1311 m
1304 m	1308 m	1300 m	1293 m	
1290 sh	1297 m	1281 m	1281 m	1262 m
1270 m	1260 m	1265 w	1273 m	1250 w
1245 w	1241 w	1249 m	1242 m	1241 m
1212 m	1213 w		1215 w	1222 w
1198 m	1183 m	1188 s	1177 s	
1167 s	1152 s	1150 s	1149 s	
1152 m	1145 sh	1101 s	1119 m	
1130 w	1125 w		1103 s	
1110 s	1098 s			
1004 sh				
1070 sh		1080 sh	1086 s	
1058 vs	1053 vs	1070 s	1071 s	
1038 s	1034 vs	1049 s	1049 s	
	1016 w	1027 s	1031 s	1030 s
1005 w	1005 w	1013 w	1012 w	1018 s
981 w	981 m	994 s	992 s	999 s
905 m	903 m	918 m	921 m	941 m
871 m	879 m	898 m	902 m	926 m
				912 w
800 s	801 s	868 sh	873 m	874 m
778 m	784 m	862 m	862 m	847 m
745 w	759 m	825 m	832 m	
		814 m	814 m	720 m
				699 sh
679 s	678 m	607 m		679 w
670 sh		587 w		
640 s	642 s	570 m		
574 m	567 m	513 w		
		502 m		
488 m	490 m	490 m		
479 m	481 sh			

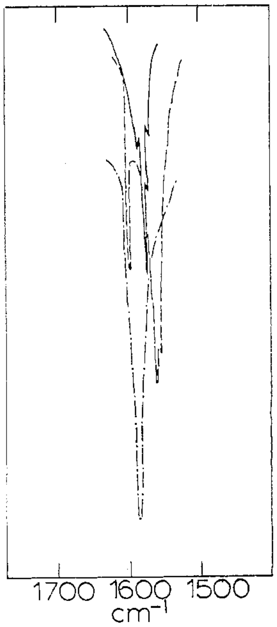

Figure 3.—Infrared spectrum of the NH asymmetric deformation region: ——, *cis*-α; - - -, *cis*-β; - · - · - *trans*.

nation sphere and can be confidently assigned to the symmetric NH_2 deformation.

The remaining three sets of bands at 1110–1160, 980–1070, and 800 cm.$^{-1}$ also show isotopic shifts but are more difficult to assign. Absorptions in these regions have been variously assigned to vibrations of the NH_2 group as a unit, wagging, twisting, or rocking,[5,7] but in this study no confident designations can be justified due to the complicated nature of the spectra in these regions.

(c) Vibrations of the Triethylenetetramine Chelate Ring.—Absorptions little affected by deuteration occur in the regions 1430–1490, 1350–1400, 1250–1290, 1030–1100, and 860–920 cm.$^{-1}$ (Table III). By a comparison with the assignments of Quagliano for similar five-membered rings[15] and assignments for the bis(ethylenediamine)cobalt(III) compounds[5,7] these may be tentatively assigned to the CH_2 bend (1430–1490, 1350–1400 cm.$^{-1}$), CH_2 wagging (1250–1290 cm.$^{-1}$), and CH_2 rocking (860–920 cm.$^{-1}$) modes. It is to be noted that the CH_2 bend at 1430–1490 cm.$^{-1}$ becomes less complicated and more intense in the order *cis*-α, *cis*-β, *trans* as would be expected from a decrease in the number of nonbonded interactions. Also the *cis*-β salts show four absorptions in the CH_2 rocking region while the *cis*-α series give only two.

The intense absorption at 1060 cm.$^{-1}$ in the *cis*-α series and those between 1070 and 1030 cm.$^{-1}$ in the *cis*-β occur in all compounds examined, are unaffected by deuteration, and may be tentatively assigned to CH_2 twisting modes.

Differences in the Spectra of *cis*-α, *cis*-β, and *trans*-Triethylenetetramine Complexes.—In general, the infrared spectrum of *cis*-α-[Co(trien)Cl_2]Cl resembles in many ways that of *cis*-[Co(en)$_2Cl_2$]Cl. This is to be expected since the two compounds are identical but for a bridging ethylene grouping. Both the secondary and

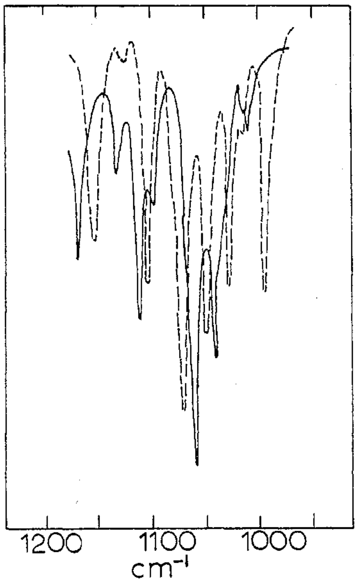

Figure 4.—Typical infrared spectrum for *cis*-α and *cis*-β compounds in the 990–1200 cm.$^{-1}$ region: ——, *cis*-α-[Co(trien)Cl_2]-Cl·H_2O; - - -, *cis*-β-[Co(trien)Cl_2]Cl·H_2O.

terminal nitrogens in trien may assume a tetrahedral configuration in the *cis*-α structure.

In the N–H stretching region (3000–3300 cm.$^{-1}$) the *cis*-α series show three strong absorptions which are shifted as a group on deuteration (Figure 2). A similar set of peaks occurs in *cis*-[Co(en)$_2$$Cl_2$]Cl. The infrared spectrum of *cis*-β-[Co(trien)Cl_2]Cl, is, however, more complicated and usually four (and, in some cases, five) strong absorptions occur in this region. These are also reproduced at lower frequencies following deuteration (Figure 2). *trans*-[Co(trien)Cl_2](ClO_4) gives four medium to strong absorptions in this region.

Such additional splitting of the NH_2 (and NH) stretching vibrations might be expected in the *cis*-β and *trans* compounds. Whereas in [Co(en)$_2$$Cl_2$]Cl and the *cis*-α series all coordinated nitrogens assume a strain-free tetrahedral arrangement, in the *cis*-β configuration one secondary nitrogen is strained into an intermediate planar-tetrahedral conformation, and in *trans*-[Co(trien)Cl_2]ClO_4 both central nitrogens are forced into such an arrangement.[17] It is therefore to be expected that both secondary N–H stretching modes in *trans*-[Co(trien)Cl_2]ClO_4 and one such vibration in *cis*-β-[Co(trien)Cl_2]Cl will occur at frequencies different from those of the unstrained terminal NH_2 absorptions. Also, molecular models show that the terminal NH_2 groups in the *cis*-α series are symmetrically arranged for hydrogen bonding to coordinated Cl atoms while in the *cis*-β arrangement they are in less favorable nonsymmetrical positions. This is substantiated in the [Co(trien)Cl_2]ClO_4 salts where there is a trend to higher frequencies in the order *cis*-α < *cis*-β < *trans* (Tables I and III).

A more immediately obvious difference in the spectra of *cis*-α and *cis*-β complexes is in the region 990–1090 cm.$^{-1}$ (Figure 4); whereas *cis*-α compounds show two strong absorptions in this region the *cis*-β forms show four. Furthermore, the *cis*-α spectra are again similar to that of *cis*-[Co(en)$_2$$Cl_2$]Cl in this region with an added peak at 1030–1040 cm.$^{-1}$. Some of the absorptions in this region shift to lower frequencies on deuteration (Table II) and may be tentatively assigned to modes involving NH_2 twisting. Similar bands at 1048, 1027, and 994 cm.$^{-1}$ in *cis*-β-[Co(trien)Cl_2]Cl shift to lower frequencies following deuteration.

Conclusions.—Infrared spectra of the following compounds have been examined. In every case it has been possible to assign configurations by comparing spectra, particularly in the 3000–3300 and 990–1100 cm.$^{-1}$ regions.

cis-α **Series**[2]**:** [(Co(trien)Cl_2]Cl; [Co(trien)Br_2]-Br[18,19]; [Co(trien)(N_3)$_2$]Cl, -I[19]; [Co(trien)(NO_2)$_2$]Cl; [Co(trien)(H_2O)$_2$](ClO_4)$_3$; [Co(trien)CO_3]Cl; [Co-(trien)(acac)]Cl_2, -I_2[19]; [Rh(trien)Cl_2]Cl[20]; [Cr(trien)-Cl_2]Cl.[21]

cis-β **Series**[2]**:** [Co(trien)Cl_2]Cl; [Co(trien)Br_2]Br[19]; [Co(trien)(N_3)$_2$]Cl, -I[19]; [Co(trien)(NO_2)$_2$]Cl; [Co-(trien)(H_2O)$_2$](ClO_4)$_3$; [Co(trien)CO_3]Cl; [Co(trien)-(acac)]Cl_2, -I_2[19]; [Co(trien)(gly)]Cl_2, -I_2[22]; [Co(trien)-(ala)]Cl_2, -I_2[22]; [Co(trien)(pyox)]Cl, -I[23]; [Co(trien)C_2-O_4]Cl.[24]

The above compounds fall into two main classes.

(1) The dinitro, diaquo, dichloro, and carbonato compounds of Searle and Sargeson[1] for which deductions made on the basis of infrared measurements agree with the configurations deduced by those authors using optical, kinetic, and chemical interconversion methods.

(2) Compounds not studied by Searle and Sargeson. These include the dibromo, diazido, acetylacetone, oxalate, glycine, alanine, and pyruvic acid oxime chelates. Particularly significant is the assignment given to the green "*trans*" and violet "*cis*" [Co(trien)-Br_2]Br isomers prepared by Bailar and Selbin.[18] Inspection of the infrared spectra of these compounds shows that the "*cis*" form is practically pure *cis*-β while the "*trans*" product is mainly *cis*-α contaminated by the *cis*-β form. This has been substantiated following the syntheses of pure *cis*-α-[Co(trien)Br_2]Br and of *cis*-β-[Co(trien)Br]Br by alternative methods.[19]

An inspection of the infrared spectra of [Rh(trien)-Cl_2]Cl prepared by the method of Basolo and Johnson[20] and of [Cr(trien)Cl_2]Cl first reported by Kling and Schlaefer[21] support the *cis*-α configuration. Deuteration of the Rh(III) compound gives further support to this assignment (Table II).

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[17] This observation has been noted in synthetic studies of this and other polydentate aliphatic amine complexes of cobalt(III): F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948); B. Das-Sama and J. C. Bailar, *ibid.*, **77**, 5480 (1955); J. Selbin and J. C. Bailar, *ibid.*, **82**, 1524 (1960); A. M. Sargeson, "Metal Chelates and Chelating Agents," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, p. 190.

[18] J. Selbin and J. C. Bailar, *J. Am. Chem. Soc.* **82**, 1524 (1960).

[19] D. A. Buckingham, unpublished results.

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

[21] O. Kling and H. L. Schlaefer, *Z. anorg. allgem. Chem.*, **313**, 187 (1961).

[22] J. P. Collman and D. A. Buckingham, publications in preparation.

[23] D. A. Buckingham and R. Kreiser, unpublished work.

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

Experimental

Infrared Spectra.—Infrared spectral measurements were recorded on either a Perkin-Elmer Model 21 recording spectrophotometer or a Perkin-Elmer Model 337 grating spectrophotometer. Solid samples in Nujol mulls were examined between potassium bromide plates. For measurements in the 1300–1500 cm.$^{-1}$ region the KBr disk technique was used. Only very minor differences in spectra were noted for the two methods.

Preparation of Compounds. (1) ***cis*-α Series.**—(a) **Chloride.** *cis*-α-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$ was prepared by the method of Sargeson and Searle[1] and recrystallized three times from boiling 3 *N* HCl. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$: C, 21.8; H, 6.1; N, 17.0; Cl, 32.3. Found: C, 21.8; H, 6.14; N, 16.8; Cl, 32.4. A saturated solution of three times recrystallized *cis*-α-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$ (28 g.) was made by shaking vigorously in dilute HOAc (800 ml., pH 3) at room temperature for 2 min. Undissolved material was quickly removed and the filtrate divided into nine fractions which were placed in an ice bath. The following crystalline salts were prepared by double decomposition and washed with a small quantity of iced water and ethanol and air dried. (b) **Bromide.** Addition of KBr gave blue-violet crystals. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{Br\cdot H_2O}$: halogen, 40.3. Found: halogen, 40.3. (c) **Iodide.** Addition of NaI gave violet crystals. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{I\cdot 0.5H_2O}$: halogen, 48.0. Found: halogen, 48.1. (d) **Perchlorate.** Addition of a little $\mathrm{NaClO_4}$ solution gave deep violet crystals. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{ClO_4}$: C, 19.2; H, 4.8. Found: C, 19.4; H, 4.91. (e) **Nitrate.** Addition of $\mathrm{KNO_3}$ gave deep violet crystals. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{NO_3}$: C, 21.3; H, 5.4. Found: C, 21.4; H, 5.44. (f) **Nitrite.** Addition of $\mathrm{NaNO_2}$ gave violet crystals. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{NO_2}$: C, 22.3; H, 5.6. Found: C, 22.4; H, 5.61. (g) **Azide.** Addition of $\mathrm{NaN_3}$ gave violet-blue crystals. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{N_3}$: C, 22.6; H, 5.7. Found: C, 22.4; H, 5.68. (h) **Oxalate.** Addition of a saturated $\mathrm{Na_2C_2O_4}$ solution gave deep blue crystals on standing overnight at 0°. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]_2\mathrm{C_2O_4\cdot H_2O}$: C, 29.2; H, 5.8. Found: C, 29.4; H, 5.94.

(2) ***cis*-β Series.**—(a) **Chloride.** *cis*-β-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$ was prepared by Sargeson and Searle's method from cis-β-$[\mathrm{Co(trien)CO_3}]\mathrm{Cl\cdot H_2O}$.[1] It was recrystallized from dilute HOAc solution by addition of concentrated HCl. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$: C, 21.8; H, 6.1; Cl, 32.3. Found: C, 21.9; H, 6.35; Cl, 32.3. A saturated solution of *cis*-β-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$ (8 g.) was made by shaking vigorously in dilute HOAc (80 ml., pH 3) for 2 min. at 5°. The filtered solution was divided into eight fractions which were immediately placed in an ice bath. The following solid salts were prepared by double decomposition, washed with 80% ethanol, and air dried. (b) **Bromide.** Addition of NaBr gave violet-red crystals. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2Br\cdot H_2O}$: C, 19.3; H, 5.4; halogen, 40.3. Found: C, 19.3; H, 5.63; halogen, 40.5. (c) **Iodide.** Addition of NaI gave violet microcrystals. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{I}$: halogen, 49.1. Found: halogen, 48.9. (d) **Perchlorate.** Addition of a little $\mathrm{NaClO_4}$ solution gave red plates on standing. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{ClO_4}$: C, 19.2; H, 4.8. Found: C, 19.2; H, 4.95. (e) **Azide.** Addition of $\mathrm{NaN_3}$ gave blue-violet crystals. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{N_3}$: C, 22.6; H, 5.7. Found: C, 22.6; H, 5.77. (f) **Thiocyanate.** Addition of a little KSCN solution gave violet-blue microcrystals on standing. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{SCN\cdot 0.5H_2O}$: C, 24.5; H, 5.6; halogen (including SCN), 40.2. Found: C, 24.3; H, 5.85; halogen, 40.8. (g) **Nitrate.** Addition of $\mathrm{NaNO_3}$ gave violet-red needles. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{NO_3}$: C, 21.3; H, 5.4. Found: C, 21.3; H, 5.43. (h) **Nitrite.** Addition of $\mathrm{NaNO_2}$ gave violet-red needles on standing. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2NO_2\cdot H_2O}$: C, 21.7; H, 5.8. Found: C, 21.9; H, 5.99. (i) **Sulfate.** Blue-violet plates formed on adding $\mathrm{NaHSO_4\cdot H_2O}$. *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{HSO_4}$: C, 19.3; H, 5.1. Found: C, 19.5; H, 5.41.

(3) ***trans*-$[\mathrm{Co(trien)Cl_2}]\mathrm{ClO_4}$.**—Prepared by the method of Sargeson and Searle.[1] *Anal.* Calcd. for $[\mathrm{Co(trien)Cl_2}]\mathrm{ClO_4}$: C, 19.2; H, 4.8; N, 14.9. Found: C, 19.3; H, 4.9; N, 14.5.

(4) **"*cis*" and "*trans*" (See Text) $[\mathrm{Co(trien)Br_2}]\mathrm{Br}$ Salts.**—These were prepared by the method of Bailar and Selbin.[18] *Anal.* Calcd. for $[\mathrm{Co(trien)Br_2}]\mathrm{Br}$: C, 16.2; H, 4.1; Br, 53.9. Found, *cis*: C, 16.0; H, 4.4; Br, 53.9. Found, *trans*: C, 15.9; H, 4.3; Br, 53.7.

(5) ***cis*-α-$[\mathrm{Rh(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$.**—Prepared by the method of Basolo and Johnson.[20] *Anal.* Calcd. for $[\mathrm{Rh(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$: C, 19.3; H, 5.4; Cl, 28.5. Found: C, 19.4; H, 5.55; Cl, 28.6.

(6) ***cis*-α-$[\mathrm{Cr(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$.**—Prepared by the Kling and Schlaefer method.[21] *Anal.* Calcd. for $[\mathrm{Cr(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$: C, 22.3; H, 6.25; Cl, 32.9. Found: C, 22.5; H, 6.41; Cl, 33.0.

Deuterated Complexes.—In alkaline solution, it has been found that the H atoms attached to the donor nitrogens of trien exchange rapidly with the solvent while at high acid concentration no exchange occurs at room temperature.[19] Deuterated *cis*-α-$[\mathrm{Rh(trien)Cl_2}]\mathrm{Cl\cdot H_2O}$ and *cis*-β-$[\mathrm{Co(trien)Cl_2)Cl\cdot H_2O}$ were prepared by dissolving in 99.8% $\mathrm{D_2O}$ made approximately 1 *M* in NaOH. After allowing to stand for some 15 min. at room temperature a large excess of concentrated HCl was quickly added and the solutions stood in the refrigerator overnight. *Anal.* Calcd. for $[\mathrm{Rh(trienD_6)Cl_2}]\mathrm{Cl\cdot H_2O}$: C, 19.0; H + D, 6.9. Found: C, 18.8; H + D, 7.11. Calcd. for $[\mathrm{Co(trienD_6)Cl_2}]\mathrm{Cl\cdot H_2O}$: C, 21.4; H + D, 7.8. Found: C, 21.1; H + D, 7.82. Similar treatment of *cis*-α-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}$ resulted in complete conversion to the *cis*-β isomer. This change is currently being investigated. Deuteration of *cis*-α-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}$ was accomplished by repeated recrystallization from $\mathrm{D_2O}$. *Anal.* Calcd. for $[\mathrm{Co(trienD_6)Cl_2}]\mathrm{Cl\cdot D_2O}$: C, 21.3; H + D, 8.3. Found: C, 21.1; H + D, 8.6.