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Reactions of Coordination Compounds in the Solid State. II. The Interconversion of the Isomers of Dichloro(triethylenetetramine)cobalt(III) Chloride, $[Co(trien)Cl_2]Cl$, upon Heating in the Solid State

Terufumi FUJIWARA and John C. BAILAR, Jr.*
School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801, U.S.A.

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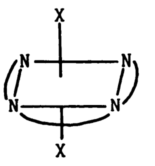
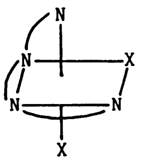
The three isomers of the ion $[Co(trien)Cl_2]^+$, where trien=triethylenetetramine, have been synthesized and their interconversion upon heating in the solid state has been studied. The trans isomer changes to the β-cis isomer, which in turn is converted to the α-cis isomer. The changes have been followed by proton NMR spectroscopy. The first change cannot be explained by a twist mechanism. Experiments with the trans monohydrate or hydrochloride in sealed tubes or in an atmosphere of HCl show that the presence of H_2O accelerates the conversion of the trans isomer to the cis-β isomer, and the presence of HCl accelerates the conversion of cis-β to cis-α, suggesting that the former conversion takes place through an aquation, followed by anation and for the latter conversion nucleophilic attack of a chloride ion on the cis-β isomer is important.

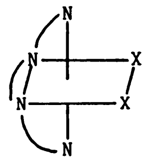
Octahedral complexes of the type $[M(trien)X_2]^+$ exist in three isomeric forms which are called trans, cis-α, and cis-β.



trans



cis-β



cis-α

Several investigators have studied the interconversion of the isomers of the cobalt(III) and chromium(III) compounds in which X represents Cl, but nearly all of their work has been concerned with the compounds in solution. Most notable is the work of Buckingham, Marzilli and Sargeson,[1] who made a thorough study of the cobalt(III) compounds. Even they has little to say about the behavior of these compounds in the solid, crystalline state. We have therefore made an extensive study of these isomers and their interconversion. In any case in which isomerization takes place, the trans isomer is converted to the cis-β form, which then goes more slowly to the cis-α form. The changes are not reversible, in which the cobalt(III) compounds seem to differ from their chromium(III) analogues.[2]

It has been pointed out[3] that the nature of X in $[Co(trien)X_2]^+$ makes a great difference in the relative stabilities of the isomers. Thus, if X=Cl, the order of stability in methanol is β-cis<trans<α-cis, but if X is H_2O, the order in aqueous solution is trans<α-cis<β-cis.

In addition, Asperger,[4] who studied the cobalt(III) complex of the analogous ligand, *N*,*N'*-bis[(*S*)-2-amino-3-phenylpropyl]-(1*R*,2*R*)-1,2-cyclohexanediamine, reported that the L-cis-β compound isomerizes to the trans compound in the solid state when heated to 110 °C. In that case, the conformation of the ring may exert an important influence.

Experimental

Preparation of Compounds. The triethylenetetramine (trien) compound, *trans*-$[Co(trien)Cl_2]Cl\cdot H_2O$, was prepared according to the published method.[1] The product was recrystallized by evaporating a saturated methanolic solution of the complex quickly in a steam of dry air to less than half of its volume. The hydrochloride of the trans form, *trans*-$[Co(trien)Cl_2]Cl\cdot 0.5HCl\cdot 2H_2O$, was prepared by recrystallizing the product from concentrated HCl, washing it with ethanol and acetone, and drying in air. The cis-isomers, *cis-α*- and *cis-β*-$[Co(trien)Cl_2]Cl$, was prepared and recrystallized as described in the literature.[3,5]

The 60—100 mesh sample of hydrochloride of the trans isomer was prepared by gently breaking larger crystals with a pestle, passing these through a 60 mesh screen, and catching the suitably sized particles on a 100 mesh screen. Samples of the finely powdered complex compounds were also prepared by grinding with a mortar and pestle. Elemental analyses of the chloride salts of the isomers are given in Table 1.

Physical Measurements. Proton magnetic resonance spectra were taken with a Varian XL-200 200-MHz FT-NMR Spectrometer fitted with a computer at the normal temperature of the probe (ca. 20 °C) and 100 transients (scanning times) were employed. Tetramethylsilane (TMS) was used as a reference standard. ^1H NMR spectra were observed in dimethyl-d_6 sulfoxide (DMSO-d_6). Although the complexes used here, especially the cis-α isomer, are sparingly soluble in DMSO, 4—5 mg of complex was dissolved in ca. 0.7 mL of solvent in the nmr tube by vigorous shaking[6] and the spectrum was recorded as soon as possible after dissolution.

Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA 7 thermogravimetric analyzer. Samples weighing 4 to 6 mg, heated in a flow of He (ca. 20 mL min^{-1}) at a rate of 10° C min^{-1}, were employed.

X-Ray powder patterns were obtained using a 114.6-mm diameter camera and nickel-filtered Cu *Kα* radiation. The samples used were contained in 0.7 mm glass capillaries, and exposure times ranged from 18 to 25 h.

Infrared spectra were obtained using a Perkin-Elmer 599B

Table 1. Analytical Data

Compound	Calcd/%				Found/%			
	C	H	N	Cl	C	H	N	Cl
cis-α-[Co(trien)Cl_2]Cl·1.5H_2O	21.29	6.25	16.55	31.42	21.36	6.11	16.57	31.24
cis-β-[Co(trien)Cl_2]Cl·H_2O	21.87	6.12	17.00	32.27	21.83	6.17	16.92	31.81
trans-[Co(trien)Cl_2]Cl·H_2O					22.00	6.11	16.54	32.48
trans-[Co(trien)Cl_2]Cl·0.5HCl·2H_2O	19.70	6.20	15.32	33.92	19.62	6.33	15.27	33.99

Infrared Spectrophotometer. The KBr-disk method was employed for all spectral runs (1 mg of sample in 100 mg of KBr) with air in the reference beam.

Rate Studies. Kinetic studies in static air were conducted by heating solid samples of the complexes in the same way as described in our previous study,[9] using an Abderhalden drying apparatus and uncapped aluminum boats. Further, some samples were contained in glass tubes (ca. 3.5 mm in diameter, ca. 4 cm in length) which were sealed off with a torch. Water (bp 100 °C) and *N,N'*-dimethylformamide (bp 152 °C) were used in the boiler as liquids of appropriate boiling points. Kinetic runs in an atmosphere of HCl were also conducted by passing HCl gas at 100 °C into the Abderhalden apparatus, in which samples were mounted in uncapped platinum boats (11 mm in length, 4 mm in width) in place of the aluminum boats. The stream of HCl was preheated to 100 °C in another Abderhalden apparatus connected to the apparatus containing the sample. The stream of HCl was very slow, so the reaction took place in an almost static atmosphere of HCl. The 60—100 mesh and the finely powdered samples were all heated in static air. Samples of the powdered material were also heated in a sealed tube and in an HCl atmosphere. Generally, two to four of the samples (8—11 mg) were heated simultaneously. As soon as possible after taking each sample out of the heating apparatus but before the ^1H NMR measurement, the mass loss accompanying the heating was measured.

Results

NMR Studies. For *cis*-α-[Co(trien)Cl_2]Cl in DMSO-d_6, there are three peaks for the NH protons at δ 5.68, 5.76, and 6.15 with the intensity ratio 2:2:2 but the first two peaks are not separated clearly and the first absorption shows some fine structure (Fig. 1).

The cis-β isomer has six clearly separated NH absorptions of equal intensity (Fig. 2). Four of them show some fine structure with centers at δ 3.86, 4.96, 5.28, and 5.64, respectively, and the other two peaks are broad singlets at δ 7.36 and 7.77, respectively.

The trans isomer shows three NH bands (two quintets with centers at δ 5.13 and 5.58, respectively, and one singlet at δ 6.87) with the intensity ratio 2:2:2 (Fig. 3). The spectrum arising from the NH and NH_2 groups for the hydrochloride are almost identical to that for the monohydrate.

All CH_2 absorptions in these isomers appear at higher field than the NH absorptions and some fine structure, which is probably the superposition of two or more multiplets, is observed. The results in the CH region are even more complex than in the NH region;

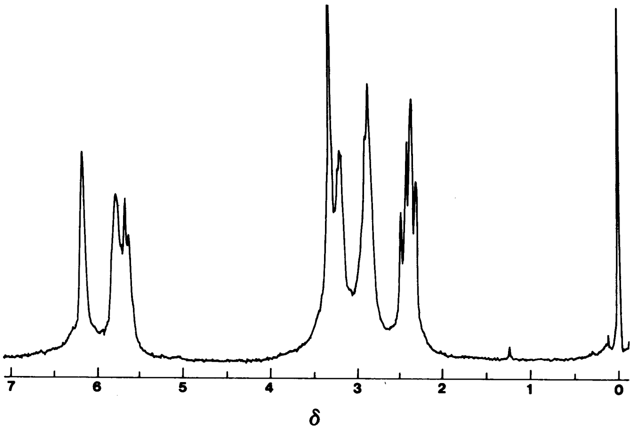


Fig. 1. ^1H NMR spectrum of *cis*-α-[Co(trien)Cl_2]Cl·1.5H_2O in DMSO-d_6.

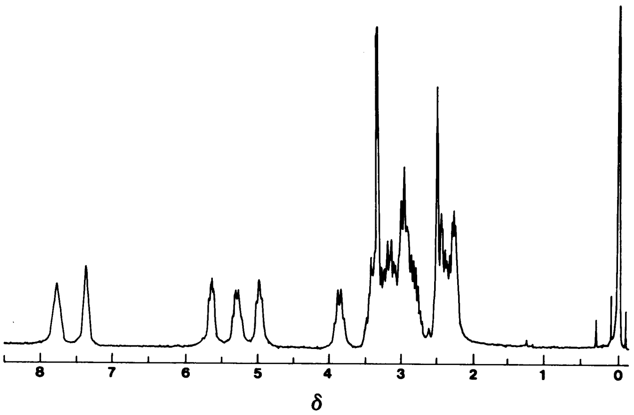


Fig. 2. ^1H NMR spectrum of *cis*-β-[Co(trien)Cl_2]Cl·H_2O in DMSO-d_6.

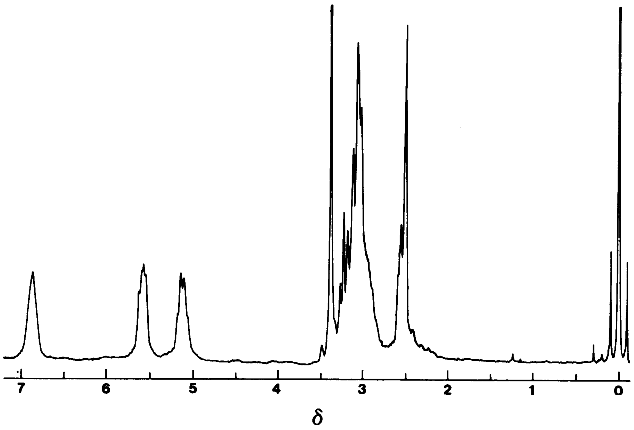


Fig. 3. ^1H NMR spectrum of *trans*-[Co(trien)Cl_2]Cl·H_2O in DMSO-d_6.

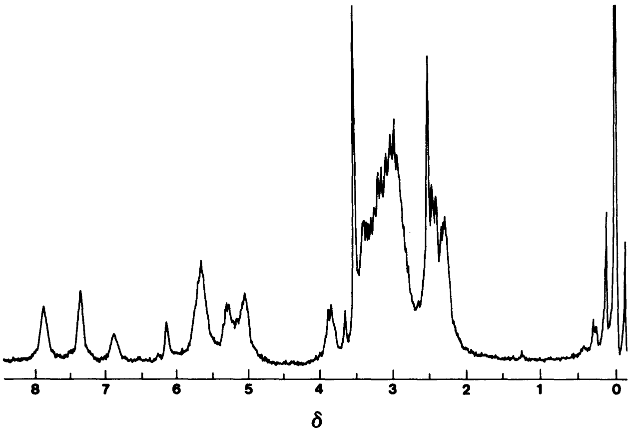


Fig. 4. ^{1}H NMR spectrum of a 60—100 mesh sample of *trans*-[Co(trien)Cl_2]Cl·0.5HCl·$2H_2O$ in DMSO-d_6 after heating at 100 °C for 20.4 h in static air.

the spectrum of the cis-α isomer is less complex than that of the cis-β isomer, as is described in the literature[3] and the CH region in the trans isomer is more symmetrical than that in the cis-α isomer. Furthermore, the signal due to H_2O in the DMSO-d_6 solutions of the isomers and the solvent signal absorb at δ ca. 3.3[10] and 2.50, respectively, and overlap the spectra arising from the CH_2 groups for the cis isomers.

In a mixture of these isomers, overlapping of some NH signals is observed while one NH absorption at δ 6.15 for the cis-α isomer, the three at δ 3.86, 7.36, and 7.77 for the cis-β isomer, and the one at δ 6.87 for the trans isomer separate clearly from each other (for example, Fig. 4). These signals can be used to estimate the relative amounts of the cis-α, cis-β, and trans isomers if no other isomer or complex is present. However, the position of the NH resonance at the lowest field (δ 7.77) is strongly dependent upon the HCl concentration; this is due to the presence of the hydrochloride of the trans isomer. Furthermore, the H_2O peak moves downfield with increase of the HCl concentration and the shift results in overlapping of the H_2O signal with the NH signal at δ 3.86 in the spectrum of the cis-β isomer. For these reasons, only the NH absorption at δ 7.36 (one proton) in the cis-β isomer is used with the NH absorptions (two protons each) in the cis-α and trans isomers for the estimation of their relative amounts by calculating from the peak areas (or intensity ratios) of the NH protons. To check the method, samples of known composition were made and estimated by ^{1}H NMR with the calculated values to within ±3%.[11] In addition, the monohydrate of the trans isomer and the hydrochloride prepared here show the NH absorptions for the cis-β isomer with very small intensities indicating that the cis isomer is present in very small amounts (less than 4%).

TGA Studies. TGA runs on the hydrated chlorides of the cis-α, cis-β, and trans isomers show that dehydration starts soon after heating is begun (at about 30—35 °C). Anhydrous weight levels are attained at 110—120 °C for the cis-α isomer and at 130—140 °C for the cis-β and trans isomers. As the temperature is raised further, no loss of weight is observed until there is a slow loss due to decomposition at 215—230 °C for all of the isomers. The TGA curve for the hydrochloride of the trans isomer shows that the loss of HCl and H_2O takes place at the same time at 90—100 °C. This mass loss is complete at 150—160 °C, and a subsequent slow loss of weight resulting from the decomposition of the complex occurs at 220—230 °C. Similar single-step loss of HCl and H_2O has been reported for the hydrochloride salts of the chloride complexes, *trans*-[Co(en)$_2Cl_2$]Cl·HCl·$2H_2O$ and *trans*-[Co(pn)Cl_2]Cl·HCl·$2H_2O$, which contain the $H_5O_2^+$ ion.[13]

Rate Studies. Heating *trans*-[Co(trien)Cl_2]Cl·0.5HCl·$2H_2O$ to 100 °C yields a mixture of the cis-α, cis-β, and trans isomers as evidenced by comparisons of infrared[14] and ^{1}H NMR spectra; for example, Fig. 4 shows an ^{1}H NMR spectrum of the 60—100 mesh sample of the trans isomer which was heated at 100 °C for 20.4 h in static air (the product is 16% cis-α, 68% cis-β, and 16% trans). The data for the relative amounts of the isomers formed as a function of time, together with the data for % weight of the remaining material are shown in Fig. 5 for the isomerization of the 60—100 mesh and the finely powdered samples of the trans isomer by heating at 100 °C in static air. A rapid initial rate of isomerization of the trans isomer, mainly to the cis-β is observed. Similar behavior has been observed for the solid state racemization of several tris chelated complexes:[15—17] $K_3[Cr(C_2O_4)_3]$, [Co(en)$_3$]X_3·nH_2O, [M(phen)$_3$]X_2 (M=Fe, Ni), [Co(phen)$_3$]X_3, and [Co(phen)$_2$en]X_3. During this initial period, a very rapid loss of weight also occurs. Subsequently, the trans isomer isomerizes more slowly to a mixture of the cis-α and β isomers; the mass loss is also very slow. Nearly complete isomerization is observed after about 45 h, at which time dehydration–dehydrochlorination of the samples is almost complete. However, there is still slow conversion of the cis-β isomer to the cis-α isomer. The 60—100 mesh sample, after heating at 100 °C for 5.32 h, does not pass through the 100 mesh screen, indicating that no change in particle size of the sample occurs during the dehydration–dehydrochlorination.

Figure 5 shows that the 60—100 mesh and the finely powdered samples isomerize at considerably different rates. The initial isomerization of the powdered samples is slower than that of the 60—100 mesh samples. After this initial period, the powdered samples show only a slightly lower rate of isomerization. This behavior is contrary to the observation that the rate of isomerization of *trans*-[Co(pn)$_2Cl_2$](H_5O_2)-

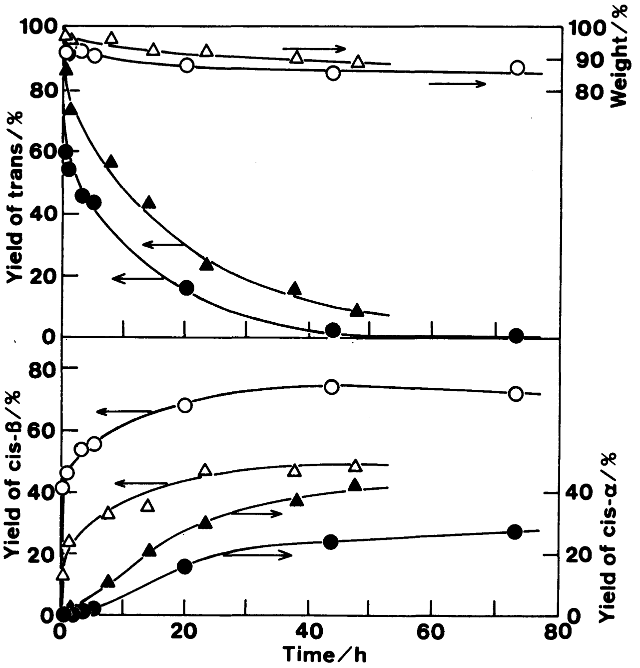


Fig. 5. Isomerization at 100 °C of 60—100 mesh (○, ●) and powdered (△, ▲) samples of *trans*-[Co(trien)Cl_2]Cl·0.5HCl·$2H_2O$ in static air, with about 10% weight of material remaining.

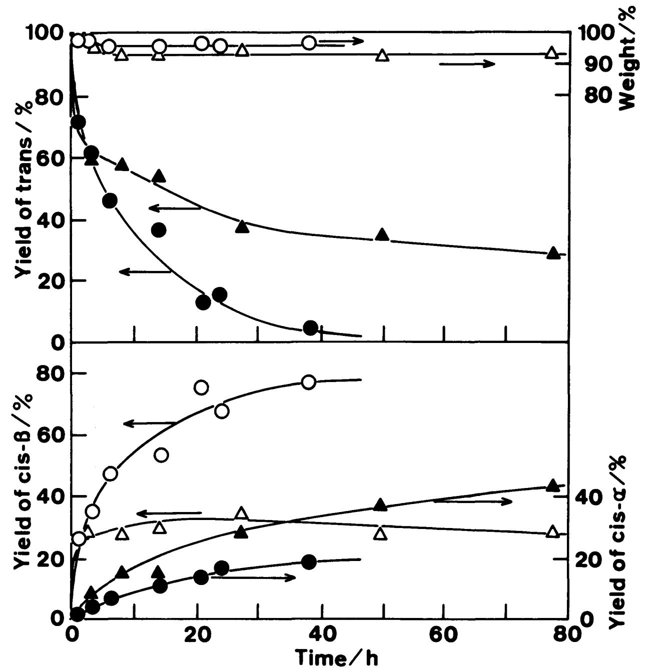


Fig. 6. Isomerization at 100 °C of powdered samples of *trans*-[Co(trien)Cl_2]Cl·H_2O in static air (○, ●) and *trans*-[Co(trien)Cl_2]Cl·0.5HCl·$2H_2O$ in an atmosphere of HCl (△, ▲), with about 6% weight of material remaining.

Table 2. Isomerization of *trans*- and *cis*-β-Dichlorotriethylenetetramine Complexes in Sealed Tubes at 100°C

Time of heating/h	% trans	% cis-β	% cis-α
	trans-[Co(trien)Cl_2]Cl·0.5HCl·$2H_2O$		
0.50	0	97	3
0.80	0	98	2
2.43	0	88	12
66.5	0	53	47
97.8	0	53	47
	95% *cis*-β-[Co(trien)Cl_2]Cl·H_2O[a]		
43.7	0	73	27
70.4	0	64	36
	cis-β-[Co(trien)Cl_2]Cl·H_2O[b]		
2.43	0	100	0
26.3	0	100	0
43.7	0	93	7
70.4	0	89	11

a) Obtained by allowing the trans monohydrate to stand at room temperature for five months. b) Obtained by crystallizing from solution.

Cl_2 increases as particle size is reduced.[18] On the other hand, for the solid-state racemization of [Co(en)$_3$]X_3, it was reported that there is little difference between the 20—40 and 200—325 mesh samples.[16] However, a higher rate of conversion to the cis-α isomer is observed for the powdered samples and apparent cessation of conversion to the cis-β isomer occurs (after about 25 h) prior to complete isomerization of the trans isomer; the extent of loss in weight for the powdered samples is smaller than that for the 60—100 mesh samples.

Heating the powdered samples of the trans isomer at 152 °C results in almost complete isomerization and dehydration–dehydrochlorination during the initial period; the product is a mixture of 42% cis-α, 57% cis-β, and 1% trans isomers. Thereafter, there is only slight conversion of the cis-β isomer into the cis-α isomer (less than 4% after about one day).

Although the trans hydrochloride undergoes no isomerization on standing at room temperature, even after one year, powdered samples of the trans monohydrate, *trans*-[Co(trien)Cl_2]Cl·H_2O,[19] (no hydrogen chloride of "crystallization") give 88% cis-β (12% trans) after three months and 95% cis-β (5% trans) after five months; neither product contains the cis-α isomer. This is similar to the reported conversion of the solid monohydrate into pure *cis*-β-[Co(trien)Cl_2]Cl by heating at 90 °C.[1] However, Fig. 6 shows that heating powdered samples of the monohydrate at 100 °C results in isomerization to a mixture of the cis-α and β isomers, although the product is mainly the cis-β isomer; for example, 77% cis-β, 18% cis-α, and 5% trans after 38.2 h. The powdered monohydrate samples show a higher rate of isomerization than those containing HCl but the rate of conversion to the cis-α isomer is lower, and during this reaction the dehydration is not complete.

Table 3. The Prominent Lines of the X-Ray Powder Patterns of Several [Co(trien)Cl$_2$]Cl Complexes

cis-α-[Co(trien)Cl$_2$]Cl·1.5H$_2$O *d*/Å	*cis*-β-[Co(trien)Cl$_2$]Cl·H$_2$O *d*/Å	*trans*-[Co(trien)Cl$_2$]Cl·H$_2$O *d*/Å
7.33(w)[a]	6.67(s)	9.29(w)
6.61(s)	6.23(s)	8.02(vw)
5.68(m)	5.45(w)	7.17(s)
5.19(vw)		5.98(s)
4.76(w)		5.39(w)
4.12(vw)		4.93(m)
3.70(vw)	3.66(w)	4.22(m)
3.45(m)	3.42(m)	3.98(vw)
3.14(vw)	3.12(vw)	3.83(vw)
2.91(w)	2.89(w)	3.18(w)
2.76(vw)	2.54(w)	2.94(w)
2.56(vw)	2.43(vw)	2.87(vw)
2.39(w)	2.28(w)	2.67(vw)
	2.16(w)	2.47(w)
		2.36(w)
		2.27(vw)
		2.17(w)
		2.02(m)
		1.93(vw)
		1.85(w)

trans-[Co(trien)Cl$_2$]Cl·0.5HCl·2H$_2$O *d*/Å	100 °C in open boat 44.03 h 74% *cis*-β-[Co(trien)Cl$_2$]Cl[b] *d*/Å	100 °C in sealed tube 0.50 h 97% *cis*-β-[Co(trien)Cl$_2$]Cl[c] *d*/Å
9.31(m)	8.87(vw)	6.69(s)
8.06(w)	6.82(s)	
7.14(s)	6.28(m)	6.25(s)
5.40(m)	5.88(s)	
4.94(s)	5.50(w)	5.48(vw)
4.20(m)	3.70(m)	3.68(w)
3.99(vw)	3.46(m)	3.44(m)
3.83(w)	3.14(vw)	3.14(vw)
3.19(m)	3.01(vw)	3.00(vw)
3.04(w)	2.91(w)	2.90(w)
2.95(vw)	2.81(vw)	
2.88(m)	2.69(vw)	2.68(vw)
2.79(w)	2.56(w)	2.55(w)
2.48(m)	2.45(vw)	2.45(vw)
2.29(vw)	2.29(m)	2.29(w)
2.19(w)	2.17(m)	2.16(w)
2.13(vw)	2.11(vw)	2.11(vw)
2.03(m)		
1.95(vw)		
1.88(vw)		
1.71(vw)		
1.69(vw)		
1.63(w)		
1.56(vw)		
1.53(w)		

trans-[Co(trien)Cl$_2$]Cl·H$_2$O room temp 5 months 95% *cis*-β-[Co(trien)Cl$_2$]Cl·H$_2$O[d] *d*/Å
7.17(w)
6.67(s)
6.23(s)

Table 3. (Continued)

5.77(vw)
5.46(w)
3.68(w)
3.42(m)
3.12(vw)
2.98(vw)
2.88(w)
2.67(vw)
2.54(w)
2.43(vw)
2.27(w)
2.16(w)
2.11(vw)

a) Intensities estimated visually: s=strong, m=medium, w=weak, vw=very weak. b) Sample 98% isomerized (contains 24% cis-α isomer). c) Sample 100% isomerized (contains 3% cis-α isomer). d) Sample 95% isomerized (contains no cis-α isomer).

When powdered samples of trans hydrochloride are heated at 100° in an atmosphere of HCl, they isomerize more slowly than when heated in air (Fig. 6). After the initial period, conversion to the cis-β isomer seems to stop while the rate of conversion to the cis-α isomer is almost the same as that in air. Thus, there is a larger amount of the cis-α isomer than of the cis-β isomer in the reaction mixtures after about 30 h. Cessation of mass loss is also observed prior to complete dehydration-dehydrochlorination after the initial mass loss.

When the chlorides of the cis-α and β are heated to 100 °C in air or in HCl, there is no observable isomerization. When kept at 152 °C for 30 h, no significant isomerization occurs, other than a very small (less than 4%) conversion of the β chloride to its α isomer. This is rather surprising in view of the report that the trans chloride is prepared by heating the moist cis isomer to 180 °C.[20] When the chlorides are heated to 152 °C for a long time they develop a greenish cast. This appears after about 30 h. This may be due to some reduction of the cobalt to the +2 state,[1] for the ^{1}H NMR and infrared spectra do not show the presence of any of the green trans isomer. These results for the *cis*-dichloro cobalt(III) complexes are very different from those reported for the dichloro chromium(III) complex, which shows a reversible cis-$\beta \rightleftarrows$cis-α isomerization on heating to 70—285 °C.[2]

Runs in sealed glass tubes show that the powdered hydrochloride samples of the trans isomer isomerize completely to the cis-β isomer on heating within 30 min at 100 °C (Table 2). After the initial rapid conversion to the cis-β isomer, subsequent conversion to the cis-α isomer occurs at a lower rate and then, apparently, the reaction stops, when the mixture is 47% cis-α and 53% cis-β.

On the other hand, under similar conditions, two samples of the cis-β isomer containing no HCl, one of which had been made by rearrangement of the trans isomer at room temperature (5 months) and the other by crystallizing from solution, were converted more slowly to cis-α form than samples which contained HCl. The sample prepared by crystallization isomerized more slowly than the one prepared from the trans isomer. Heating the samples of the cis-β isomer at 152 °C in sealed tubes for 1.10 h gives a mixture of 2% cis-α and 98% cis-β isomers, but heating the cis-α isomer for 2.02 h gives no observable conversion.

X-Ray Studies. The main reflections from the X-ray powder photographs of samples of a series of the [Co(trien)Cl$_2$]Cl complexes are given in Table 3. As samples of the hydrochloride of the trans isomer are isomerized along with dehydration–dehydrochlorination, great changes occur in the X-ray powder patterns, indicating that the crystal structure undergoes a change during the reaction. Similar behavior has been reported for the solid-state racemization of *l*-*cis*-[Cr(en)$_2$Cl$_2$]Cl·H$_2$O, which occurs only during dehydration;[21] this is in contrast to the observation that the powder patterns taken before and after dehydration for (+)-[Co(en)$_3$]X$_3$·H$_2$O (X=I$^-$ and Br$^-$) are different, while heating the anhydrous complexes caused partial racemization but no changes in the powder patterns.[16] When the trans monohydrate isomerized at room temperature without dehydration, changes were evident in the powder patterns, suggesting that in this case, the crystal change seems to parallel isomerization. The products which form when the trans monohydrate is allowed to stand at room temperature for five months (almost pure cis-β isomer) and by heating the trans hydrochloride in a sealed tube at 100 °C for 0.5 h have almost the same crystal structure as a sample of the cis-β isomer crystallized from solution, as shown in Table 3. However, they isomerize at different rates.

Discussion

One can imagine several ways in which the

$[\mathrm{Co(trien)Cl_2}]^+$ ion can isomerize, chief of which are (1) a twist mechanism, (2) a dissociation mechanism, in which the metal momentarily has a coordination number of five, and (3) an associative mechanism, in which the coordination number is seven. Twist mechanisms have been discussed for the isomerization of the complex of a tetradentate ligand.[22] The tetragonal (Rây-Dutt) twist[23] is not applicable to rearrangements of compounds of this type. The trigonal (Bailar) twist[24] and the rhombic (Springer-Sievers) twist[25] do not allow the trans isomer to isomerize to the cis-β isomer but lead to the α-isomer. Therefore, these twist mechanisms can be ruled out for the conversion of the trans isomer to the cis-β isomer. On the other hand, the cis-β isomer can be formed by a dissociation mechanism, with one of the primary nitrogen atoms moving to a position originally occupied by a chloro group in the trans isomer. In the solid state, such a dissociation mechanism seems to be a particularly unfavorable one since there is no possibility of solvation, either of the complex or of the freed amino group which would moderate the large energy required for the charge separation in the transition state caused by the bond breaking. In this study, the presence of water and/or HCl is found to be important to the conversion of the trans isomer to the cis-β isomer. This occurs during dehydration, is accelerated in sealed tubes, and is retarded in an atmosphere of HCl; these observations parallel dehydration and/or dehydrochlorination behavior. This behavior of the trans isomer can be explained by an aquation-anation pathway as proposed for the solid-state racemization of *l*-*cis*-$[\mathrm{Cr(en)_2Cl_2}]\mathrm{Cl}\cdot\mathrm{H_2O}$[21] and the solid-state isomerization of *trans*-$[\mathrm{Co(pn)_2Cl_2}](\mathrm{H_5O_2})\mathrm{Cl_2}$.[18] It has been reported that in aqueous solution the trans isomer aquates stereospecifically to the cis-β-$[\mathrm{Co(trien)ClOH_2}]^{2+}$ ion.[8] Assuming that the cis-β-chloroaqua complex is formed as an intermediate, it is also supposed that the rate-determining step is the first reaction in the following scheme:

$$\textit{trans}\text{-}[\mathrm{Co(trien)Cl_2}]^+ \xrightarrow[-\mathrm{Cl}^-]{+\mathrm{H_2O}} \textit{cis}\text{-}\beta\text{-}[\mathrm{Co(trien)ClOH_2}]^{2+}$$

$$\xrightarrow[-\mathrm{H_2O}]{+\mathrm{Cl}^-} \textit{cis}\text{-}\beta\text{-}[\mathrm{Co(trien)Cl_2}]^+$$

in which in the presence of HCl the activity of $\mathrm{H_2O}$ is diminished by protonation and the dissociation of the Co–Cl bond is unfavorable.

Conversion of the trans isomer to the cis-α isomer by a twist (Bailar or Springer-Sievers) mechanism is unlikely, for heating the trans isomer in a sealed tube causes the immediate formation of the pure cis-β isomer; the subsequent conversion of the cis-β isomer to the cis-α isomer occurs slowly.

Runs in an atmosphere of HCl or in sealed tubes show that the conversion of the cis-β isomer to the cis-α isomer is accelerated by the presence of HCl, in direct contradiction to the conversion of the trans isomer into the cis-β isomer, and heating the hydrochloride in open boats yields larger amounts of the cis-α isomer compared with the monohydrate. However, there is little influence of a water molecule on the reaction. The effect of HCl cannot be understood on the basis of a twist mechanism. For the isomerization of *cis*-$[\mathrm{Co(trien)X_2}]^+$, a pathway involving a "back-side attack" on the cis isomers by an incoming group has been postulated.[12] The isomerization pathway may explain the conversion behavior of the cis-β isomer if it is assumed that the chloride ion plays the role of a base as an incoming group,[26] although the "back-side attack" on the cis-β isomer will give equal amounts of the trans and cis-α isomers, and so the following reaction scheme may be assumed:

$$\textit{trans}\text{-}[\mathrm{Co(trien)Cl_2}]\mathrm{Cl} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \textit{cis}\text{-}\beta\text{-}[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}$$

$$\xrightarrow{k_2} \textit{cis}\text{-}\alpha\text{-}[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}$$

where $k_1 > k_2 \simeq k_{-1}$.

It is found that as particle size is reduced, the rate of isomerization of the trans hydrochloride decreases and the rate of dehydration–dehydrochlorination also decreases while the conversion of the resultant cis-β isomer to the cis-α isomer increases (Fig. 5). An explanation of this by the process proposed here is reasonable if it is assumed that the rate of dehydrochlorination decreases more than that of dehydration as particle size is reduced. This follows from the fact that the presence of HCl causes a decrease in k_1 (conversion of the trans isomer) but an increase in k_2 (conversion of the cis-β isomer). Moreover, it has been reported that the *cis*-α-$[\mathrm{Co(trien)Cl(H_2O)}]\mathrm{Cl_2}\cdot\mathrm{H_2O}$ complex in the solid state dehydrates completely to the *cis*-α-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}$ complex with retention of configuration,[27] suggesting that the cis-α form is the stable one.

The importance of lattice defects in determining the rate of racemization of some tris complexes in the solid state has been discussed;[16,17] the complex ions near a defect experience enhanced reactivity.[28] We found that the two substances, one of which is the almost pure cis-β isomer formed when the trans monohydrate is allowed to stand at room temperature for five months, and another, which is the cis-β monohydrate crystallized from solution, have almost the same lattices as evidenced by the X-ray powder patterns but isomerize at different rates in sealed tubes. This result may be explained by a difference in number of defects in the solid.

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