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Reactions of Coordination Compounds in the Solid State. III. The Behavior of the Isomers of Dichloro(triethylenetetramine)cobalt(III) Bromide and Iodide, $[Co(trien)Cl_2]X$

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 rearrangement of the isomers of dichloro(triethylenetetramine)cobalt(III) bromide and iodide upon heating in the solid state has been studied in relation to the corresponding isomers of the chloride. The behavior of the bromide and iodide has been found to be different from that of the chloride, supporting the existence of anion effects in the solid-state reactions. With respect to the nature of the anions, several factors which are responsible for the differences are discussed in relation to mechanism.

In the second paper of this series, the rearrangement of the geometrical isomers of dichloro(triethylenetetramine)cobalt(III) chloride was considered.1) It has been found that the anion plays an important role in these isomerizations, and that the dichloro bromide and dichloro iodide do not behave in the same way as the chloride. These differences are described here. It is not yet clear whether these differences arise from differences in the crystal lattices, from charge transfer effects, from differences in hydrogen bonding of the hydrates or from some other cause. We hope to clarify this point in later communications. Here we record only the observed differences in behavior, with preliminary comments on possible causes.

Experimental

Preparation of Compounds. The bromide salts of the triethylenetetramine (trien) compound, *trans*-$[Co(trien)Cl_2]Br\cdot 0.5HBr\cdot 2H_2O$, *cis*-$\alpha$-$[Co(trien)Cl_2]Br$, and *cis*-$\beta$-$[Co(trien)Cl_2]Br\cdot H_2O$, were prepared by grinding a slurry of the solids of the corresponding chloride salts1) in a mortar with concentrated HBr (twice) followed by filtration, washing with ethanol and acetone, and drying in air. The crystalline bromide salt of the trans isomer was identified as the dihydrate by a coulometric determination of lattice water with a Hiranuma AQ-3 Aquacounter and a Karl Fischer reagent in which the bromide salt was dissolved.

The cis-β complex was resolved by the method given by Sargeson and Searle.2) The optically active salt, (−)D-sodium bis(oxalato)(ethylenediamine)cobaltate, prepared following the improved procedure of Worrell,3) was used as the resolving agent for the cis-β isomer and the optically active product was obtained as the iodide. A DMSO solution of (+)D-*cis*-β-$[Co(trien)Cl_2]I\cdot 0.5H_2O$ (3.02 mg in 25 ml) gave α_D +0.046, whence $[\alpha]_D=+190$. The optically active cis-β isomer has a CD curve similar to the curve for the corresponding cis isomer.4) Elemental analyses of the bromide and iodide salts of the isomers are given in Table 1.

Physical Measurements. Proton magnetic resonance measurements were made as before1) on a Varian XL-200 200-MHz FT-NMR Spectrometer operating at the normal temperature of the probe (ca. 20 °C). All spectra were run in dimethyl-d_6 sulfoxide (DMSO-d_6) solutions (ca. 0.5—0.6 wt% complex),5) as described previously,1) as soon as possible after dissolution and chemical shifts were measured relative to tetramethylsilane as a reference standard.

Optical rotations were measured in a 2-dm tube with a Rudolph Research Autopol III Automatic Polarimeter using a sodium lamp. CD curves were measured on a JASCO Model J-40/J-41 Automatic Recording Spectropolarimeter in a 1-cm cell. DMSO was used as solvent for the polarimetric measurements.6) Thermogravimetric analysis (TGA) was obtained as before1) but by using a Sinku-Riko Model TGD-3000-RH thermogravimetric analyzer and a flow of N_2 (ca. 40 ml min^{-1}).

Rate Studies. Powdered samples (8—11 mg) of the

Table 1. Analytical Data

Compound	Calcd/%						
	C	H	N	Cl	Br	I	Co
cis-α-$[Co(trien)Cl_2]Br$	20.24	5.10	15.74	19.92	22.45	—	—
cis-β-$[Co(trien)Cl_2]Br\cdot H_2O$	19.27	5.39	14.98	18.96	21.37	—	—
trans-$[Co(trien)Cl_2]Br\cdot 0.5HBr\cdot 2H_2O$	16.66	5.24	12.96	16.40	27.72	—	—
(+)D-*cis*-β-$[Co(trien)Cl_2]I\cdot 0.5H_2O$	17.49	4.65	13.60	17.21	—	30.80	14.30

Compound	Found/%						
	C	H	N	Cl	Br	I	Co
cis-α-$[Co(trien)Cl_2]Br$	20.03	5.06	15.59	19.74	22.66	—	—
cis-β-$[Co(trien)Cl_2]Br\cdot H_2O$	19.13	5.45	15.14	19.01	21.38		
trans-$[Co(trien)Cl_2]Br\cdot 0.5HBr\cdot 2H_2O$	16.80	5.28	12.77	16.40	27.78		
(+)D-*cis*-β-$[Co(trien)Cl_2]I\cdot 0.5H_2O$	17.68	4.59	13.66	17.04	—	32.10	14.46

complex salts used here were mounted in uncapped aluminum boats and were heated in an Abderhalden apparatus containing water (bp 100 °C) or *N*,*N*-dimethylformamide (bp 152 °C) as a liquid of appropriate boiling point in the same way as described in our previous studies.(1,7) Also samples of the optically active iodide were heated at 100 °C in glass tubes (ca. 3.5 mm in diameter, ca. 4 cm in length) which were sealed off with a torch.

Before the ^{1}H NMR and/or polarimetric measurements, the mass loss accompanying the heating was measured as soon as possible after removing the samples from the heating apparatus at fixed times. For the CD measurements, samples of the optically active cis isomer were weighed (4—5 mg) into a 5 mL volumetric flask, dissolved in DMSO by vigorous shaking, and diluted to volume.

Results and Discussion

The ^{1}H NMR spectra of the bromide and iodide of the cis-α isomer are similar to that of the chloride, for which there are three peaks for the NH protons with the intensity ratio 2:2:2 (Figs. 1 and 2). One of the NH absorptions, which shows fine structure, appears slightly downfield (a triplet at δ 5.70 for the bromide and a quintet with center at δ 5.75 for the iodide) while the other two peaks shift upfield (at δ 5.58 and 5.94 for the bromide and at δ 5.53 and 5.89 for the iodide, respectively). In the bromide and iodide of the cis-β isomer, four of the six NH absorptions of equal intensity appear at positions similar to those of the corresponding NH absorptions in the chloride (Figs. 3 and 4); three quintets with centers at δ 3.94, 5.32, and 5.60, respectively, and one singlet at δ 7.40 for the bromide, and the three quintets with centers at δ 3.95, 5.32, and 5.58, respectively, and one singlet at δ 7.43 for the iodide). On the other hand, the other two absorptions shift upfield; one quintet with the center at δ 4.34 and one singlet at δ 6.75, for the bromide and the quintet centered at δ 4.08 and the singlet at δ 6.26 for the iodide. An ^{1}H NMR spectrum arising from the NH and NH$_2$ groups for the hydrobromide of the trans bromide is almost identical to that for the corresponding chloride monohydrate, which 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. 5).

All CH$_2$ absorptions in these isomers appear at higher field than the NH absorptions and show some fine structure, which is probably the superposition of two or more multiplets, as well as those for the

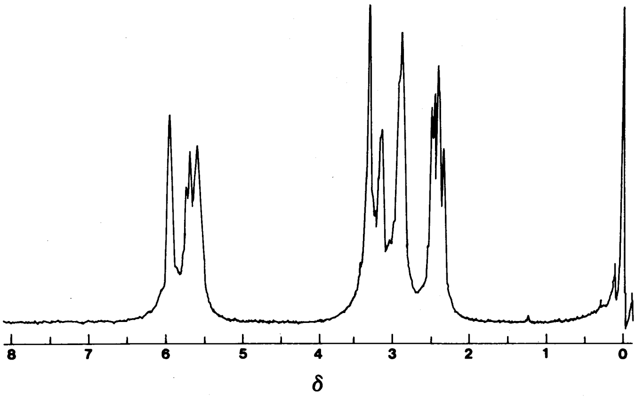

Fig. 1. ^{1}H NMR spectrum of *cis*-α-[Co(trien)Cl$_2$]Br in DMSO-d_6.

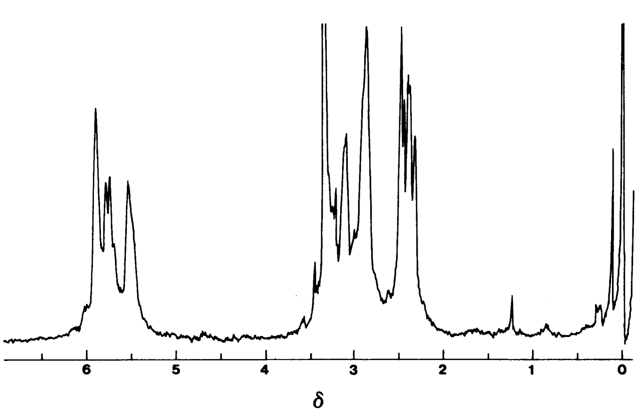

Fig. 2. ^{1}H NMR spectrum of *cis*-α-[Co(trien)Cl$_2$]I in DMSO-d_6.

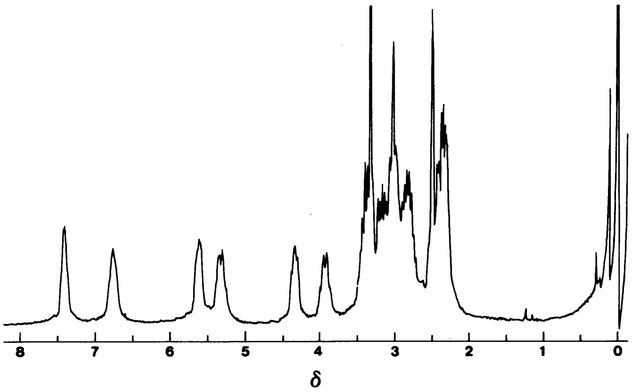

Fig. 3. ^{1}H NMR spectrum of *cis*-β-[Co(trien)Cl$_2$]Br·H$_2$O in DMSO-d_6.

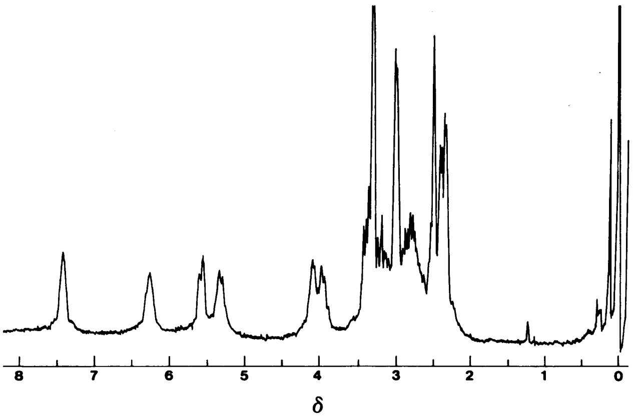

Fig. 4. ^{1}H NMR spectrum of *cis*-β-[Co(trien)Cl$_2$]I·0.5H$_2$O in DMSO-d_6.

corresponding cis-α, cis-β, and trans chlorides.1) Furthermore, the signal due to H_2O (mainly as an impurity) in the DMSO-d_6 solutions of the isomers and the solvent signal overlap the spectra arising from the CH_2 groups for the cis isomers as observed for DMSO-d_6 solutions of the chlorides.1) For the estimation of the relative amounts of the cis-α, cis-β, and trans isomers for a mixture of them (or a product) by calculation of the peak areas (or intensity ratios) of the NH protons, the NH absorptions at δ 7.40, 5.94, and 6.87 for the bromides of the cis-β, cis-α, and trans isomers, respectively, can be used.1)

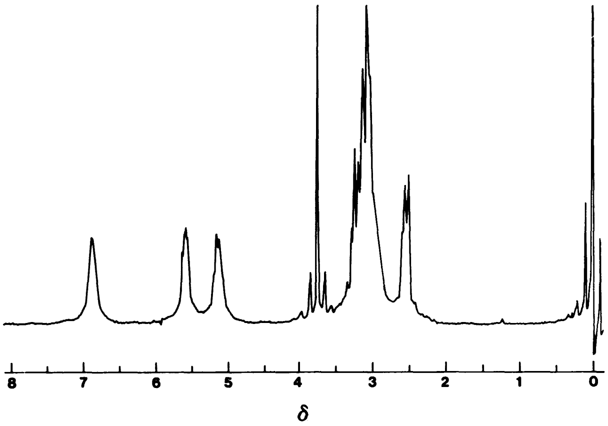

Fig. 5. ^{1}H NMR spectrum of *trans*-[Co(trien)Cl_2]Br·0.5HBr·2H_2O in DMSO-d_6.

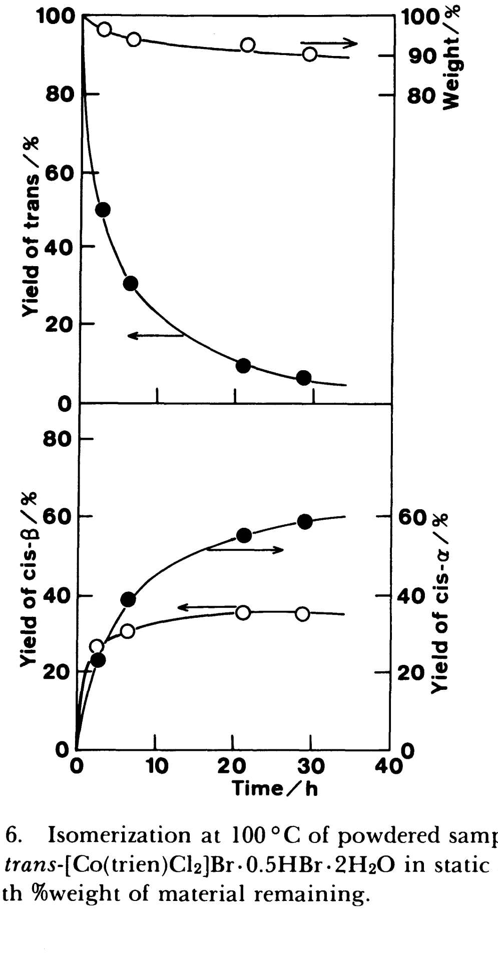

Fig. 6. Isomerization at 100 °C of powdered samples of *trans*-[Co(trien)Cl_2]Br·0.5HBr·2H_2O in static air, with %weight of material remaining.

In a previous study,1) we found that heating the green chloride salt, *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. 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. Similarly, finely powdered samples of the trans hydrobromide, *trans*-[Co(trien)Cl_2]Br·0.5HBr·2H_2O, are isomerized to a mixture of the cis-α and -β isomers when heated at 100 °C in air (Fig. 6). Also, a TGA curve for the trans hydrobromide is similar to the curve for the trans hydrochloride.1) There is a single-step loss of HBr and H_2O at 85—95 °C and the mass loss is complete at 150—160 °C. A subsequent slow loss of weight due to decomposition occurs at 230—240 °C.

The conversion of the trans isomer to the cis-β isomer cannot be expected by the Rây-Dutt,10) Bailar,11) or Springer-Sievers12) twists, as discussed in previous papers.1,13) Moreover, the green crystals of the dibromo bromide, *trans*-[Co(trien)Br_2]Br·HCl, show no isomerization during drying overnight at 90 °C or dehydrochlorination at 110 °C for two days.14) The difference between the dichloro and dibromo complexes indicates that the rate of isomerization may be affected strongly by the Co–X bond strength. In the reaction mixtures, two new NH absorptions for the cis-α isomer appear at δ 5.88 and 6.08 in addition to the NH absorption at δ 5.98 which is similar to that of the bromide, *cis*-α-[Co(trien)Cl_2]Br. When the bromide of the cis-α isomer is prepared by the method described above, the ^{1}H NMR spectrum of the product has similar NH absorptions if the chlorobromo complex, *cis*-α-[Co(trien)ClBr]Br, is present as a byproduct. These indicate that the *cis*-α-[Co(trien)ClBr]$^+$ ion is formed as one of the products when the *trans*-[Co(trien)Cl_2]Br·0.5HBr·2H_2O is heated; such a ligand substitution cannot be expected by a twist mechanism. The conversion behavior of the trans bromide to the cis-β and the subsequent conversion of the cis-β bromide to the cis-α, as well as those of the corresponding trans and cis-β chlorides,1) respectively, can be explained by an aquation-anation pathway15) and a pathway involving a "back-side attack" on the cis isomer by an incoming group,16) respectively.

The nature of the counterion and/or the HX is also important, as shown by the fact that the rate of isomerization for the hydrobromide is higher than for the hydrochloride but the rate of mass loss caused by dehydration–dehydrobromination is lower (dehydration–dehydrobromination is not complete, which was confirmed by a TGA run on the trans hydrobromide at a constant temperature of 100 °C). For example, a powder sample of *trans*-[Co(trien)Cl_2]Cl·0.5HCl·2H_2O, on heating to 100°C, yields 49% cis-β and 42% cis-α in 48 h, whereas the corresponding bromide, *trans*-[Co(trien)Cl_2]Br·0.5HBr·$2H_2O$, upon heating for only 29.4 h, yields 35% cis-β and 58% cis-α (after about 3 h, there is more cis-α isomer in the mixture than cis-β). Similar effects appear in reactions of the solid-state racemization of $(+)_D$-[Co(en)$_3$]$X_3 \cdot nH_2O$$^{17)}$ and thermal decomposition of [Co(NH_3)$_6$]X_3 in the solid state.$^{18)}$ In the case of $(+)_D$-[Co(en)$_3$]X_3, the iodide was found to racemize the most readily, the bromide somewhat less so, and the chloride, hardly at all and it was presumed that hydrogen bonding of the type N–H···X is responsible for the rate differences in the series. In the case of [Co(NH_3)$_6$]X_3, the rate of decomposition decreases in the order of anions $I^- > Br^- > Cl^-$ and it was considered that electron transfer from an outer-sphere anion to the central cobalt(III) ion plays a role in forming the thermally less stable cobalt(II) complex. It may be that both factors are responsible for the above difference in the rate of conversion between the chloride and bromide of the trans or cis-β isomer of the trien complex studied here but it is not clear whether the rate differences arise from charge transfer effects or from differences in hydrogen bonding. The anion effects on the conversion of the trans and cis-β isomers may also be explainable in terms of a defect-diffusion mechanism proposed for solid-state reactions of coordination compounds by House.$^{19)}$ For the conversion, the process involving anation would require that the anion leave a lattice site and migrate to the complex ion to form a transition state, which would involve the vacating of an anion site with the formation of a Schottky type defect (Fig. 2 of Ref. 19), and the activation energy required by the process would be expected to increase with increasing lattice energy. Since for a given cation the lattice energy would increase as the size of the anion decreases, it is reasonable that the chloride should have a higher lattice energy and so a higher activation energy than the bromide.

On the other hand, when the bromides of the cis-α and β are heated to 100 °C in air there is no observable isomerization. When the α or β bromides are kept at 152 °C for 30 h, no significant isomerization occurs, while a very small (less than 4%) conversion of the β chloride to its α isomer is observed in a previous study.$^{1)}$ The optically active iodide $(+)_D$-*cis*-β-[Co(trien)Cl_2]I·$0.5H_2O$ does not undergo significant racemization or isomerization upon heating in an open boat at 152 °C for 22.8 h or even in a sealed tube at 100 °C for 237 h whereas the cis-β chloride in a sealed tube at 100 °C is converted to cis-α form (11% after 70.4 h in Table 2 of Ref. 1), although TGA runs on the iodide and chloride of the cis-β isomer show that the iodide decomposes at a lower temperature (190—200 °C) than the chloride (215—230 °C$^{1)}$). A similar trend in anion effects on the conversion of the cis-β isomer to the cis-α isomer is observed for the solid-state racemization of [M(phen)$_3$]X_2 (M=Fe, Ni) and [Co(phen)$_3$]X_3,$^{20)}$ where the rate differences would be attributed to a nucleophilic interaction of the counterions with the central metal: the donor ability of the chloride ion is larger than that of the bromide or iodide ion. On the other hand, these effects "opposite" to the above ones observed for the hydrobromide and hydrochloride salts of the trans isomer suggest that the rearrangements depend to a large extent on the packing of ions in the crystal, rather than upon any specific chemical property.

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