Reactions of Coordination Compounds in the Solid State. IV.* The Behavior of the Optically Active Salt of *cis*-α-Dichloro-(triethylenetetramine)cobalt(III) Chloride, [Co(trien)Cl₂]Cl

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Abstract

The behavior of the optically active *cis*-α-dichloro-(triethylenetetramine)cobalt(III) chloride, [Co(trien)-Cl₂]Cl, upon heating, has been examined in the solid state. CD and NMR measurements showed that the solid salt of the *cis*-α isomer racemizes by heating at 100 °C in a sealed glass tube, retaining the *cis*-α configuration completely. Concerning this observation, several mechanisms for the rearrangement of the isomer are discussed.

Introduction

The racemization of *cis*-α-dichloro(triethylene-tetramine)cobalt(III) chloride, [CotrenCl₂]Cl, deserves special consideration, for although this isomer is more stable than either of the other two isomers [1], it racemizes upon heating, retaining its *cis*-α configuration. The fact that it is the most stable does not preclude an instantaneous, reversible change into a slightly less stable form, and we believe that the racemization does involve such a change into the symmetrical *trans*-form although in a previous study [1], we found that the *trans* isomer changes first to the *β-cis* isomer, which in turn is converted to the *α-cis* isomer. The postulated reaction is most readily effected by a trigonal twist mechanism. Several other mechanisms for the racemization are also discussed but they are less likely.

Experimental

Preparation of Compounds

The triethylenetetramine (trien) compound, *cis*-α-[Co(trien)Cl₂·1.5H₂O, was prepared and resolved as described in the literature [2, 3]. The optically active salt, (+)$_D$-bis(oxalato)ethylenediaminecobaltate, prepared according to Worrell [4], was used

as the resolving agent. The iodide of the resolved *cis*-α isomer was converted to the chloride by shaking it vigorously with excess AgCl in water containing a drop of acetic acid. AgI was filtered off and the *cis*-α chloride was crystallized by adding acetone. A DMSO solution of (+)$_D$-*cis*-α[Co(trien)Cl₂]Cl·1.5H₂O (3.33 mg in 25 ml), which has a CD curve similar to that of the corresponding optically active *cis* isomer [5], gave α$_D$ + 0.361, whence [α]$_D$ + 1360. *Anal.* Calc. for [CoCl₂C₆H₁₈N₄]Cl·1.5H₂O: C, 21.29; H, 6.25; N, 16.55; Cl, 31.42. Found: C, 20.95; H, 5.91; N, 16.33; Cl, 31.72%.

Physical Measurements

Proton magnetic resonance spectra were recorded as before [1] on a Varian XL-200 200-MHz FT-NMR Spectrometer at the normal temperature of *ca.* 20 °C using dimethyl-d₆ sulfoxide (DMSO-d₆) as solvent† and tetramethylsilane as a reference standard. Optical rotations and CD curves were measured with a Rudolph Research Autopol III Automatic Polarimeter using a sodium lamp and a 2-dm tube and on a Jasco Model J-40/J-41 Automatic Recording Spectropolarimeter in a 1-cm cell, respectively. For the CD measurements, DMSO solutions of the optically active *cis*-α chloride (4–5 mg in 5 ml) were prepared as described previously [6]. The DMSO solutions show no rotational change in several days.

Rate Studies

Kinetic runs were conducted by heating 8–11 mg powdered samples of the optically active complex in uncapped aluminum boats or sealed glass tubes††, using an Abderhalden drying apparatus containing *N,N*-dimethylformamide (boiling point (b.p.) 152 °C) or water (b.p. 100 °C) as described in our previous papers [1, 7]. As soon as possible after taking the samples out of the heating apparatus, mass loss

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*Part III is ref. 6, Part II is ref. 1.
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†The chloride of the optically active *cis*-α isomer is more soluble in DMSO than the corresponding racemic chloride and DMSO solutions of *ca.* 0.5–0.6 wt.% were used.
††The glass tubes (*ca.* 3.5 mm in diameter, *ca.* 4 cm in length) used here were sealed off with a torch.

measurements were made before the PMR and polarimetric measurements.

Results and Discussion

When the optically active $(+)_D$-cis-α-[Co(trien)-Cl_2]Cl·$1.5H_2O$ is heated in an open boat at 152 °C for 22.6 h, it shows no isomerization or racemization, but in a sealed glass tube, within 2 h at 100 °C, it racemizes completely as shown in Table I, but shows no conversion to the β-isomer (shown by PMR spectra*). The solid-state racemization of the optically active cis-α isomer in a sealed tube at 100 °C is rather surprising in view of the fact that no conversion of the cis-α isomer to the corresponding cis-β and/or trans isomers was observed under similar conditions [1]: theories involving association, dissociation and twist mechanisms are to be considered as follows:

Even though the cis-α isomer is thermodynamically the most stable one in the solid state [1], it is quite possible that a small bit of it changes momentarily into a less stable form when it is heated (and then goes back to the α-cis form). If it changes to the trans form, racemization takes place, for the trans form is symmetrical. Twist mechanisms have been discussed for the isomerization of the complex of a tetradentate ligand [8]. If, for example, the face numbered 145 in picture A in Fig. 1 turns in the direction shown by the curved arrow, it gives the trans form, B. This can, of course, twist back to give the original material, but equally well, face 123 of the trans isomer can twist clockwise to give C, which is the mirror-image isomer of A. Further, other twists of this type allow the cis-α isomer to isomerize to the cis-β isomer. Instantaneous, reversible conversion of the cis-α isomer to the cis-β isomer may be postulated for the racemization but an optical inversion of the cis-β isomer is necessary to perform the racemization: as shown in Fig. 1b, for example, counterclockwise rotation of face 346 of the Δ-cis-α isomer gives the Λ-cis-β isomer and subsequently face 136 of it may twist counterclockwise to give the Δ-cis-β isomer, which then goes back by counterclockwise rotation of face 134 to the cis-α isomer but in the Λ form (the mirror-image isomer of the original material). The fact that three steps are necessary may make this mechanism less likely.

In considering one-bond dissociation mechanisms, there are two possibilities: (a) a Cl atom dissociates, (b) an NH_2 group dissociates (Fig. 2). If either Cl dissociates, we'll get a triangular bipyramid (Fig. 2a).

*The spectrum arising from NH, NH_2, and CH_2 groups for the optically active cis-α isomer is almost identical to that reported for the corresponding racemic isomer in ref. 5.

TABLE I. Racemization of $(+)_D$-cis-α-[Co(trien)Cl_2]Cl·$1.5H_2O$ in Sealed Tubes at 100 °C

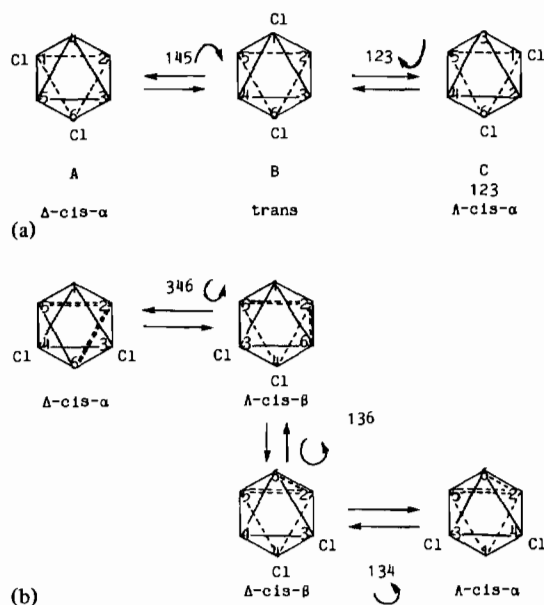| Time of heating (h)	Loss of optical activity (%)	cis-α (%)
0.50	4	100
1.02	86	100
2.20	100	100

Fig. 1. Racemization of cis-α-[Co(trien)Cl_2]Cl by twist mechanisms involving changes into the trans form (a) and into the cis-β form (b).

This mechanism can account for the racemization if the trans isomer now reverts to the cis-α form, but otherwise, the cis-isomer is formed if dissociation is not followed by a twist, so it is less likely than the twist mentioned earlier. Now consider the dissociation of an NH_2 group. Either NH_2 group can dissociate and then replace the adjacent Cl atom, pushing it into the spot which it (the NH_2 group) has just vacated: D → E → F or D → G → H. However, F and H are identical (see this by turning H upside down and then rotating it 180° about its vertical axis in Fig. 2b), so in their formation, no racemization has taken place. Another step necessary to give a racemic product: the cis-β isomer must undergo an optical inversion before going back to the cis-α isomer as described above.

Dissociation of the two trans Co—N bonds (Fig. 3a) can lead to the racemization of the cis-α isomer without geometric isomerization, assuming that only the primary nitrogen atoms of the freed amino groups interchange positions. However, the lack of solvation energy required for the charge separation

(a)

(b)

Fig. 2. Dissociation mechanisms for racemization of *cis*-α-[Co(trien)Cl₂]Cl: (a) a Cl atom dissociates; (b) an NH₂ group dissociates.

in the transition state caused by the bond breaking makes such a dissociation an unfavorable pathway in the solid state as discussed in our previous paper [1]. In addition, another dissociation may be also postulated for the racemization. When the optically active *cis*-α isomer is heated in a sealed tube the H₂O molecule hydrogen binds to the amine groups of the trien ligand, weakening their hold on the

(a) **(b)**

Fig. 3. Structures of possible intermediates for the mechanism of racemization of *cis*-α-[Co(trien)Cl₂]Cl.

metal ion; additionally, the bond between the secondary amine group and the metal is weakened due to the moderate *trans* effect of the chloro groups. This process results in temporary formation of a five-coordinate intermediate with an unattached hydrated secondary amine group (Fig. 3b) like the central nitrogen atom of the triamine in the platinum complex, [Pt(II)(L·HCl)(NH₃)₂](BPh₄)₂ (L = CH₃N-(CH₂CH₂NH₂)₂), which has been found to be unattached to the platinum(II) [9]. However, it is quite improbable that an —NH— group dissociates, for, as a member of two chelate rings, each NH must be held very tightly. It has been reported that aquation of the optically active *cis* isomers takes place with retention of configuration but some isomerization of the α-diaquo to the β-diaquo ion is observed in aqueous solutions [10]. So, the racemization behavior of the *cis*-α isomer in sealed tubes (where no lattice water can escape) may be explainable in terms of an aquation–anation mechanism (as for the solid-state racemization of 1-*cis*-[Cr(en)₂Cl₂]Cl·H₂O [11]) if it is assumed that the *cis*-α diaquo complex is formed as an intermediate

Cl⁻ attack on face 145 or face 456 (opposite Cl).

Attack on 134 pushes 1 to 2

Attack on 346 pushes 6 to 3

Attack on 125 pushes 1 to 2

Attack on 256 pushes 6 to 3

Fig. 4. Association mechanisms involving attack of a Cl⁻ ion for racemization of *cis*-α-[Co(trien)Cl₂]Cl.

and a small bit of it changes into the β-diaquo ion, which rapidly undergoes an optical inversion and subsequent reversion to the α-diaquo ion would be followed by a rapid anation with retention of configuration*. However, there is no experimental justification for such an assumption. On the other hand, it has been pointed out that (even though for the solid state racemization of $[Co(en)_3]X_3$ [13] and $[Fe(phen)_3]X_2$ [14] a twist process is likely) lattice water would play an important role in the racemization reactions: the racemization of the complexes would be accelerated by a large number of defects introduced into the solid upon dehydration since complex ions near a defect are known to experience enhanced reactivity [15]. In a sealed tube, such an effect on the solid-state racemization of the cis-α isomer may be expected: water vapor in the sealed tube would extensively crack the crystal lattice which would be accompanied by production of defects, and thus the racemization would be accelerated. In solution, the base hydrolysis of the optically active cis-α isomer [3] and in the reaction of the isomer with ammonia or with ethylenediamine [16] leads to optical inversions but with isomerization to the cis-β form, for which a 'back-side attack' by an incoming group has been postulated [17]. If we consider an associative mechanism, attack of one of the Cl^- ions on one of the faces of the octahedral furthest from the two coordinated chlorine atoms is the only reasonable possibility. However, Fig. 4 shows attack on faces opposite only one chloride atom, too. In any case, we get the same β-cis isomer, so no racemization takes place.

In summary, it is concluded that the most probable mechanisms for the racemization of cis-α is a twist which gives the optically inactive trans isomer as a transient intermediate.

In addition, the nature of the counter ion is important, as shown by the fact that in contrast to the chloride of the optically active cis-α isomer, the optically active iodide $(+)_D$-cis-β-$[Co(trien)Cl_2]I \cdot 0.5H_2O$ does not undergo significant racemization or isomerization upon heating in an open boat at 152 °C or even in a sealed tube at 100 °C [6].

Acknowledgement

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*The cis-α-$[Co(trien)Cl(H_2O)]Cl_2 \cdot H_2O$ complex in the solid state dehydrates completely to the cis-α-$[Co(trien)Cl_2]Cl$ complex with retention of configuration [12].