Reactions of Coordination Compounds in the Solid State
V. The Racemization of Potassium Ethylenediaminetetraacetate Cobaltate(III)

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Abstract

The racemization of the optically active solid salt K[Coedta]·$2H_2O$ has been studied at 152 and 174 °C. Some decomposition takes place at the higher temperature. When heated to 152 °C for 2.3 h, the material is completely dehydrated, but shows no loss of optical activity. On longer heating, racemization becomes apparent. When heated in a sealed glass tube to 174 °C, racemization occurs rapidly (accompanied by some decomposition of the sample). Possible mechanisms are discussed.

Introduction

The ethylenediaminetetraacetate ion is one of the strongest complexing agents known; it may utilize four, five or all six of its ligating atoms in complex formation. It has been shown that in the salt K[Coedta]·$2H_2O$, the ligand is hexadentate [1]. Thus, the complex exists in two stereoisomeric forms. When the optically active material is heated to 152 °C in an open vessel, the water escapes with negligible loss of optical activity. On longer heating, the loss of optical activity becomes apparent.

When samples of the hydrate are heated in a sealed tube at 174 °C, rapid racemization takes place, accompanied by extensive decomposition of the complex. It is possible that when the hydrated complex is heated, the water molecules displace carboxyl groups from the coordination sphere (Fig. 1a), but this is energetically unfavorable. A trigonal twist mechanism, giving a prismatic intermediate (Fig. 1b), seems to offer a more logical explanation.

Experimental

Preparation and Optical Resolution

The ethylenediaminetetraacetato (edta) complex, K[Co(edta)]·$2H_2O$, was prepared by the method given by Dwyer *et al.* [2]. The potassium salt was resolved by the method of Dwyer and Garvan [3], which utilized d-*cis*-dinitrobis(ethylenediamine) cobalt bromide as the resolving agent. The dextro isomer, d-K[Co(edta)]·$2H_2O$, with $\Delta\epsilon = -1.28$ at 584 nm and +0.65 at 506 nm (for the levo isomer, $\Delta\epsilon = +1.50$ at 585 nm and −0.69 at 505 nm [4], and +1.7 at 588 nm and −0.9 at 515 nm [5]), was obtained from the filtrate which was reserved after removing the diastereoisomer containing the levo isomer, by adding ethanol to the ice cold filtrate. It was washed with cold 50% ethanol, ethanol and acetone in that order, and dried in air. *Anal.* Found: C, 28.36; H, 3.87; N, 6.71; Co, 13.96; K, 9.22. Calc. for $C_{10}H_{16}O_{10}N_2CoK$: C, 28.44; H, 3.82; N, 6.63; Co, 13.96; K, 9.26%.

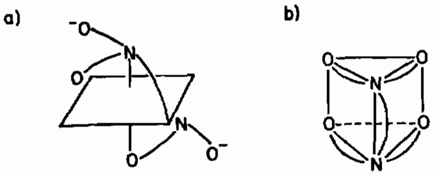

Fig. 1. Structure of possible activated complexes for the mechanisms of racemization of the edta complex: (a) dissociation; (b) trigonal twist.

Physical Measurements

Visible absorption spectra were measured on a Varian 2300 UV-VIS-NIR Spectrophotometer. The CD curves were recorded with a JASCO Model J-40/J-41 Automatic Recording Spectropolarimeter in a 1-cm cell. Spectra were measured at room temperature. Thermogravimetric analysis (TGA) was carried out as before [6, 7] with a Sinku-Riko Model TGD-3000-RH thermogravimetric analyzer.

Rate Studies

Kinetic studies were concluded as described in our previous study [6, 7] by using an Abderhalden drying apparatus in which *N*,*N*-dimethylformamide (boiling point (b.p.) 152 °C) and n-decane (b.p. 174 °C) were used as liquids of appropriate boiling points. Un-

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capped platinum boats (11 mm in length, 4 mm in width) and glass tubes (*ca.* 3.5 mm in diameter, *ca.* 4 cm in length) which were sealed off with a torch were used as containers in which powdered samples (8–11 mg) of the complex were mounted. Each sample was removed from the heating apparatus at a fixed time and then mass loss accompanying the heating was measured as soon as possible in the case of the samples in the uncapped platinum boats. For the visible absorption and CD measurements, 4–5 mg of the sample was weighed into a 5-ml volumetric flask, dissolved in water, and diluted to volume.

Results and Discussion

TGA runs on the dihydrate of the edta complex, d-K[Co(edta)]·2H_2O, shows that a loss of one of the two H_2O molecules takes place at 75–80 ℃. This mass loss is complete at 110–115 ℃ and a subsequent loss of weight resulting from loss of another water molecule occurs. An anhydrous weight level is reached at 155–160 ℃. As the temperature is raised further, a slow loss in weight due to decomposition starts at 200–210 ℃.

It has been reported that in aqueous solution the edta complex undergoes no loss in rotation at 20 to 25 ℃ in a month but slowly racemizes at 100 ℃ with a half-life of 168 min [3]. Heating the optically active complex in the solid state at 152 ℃ for 2.3 h causes no observable loss of optical activity although there is complete loss of water, as shown by the loss in weight (8.5%)*, which is in good agreement with the above TGA data. The visible spectra measured before and after the heating are almost identical and agree well with that reported for the hexadentate edta complex [4]. After 45.6 h, under the same conditions, there is a slight decrease in intensity of the visible absorption band at 538 nm (less than 3% loss of absorbance) while 12% loss of optical activity is observed, indicating that the complex in the solid state racemizes mainly without decomposition. When heated at 174 ℃ for 50.3 h, the complex undergoes 41% loss of optical activity but simultaneously, changes in color from violet to a reddish hue; there is a 35% loss of absorbance due to decomposition and 15.8% loss in weight (the H_2O molecule amounts to about 8.5% of the total weight). The behavior is similar to the decomposition and loss of optical activity of the *cis*-ℓ-$[Co(en)_2(NH_3)_2](PF_6)_3$ complex [7]; it is more prominent at a higher temperature than at a lower temperature.

Heating the edta complex in sealed glass tubes at 174 ℃ for 2.2 h results in complete loss of optical activity while the above absorption band for the edta complex still appears on the visible spectrum with a large decrease in the intensity (51% loss of absorbance), although the maximum is shifted slightly (only about 2 nm) toward the blue. This indicates that the edta complex remaining has racemized at a higher rate in the sealed tube than in the open boat. Moreover, a brown product which shows no optical activity is obtained under the same conditions after 6.6 h. The visible spectrum of the product shows no observable absorption band at 538 nm for the edta complex, indicative of complete decomposition. The racemization of the hydrated edta complex can be explained by a dissociation mechanism if one assumes the breaking of the two *trans* Co–O bonds and the formation of an activated complex containing tetradentate edta in a transition state as shown in Fig. 1a.

The large energy required for dissociation of these bonds would be somewhat moderated by solvation of the complex or of the freed carboxyl groups, but in the solid state in which there is no possibility of solvation, this mechanism seems to be an unfavorable one. An intermediate containing pentadentate edta and a second substituent, for example, $[Co(edta)(H_2O)]^-$, which was prepared by Schwarzenbach [8], may facilitate such a pathway if it is formed as a precursor of the activated complex. On the other hand, it has been demonstrated that elimination of the second substituent from an optically active complex ion containing pentadentate edta proceeds without loss of optical activity [1]. We have found that the edta complex in the solid state does not undergo racemization during dehydration but that the solid-state racemization of the complex occurs after the dehydration. This result suggests that the most probable mechanism for the solid-state racemization of the edta complex is a twist which forms a trigonal prismatic structure (Fig. 1b) in the transition state**. The decomposition of the edta complex has not been investigated in detail in this study so there is insufficient evidence to indicate whether the decomposition mechanism for the edta complex is related to the racemization mechanism in the solid state.

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*It was reported in ref. 1 that the racemic edta complex is dehydrated at 105 °C.

**A trigonal (Bailar) twist mechanism was proposed for the racemization of the cobalt complex of edta by Bailar [9].

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