CHEMISTRY LETTERS, pp. 719-722, 1972. Published by the Chemical Society of Japan

REACTIONS OF THE β-CIS ISOMERS OF ETHYLENEDIAMINE-N,N'-DIACETATO(ETHYLENEDIAMINE)COBALT(III) AND ETHYLENEDIAMINE-N,N'-DIACETATO(DIAMMINE)COBALT(III) COMPLEXES IN BASIC AQUEOUS SOLUTIONS

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Reactions of the β-cis isomers of ethylenediamine-N,N'-diacetato-(ethylenediamine)cobalt(III) and ethylenediamine-N,N'-diacetato(diammine)-cobalt(III) ions, β-cis-$[Co(EDDA)(en)]^+$ and β-cis-$[Co(EDDA)(NH_3)_2]^+$, have been examined in basic aqueous solutions. It has been found that, whereas the diammine complex hydrolyzes, the ethylenediamine complex isomerizes to the α-cis isomer. The routes of the reactions have been discussed.

Although great many pairs of geometrical isomers have been synthesized among the cobalt(III) complexes, only a small amount of studies, in which the rates of isomerization in aqueous solutions have been measured, are found in the literature.[1] This is in contrast to the many kinetic studies on the substitution reactions including acid and base hydrolyses. Isomerization reactions are in general difficult to measure kinetically, since one isomer does not necessarily isomerize to the other, but substitutes its ligand with a molecule or an ion present in the solution. In the course of our study on the ethylenediamine-N,N'-diacetatocobalt(III) complexes, we noticed that the β-cis isomer of ethylenediamine-N,N'-diacetato(ethylenediamine)-cobalt(III) ion, β-cis-$[Co(EDDA)(en)]^+$, isomerized to the α-cis isomer in a basic solution. Therefore, measurements of the rates of the isomerization have been carried out spectrophotometrically. Reaction of the β-cis isomer of ethylenediamine-N,N'-diacetato(diammine)cobalt(III) ion, β-cis-$[Co(EDDA)(NH_3)_2]^+$, has also been examined under the similar conditions.

All of the complexes used in this study were prepared by the procedures described previously.[2] The kinetic runs were performed in the usual manner. Fig. 1

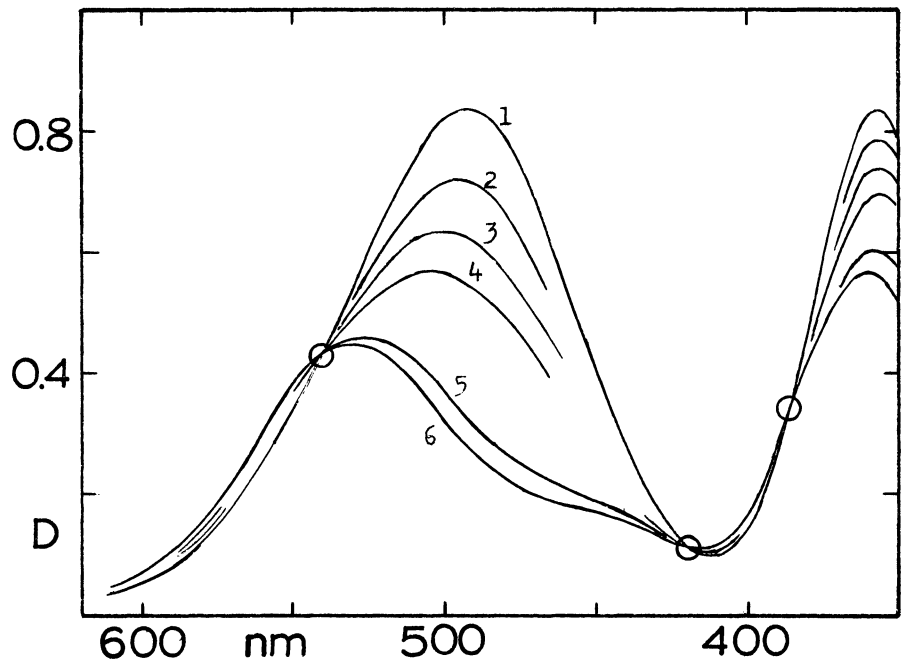


Fig. 1. Change of the Absorption Curve of β-cis-[Co(EDDA)(en)]$^+$ at 65°C in 0.3M $NaHCO_3$-0.1M Na_2CO_3 Solution.
1, the β-cis isomer;
2, after 60 min;
3, after 120 min;
4, after 180 min;
5, at equilibrium;
6, the α-cis isomer.

illustrates a change of the absorption curve of the ethylenediamine complex. As may be seen in the figure, three isosbestic points, which are on the curve of the α-cis isomer, maintain their positions during the reaction. This means that no reaction but the isomerization took place. The rate constants were calculated, assuming that the opposing β-to-α and α-to-β reactions are both first order with respect to the complex ions:

$$k = \frac{1}{t} \cdot \frac{x_\infty}{a} \ln \frac{x_\infty}{x_\infty - x_t}$$

where

$$x_t = \frac{D_\beta - D_t}{D_\beta - D_\alpha} \times a \qquad \text{and} \qquad x_\infty = \frac{D_\beta - D_\infty}{D_\beta - D_\alpha} \times a$$

a = initial concentration of the β-cis isomer (0.005 mole/l)

D's = absorbances at 493 nm

The rate constants calculated at different reaction times of a run satisfactorily agreed, verifiing the opposing first order reactions with respect to the complex ions. Table 1 summarizes the rate constants. It may be seen in the table that the isomerization is highly dependent on the hydroxyl ion concentration and approximately first order with respect to the concentration.

On the other hand, the diammine complex showed a quite different spectral change, as is illustrated in Fig. 2. The isosbestic points at 436 and 517 nm observed during the earlier period of the reaction suggest that the complex turns into a different species of complex, since the points are not on the absorption curve of the α-cis

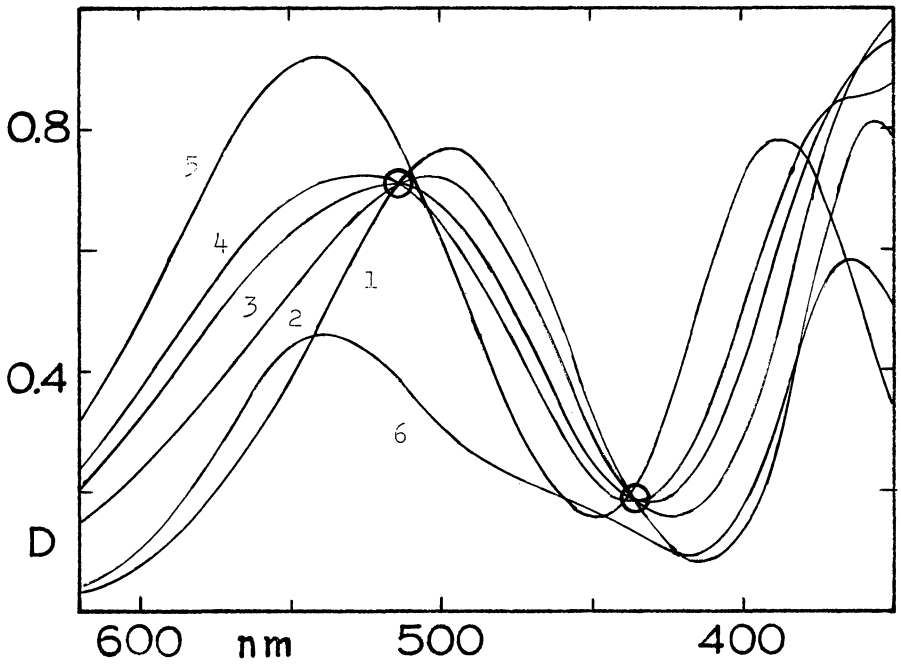


Fig. 2. Change of the Absorption Curve of β-cis-$[Co(EDDA)(NH_3)_2]^+$ at 50°C in 0.3M $NaHCO_3$-0.1M Na_2CO_3 Solution.
1, the β-cis isomer;
2, after 20 min;
3, after 40 min;
4, after 60 min;
5, at equilibrium;
6, the α-cis isomer.

isomer. This species has not yet been identified. However, the spectral curves observed at the later period of the reaction gradually became distant from the isosbestic points, and the curve at equilibrium was identical with that obtained with the diaquo complex, $[Co(EDDA)(H_2O)_2]ClO_4$, in the same condition. These facts clearly indicate that the reaction of the diammine complex is not the isomerization but the substitution of the coordinated ammonia with possibly hydroxyl ion.

Table 1. Rate Constants, $k(\times 10^{-3}min^{-1})$, of the Isomerization of β-cis-$[Co(EDDA)(en)]^+$.

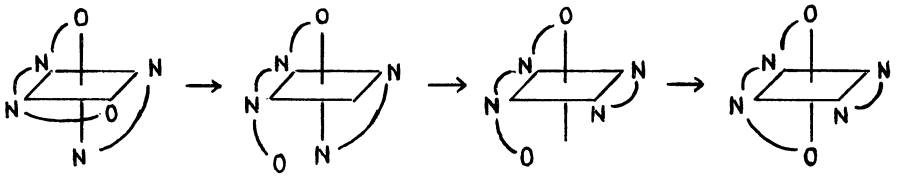
Condition	pH at 65°C	60°C	65°C	70°C
0.3M $NaHCO_3$ 0.1M Na_2CO_3	9.47		4.28	
0.2M $NaHCO_3$ 0.2M Na_2CO_3	9.79	4.09	10.7	26.0
0.1M $NaHCO_3$ 0.3M Na_2CO_3	10.15		18.8	

Since the electronic configurations of the two reactants are quite similar and the bond energies of the cobalt-nitrogen bonds in the complexes are likely to be nearly equal, it may be assumed that the activation processes of the reactions are not different. On this assumption, the route of the isomerization of the ethylenediamine complex is estimated as follows:

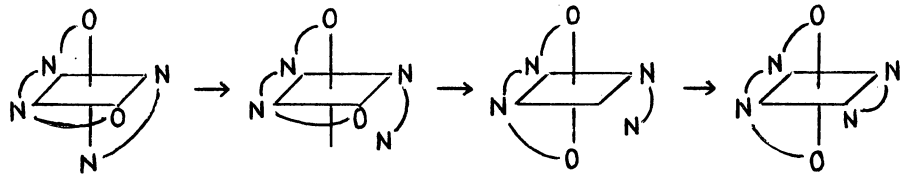
The following three routes should be taken into consideration; any other route, such as a route through a seven-coordinated intermediate, can not bring the reactant into the product.

(1) Route through a trigonal prismatic intermediate without bond breaking,

(2) Route with bond breaking between the cobalt and the in-plane oxygen of EDDA,



(3) Route with bond breaking between the cobalt and the trans-to-O nitrogen of en,



The rate via the route (1) would depend on temperature alone and not on pH. The diammine complex could also isomerize via this route, since it involves no bond breaking. The experimental results, therefore, exclude this route without any question. If the reaction proceeds without bond breaking between the cobalt and the nitrogen of en (the route (2)), the diammine complex would also isomerize by the similar way. Since the diammine complex exhibited no sign of isomerization at all, the route (2) can also be excluded.

The route (3) alone can explain the observed reaction characteristics. Since the probability of simultaneous bond breaking of both the cobalt-nitrogen (of en) bonds must be extremely small, the ethylenediamine complex isomerizes via this route without hydrolysis. In contrast, the bond breaking of the cobalt-ammonia bond can not retain the released ammonia molecule in the vicinity of complex, and the coordination of a water molecule or a hydroxyl ion to the vacant coordination site must be much more probable. Thus, the hydrolysis of the diammine complex can also be explained. Details on the experimental results and a more thorough discussion will be reported shortly.

References:

1) See, for example, F. Basolo and R. G. Pearson, " Mechanisms of Inorganic Reactions ", 2nd Ed., John Wiley and Sons, Inc., New York, (1967), p. 274.

2) K. Kuroda, This Letters, 1972, 197.

(Received June 12, 1972)