CHEMISTRY LETTERS, pp. 17-20, 1974. Published by the Chemical Society of Japan

PREPARATION AND ISOMERIZATION OF THE ISOMERS OF ETHYLENEDIAMINE-N,N'-DIACETATO(TRIMETHYLENEDIAMINE)COBALT(III) ION

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Two isomers of ethylenediamine-N,N'-diacetato(trimethylenediamine)-cobalt(III) perchlorate, α- and β-[Co(EDDA)(tn)]ClO_4, have been synthesized, and the isomerization from the β-isomer to the α-isomer has been examined kinetically in carbonate buffer solutions. The reaction character has been compared with that of the corresponding ethylenediamine complex.

Although great many pairs of geometrical isomers have been synthesized among the cobalt(III) complexes, only a few isomerizations between the isomers have been examined kinetically in aqueous solutions.[1] The reason for such situation is simply that one isomer does not necessarily isomerize to the other, but substitutes its ligand with a molecule or an ion present in the solutions. We have previously reported on the isomerization of β-isomer of ethylenediamine-N,N'-diacetato(ethylenediamine)cobalt(III) ion to the α-isomer.[2] In order to extend observations on isomerizations, α- and β-isomers of ethylenediamine-N,N'-diacetato(trimethylenediamine)cobalt(III) perchlorate, α- and β-[Co(EDDA)(tn)]ClO_4, were newly synthesized, and the isomerization from the β- to the α-isomer was examined in carbonate buffer solutions.

Preparations. (1) β-Ethylenediamine-N,N'-diacetato(trimethylenediamine)-cobalt(III) Perchlorate Monohydrate, β-[Co(EDDA)(tn)]$ClO_4 \cdot H_2O$. Into 5 ml of water containing 0.15 g of trimethylenediamine, was added 0.4 g of α-*cis*-ethylenediamine-N,N'-diacetato(diaquo)cobalt(III) perchlorate.[3] The color of the solution was blue owing to the formatiom of the hydroxo species. (The aqueous solution of the diaquo complex alone is red-violet.) The mixture was warmed at ~50°C with stirring. The color turned to reddish violet and at the same time a red precipitate began to appear. After the warming for 10 min, the mixture was cooled to 0°C. The precipitate was collected, and then recrystallized from 25 ml of warm(~60°C) water with the addition of a few drops of 6N $HClO_4$. Yield, 0.25 g. Found: C, 25.26; H, 5.43; N, 13.20%.[4] Calcd for [Co(EDDA)(tn)]$ClO_4 \cdot H_2O$ = $CoC_9H_{22}O_9N_4Cl$ (424.68): C, 25.46; H, 5.22; N, 13.19%. The solubility in water is 4.1 g/l at 20°C.

(2) α-Ethylenediamine-N,N'-diacetato(trimethylenediamine)cobalt(III) Perchlorate, α-[Co(EDDA)(tn)]ClO_4. The filtrate in the above preparation was diluted to 20 ml with water, and 0.1 g of active charcoal and a drop of trimethylenediamine were added. The mixture was warmed at ~60°C for 30 min with stirring. After the removal of charcoal by filtration, the filtrate was acidified with 1 ml of 6N $HClO_4$. Red-violet

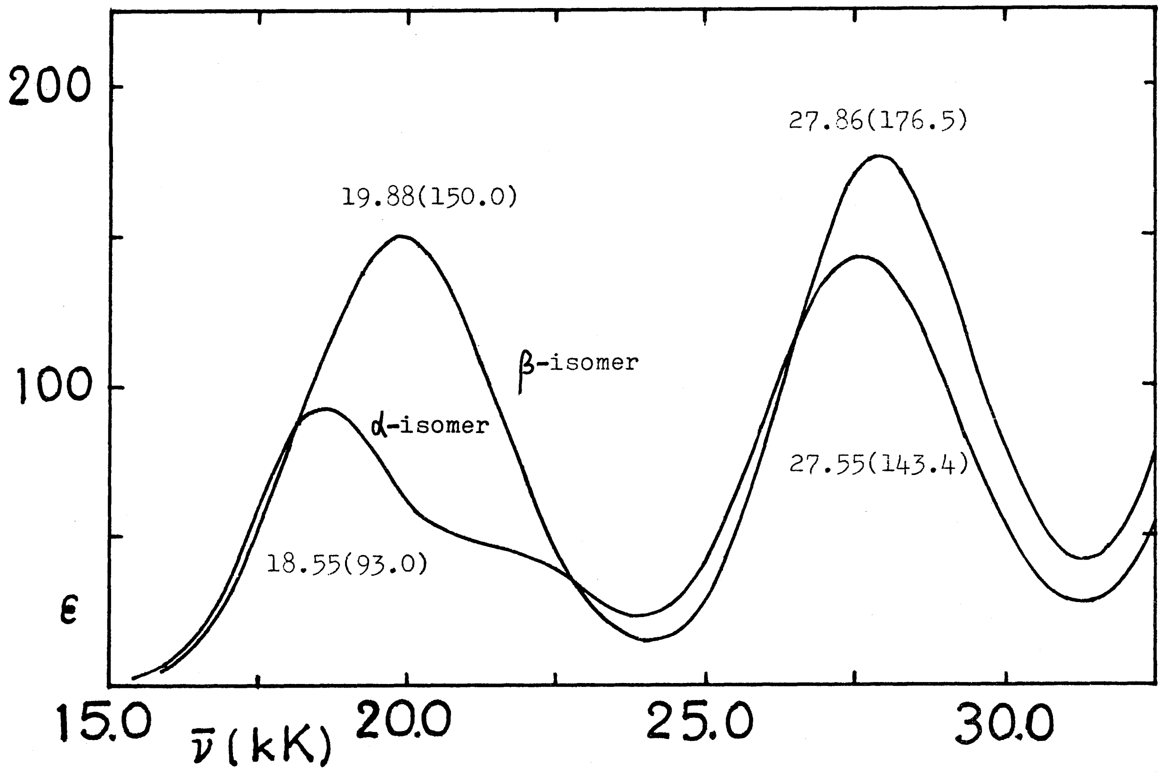


Fig. 1. Electronic Spectra of [Co(EDDA)(tn)]ClO_4.

crystals came out upon the evaporation to 10 ml followed by cooling. The deposit was recrystallized from 5 ml of warm water. Yield, 0.15 g. The α-isomer can also be obtained directly by the reaction of the diaquo complex with trimethylenediamine at the presence of charcoal. The yield is nearly quantitative. Found: C, 26.43; H, 5.07; N, 13.74%.[4] Calcd for [Co(EDDA)(tn)]ClO_4 = $CoC_9H_{20}O_8N_4Cl$ (406.67): C, 26.58; H, 4.96; N, 13.78%. The solubility in water is 14.5 g/l at 20°C.

In the case of the preparation of the corresponding ethylenediamine complex, the β-isomer is obtained by the reaction of the diaquo complex with en at 100°C.[5] In contrast, the β-isomer of the present complex is obtained by the reaction at 50°C or even at lower temperatures. We have discussed previously[5] that, since the β-configuration of the tetradentate is more unstable than the α-configuration, high temperature is necessary to prepare β-isomers from the starting α-*cis* diaquo complex. The apparent contradiction of the present preparation against the discussion is obviously due to the low solubility of β-[Co(EDDA)(tn)]$ClO_4 \cdot H_2O$. Owing to the deposition of the salt, the β-isomer is supplied by the shift of the equilibrium between the isomers:

$$\alpha\text{-isomer} \rightleftharpoons \beta\text{-isomer} \quad \text{(fast in basic media)}$$
$$\downarrow$$
$$\text{deposit as perchlorate}$$

At the presence of charcoal and in dilute solutions, the complex exists mostly as the α-isomer. It is precipitated as the perchlorate by the evaporation of the solution after acidifiing with perchloric acid. (Both isomers are inert in acidic media.)

Identification of the Isomers. Absorption spectra (Fig. 1) clearly indicate the coordination mode of the tetradentate in the isomers. As may be seen, the red-

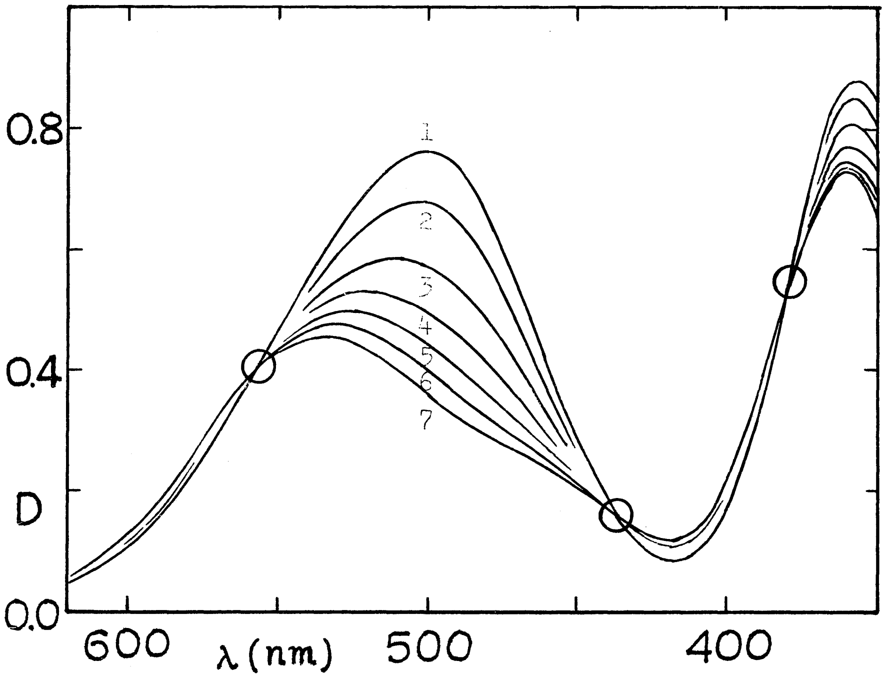


Fig. 2. Change of the Absorption Curve of β-$[Co(EDDA)(tn)]^+$ at 65°C in 0.2M $NaHCO_3$-0.2M Na_2CO_3 Solution.
1, the β-isomer;
2, after 10 min;
3, after 30 min;
4, after 50 min;
5, after 70 min;
6, after 100 min;
7, at equilibrium.

violet isomer shows a large splitting in the first band, which indicates trans configuration with respect to O (the α-configuration). The red isomer shows an intense first band with no distinct split, which indicates the cis configuration with respect to O (the β-configuration). Furthermore, both spectra are in good similitude with those of the corresponding isomers of the ethylenediamine complex.5) Thus, there remains no question on the configuration of the isomers.

Kinetic Measurements and Reaction Character of the Isomerization. The kinetic runs were performed in the usual manner. Fig. 2 illustrates a change of the absorption curve of the β-isomer. As may be seen, three isosbestic points occurred at 377, 436, and 557 nm, and the spectra approached to that of the α-isomer. 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 were both first order with respect to the complex ions, from the equation:

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

where

$$x_{t(\infty)} = \frac{D_\beta - D_{t(\infty)}}{D_\beta - D_\alpha} \times a$$

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

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

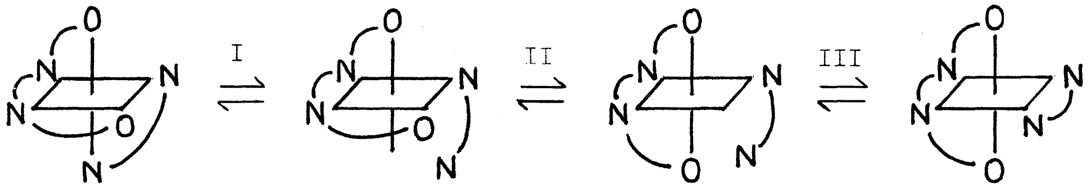
Condition	55°C	60°C	65°C	70°C
0.3M $NaHCO_3$ 0.1M Na_2CO_3 (1)			12.0	
0.2M $NaHCO_3$ 0.2M Na_2CO_3 (2)	3.70	8.35	18.4	41.1
0.1M $NaHCO_3$ 0.3M Na_2CO_3 (3)			33.5	
0.1M $HClO_4$			inert	

The pH value of the buffer solutions at 65°C was 9.47 (1), 9.79 (2), and 10.15 (3), respectively.

D's = absorbances at 500 nm

The absorbance at "infinite time" (D_∞) was measured after about 8 half-lives in each run, and x_∞'s were in the range of 88.3 ~ 89.5% (average 88.8%). The average value was used for the calculation of the rate constants. The rate constants calculated at different reaction times of a run agreed satisfactorily, verifiing the opposing first order reactions with respect to the complex ions. They are summarized in Table 1. It may be seen that the rates are highly dependent on the temperature, and also on the hydroxide ion concentration. These characters are quite similar to those of the isomerization of β-$[Co(EDDA)(en)]^+$.[2] The Arrhenius plots are satisfactorily straight, and the activation energy and the frequency factor obtained from the plots are 36.0 kcal and 3.5×10^{21} min^{-1}, respectively. These values are compared with 42.1 kcal and 1.7×10^{25} min^{-1} for the ethylenediamine complex. The activation energy, though high among the various reactions of the cobalt(III) complexes, is considerably lower than that of the ethylenediamine complex. The frequency factor is also lower with a factor of $\sim 10^4$. These differences in quantity are considered as follows:

We have proposed the following route for the isomerization of β-$[Co(EDDA)(en)]^+$,[2]



and the present isomerization is not contradictory to this route. In the case of substitution reactions of a series of complexes such as $[CoX(NH_3)_5]^{n+}$, there seems to be a parallel relation between the activation energies and the wave numbers of the absorption maxima of the complexes. As the present complex absorbs at lower wave number than the ethylenediamine complex, the lower activation energy is considered to be reasonable on the proposed reaction route which involves a bond rupture as the activation process. Furthermore, on the above reaction route, if the probability of the recombination of the released amino group to the vacant coordination sites (the probability of the forward III and the backward I) depends on the lengths between the two amino groups of the diamines, this may be a cause of the difference in the frequency factors. However, a more detailed studies are necessary about this assumption and are now in progress using other kinds of diamines.

References and Footnote:

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 and F. Mohri, This Letters, 1972, 719.
3) K. Kuroda and K. Watanabe, Bull. Chem. Soc. Japan, 44, 1034 (1971).
4) The elements were analysed by the Analyses Center in the Institute for Chemical Research in Kyoto University.
5) K. Kuroda, Bull. Chem. Soc. Japan, 45, 2176 (1972).

(Received November 2, 1973)