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PREPARATION AND REACTION OF THE UNSYMMETRICAL-FACIAL ISOMERS OF THE BIS(N-ALKYLIMINODIACETATO)COBALTATE(III) IONS

Tomoharu AMA, Hiroshi KAWAGUCHI, and Takaji YASUI
Department of Chemistry, Faculty of Science,
Kochi University, Akebono-cho, Kochi 780

The u-fac isomers of the bis(N-methyliminodiacetato)cobaltate-(III) ($[Co(mida)_2]^-$) and bis(N-ethyliminodiacetato)cobaltate(III) ($[Co(eida)_2]^-$), which have large steric compression, were newly prepared and characterized on the basis of the electronic absorption and circular dichroism spectral data. The first absorption maxima of these complexes are shifted to the lower energy side than that of the u-fac-$[Co(ida)_2]^-$. In basic aqueous solution, the u-fac-$[Co(mida)_2]^-$ and -$[Co(eida)_2]^-$ were reduced to Co(II) complexes.

The bis(N-methyliminodiacetato)cobaltate-(III) ($[Co(mida)_2]^-$) ion provides three geometrical isomers; mer, u-fac and s-fac isomers (Fig. 1.). Though the s-fac and mer isomers were isolated,[1 – 4] the u-fac isomer has not been reported. Previously, it was asserted that the preparation of the u-fac isomer of the $[Co(mida)_2]^-$ was difficult because of the intramolecular steric complession,[2, 3] that is, the $-CH_3$ part of the mida in a u-fac-$[Co(mida)_2]^-$ ion is very close to the $-CH_3$ and $-CH_2-$ parts of another mida in the complex ion. However, we succeeded to prepare the u-fac-$[Co(mida)_2]^-$ and -$[Co(eida)_2]^-$ (H_2eida = N-ethyliminodiacetic acid; of which steric compression is larger than that of the u-fac-$[Co(mida)_2]^-$), and succeeded to resolve these u-fac isomers into the optical isomers. The u-fac-$[Co(mida)_2]^-$ and -$[Co(eida)_2]^-$ decomposed in basic aqueous solution, accompanying the decomposition of the ligands and the reduction of Co(III) to Co(II). On the other hand, u-fac-$[Co(ida)_2]^-$ (H_2ida = iminodiacetic acid), which is less strained, did not indicate such reactions in basic aqueous solution, and it was isomerized to the s-fac isomer.[3] In the present letter, we will describe the preparation and optical resolution of the u-fac-$[Co(mida)_2]^-$ and -$[Co(eida)_2]^-$, and compare the properties and reactions of the $[Co(mida)_2]^-$ with those of the $[Co(ida)_2]^-$.[1 – 12]

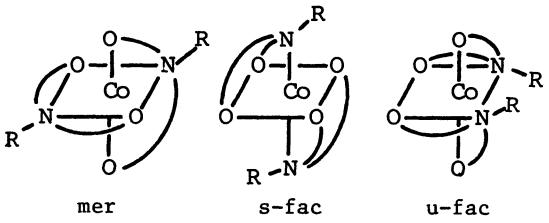

Fig. 1. Three isomers of the $[Co(Rida)_2]^-$ (R = -H, $-CH_3$, and $-C_2H_5$).

Three isomers of the K$[Co(mida)_2]$ complex were prepared as follows. To a solution containing Co(II) chloride hexahydrate (5.95 g) in 20 cm^3 of water was added a solution of N-methyliminodiacetic acid (7.4 g) in 80 cm^3 of water. Lead dioxide (9.0 g) was added gradually to the mixed solution, adjusting pH 3.5 – 4.0, and then the solution was stirred for 1 h at room temperature. After insoluble materials in the reactant solution were removed by filtration, the filtrate was poured into a

QAE-Sephadex column (4.7 X 60 cm, Cl^- form) and the adsorbed band was developed with 0.05 mol dm^{-3} solution. The overlapped red and pinkish-brown isomers were eluted early and the blue one late. The solution obtained from the eary eluted band was concentrated using a rotary evaporator. A sparingly soluble pinkish-brown isomer (s-fac) was precipitated from the concentrated solution and an easily soluble red isomer (mer) was obtained from the filtrate of the s-fac isomer. A blue isomer (u-fac) was obtained from the concentrated solution of the late eluted one. The each crude complex was recrystallized from water by adding methanol. Anal. Found for the u-fac isomer: C, 29.06; H, 4.08; N, 6.76%. Calcd for $K[Co(mida)_2]\cdot 1.5H_2O$: C, 28.92; H, 4.13; N, 6.75%.

The isomers of the $K[Co(eida)_2]$ were obtained by the same way as used for the $K[Co(mida)_2]$. Anal. Found for the s-fac isomer: C, 34.54; H, 4.13; N, 6.64%. Calcd for $K[Co(eida)_2]$: C, 34.62; H, 4.36; N, 6.73%. Found for the mer isomer: C, 34.22; H, 4.35; N, 6.59%. Calcd for $K[Co(eida)_2]$: C, 34.62; H, 4.36; N, 6.73%. Found for the u-fac isomer: C, 31.79; H, 4.60; N, 6.17%. Calcd for $K[Co(eida)_2]\cdot 2H_2O$: C, 31.86; H, 4.90; N, 6.19%.

Optical resolution of the u-fac-$[Co(mida)_2]^-$ was carried out in the following manner. The u-fac-$K[Co(mida)_2]\cdot 1.5H_2O$ (3.12 g) was dissolved in 50 cm^3 of water and potassium ion in the solution was converted to lithium one using a small column containing Dowex 50W X 8 resin (200 – 400 mesh, Li^+ form). A solution containing $(-)_{589}$-$[Co(NO_2)_2(en)_2]Br$ (1.40 g) in 80 cm^3 of water (60°C) and a solution containing $Ag(CH_3COO)$ (0.68 g) in 100 cm^3 of water were mixed rapidly and filtered to remove AgBr precipitated. The filtrate was mixed with the $Li[Co(mida)_2]$ solution mentioned above. This mixed solution was evaporated using a rotary evaporator at 30 – 35°C until diastereomer began to deposite. The concentrated solution was cooled in an ice bath for 30 min. The dark green crystals which deposited were filtered and washed with small amount of ice water. The diastereomer was dissolved in a warm water (40 – 45°C) and poured into a small SP-Sephadex column (Na^+ form) to remove $(-)_{589}$-$[Co(NO_2)_2(en)_2]^+$. The solution obtained by elution with water was concentrated to a few milliliters. Methanol was added to the concentrated solution until crystals began to appear and allowed to stand in an ice bath for 1 h. The blue complex deposited as needle crystals was filtered and washed with ethanol. $[\alpha]_{589}$ = -3100°. Anal. Found: C, 28.16; H, 4.35; N, 6.61%. Calcd for $Na[Co(mida)_2]\cdot 3H_2O$: C, 28.18; H, 4.73; N, 6.57%.

The u-fac-$[Co(eida)_2]^-$ was resolved by the similar way as mentioned above, using $(+)_{589}$-$[Co(ox)(en)_2]Br$ as the resolving agent. However, as the solubilities of the two diastereomers formed were resemble to each other, fractional crystallization was carried out to obtain pure less soluble diastereomer. The less soluble diastereomer was converted to the potassium salt by using cation exchange resin (Dowex 50W X 8, 200 – 400 mesh, K^+ form). $[\alpha]_{589}$ = + 3150°. Anal. Found: C, 33.16; H, 4.35; N, 6.26%. Calcd for $K[Co(eida)_2]\cdot H_2O$: C, 33.18; H, 4.64; N, 6.45%.

The absorption spectra of the three isomers of the $[Co(mida)_2]^-$ are shown in Fig. 2. The spectral data of the mer and s-fac isomers are in agreement with those in the references.[1, 2] The spectral patterns of the newly prepared u-fac isomers of the $[Co(mida)_2]^-$ and $[Co(eida)_2]^-$ were quite similar to that of the u-fac-$[Co(ida)_2]^-$. Similarly, the CD patterns of the $(-)_{589}$-u-fac-$[Co(mida)_2]^-$ and

-$[Co(eida)_2]^-$ are similar to that of the u-fac-$[Co(ida)_2]^-$,[11] as shown in Fig. 3. These results make it possible to assign the configuration of the newly prepared complexes to u-fac.

The first and second absorption maxima of the u-fac-$[Co(mida)_2]^-$ (17000 and 24700 cm^{-1}) and -$[Co(eida)_2]^-$ (16900 and 24500 cm^{-1}) were observed in the lower energy side than those of the u-fac-$[Co(ida)_2]^-$ (17800 and 26300 cm^{-1}),[4] while those of the $[Co(edta)]^-$ (18600 and 26300 cm^{-1})[5] and $[Co(1,3\text{-pdta})]^-$ (18200 and 26400^{-1})[5] located at the higher energy side. The CD spectra of the u-fac-$[Co(mida)_2]^-$ and -$[Co(eida)_2]^-$ are shifted to the lower energy side in comparison with that of the u-fac-$[Co(ida)_2]^-$, though the spectral patterns of them are very similar. The large steric compression of the u-fac-$[Co(mida)_2]^-$ and -$[Co(eida)_2]^-$ will lower the ligand fields.

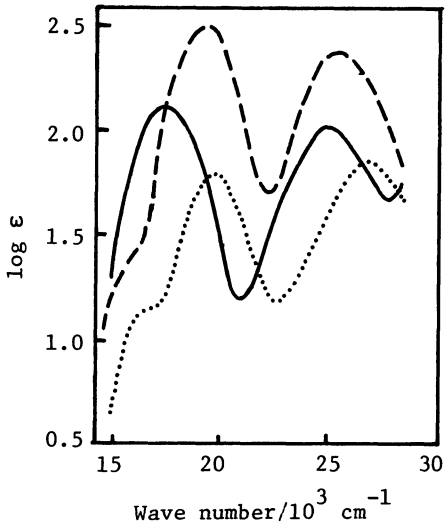

Fig. 2. Absorption Spectra of the $[Co(mida)_2]^-$ ions. —— u-fac, ---- mer, and ..... s-fac.

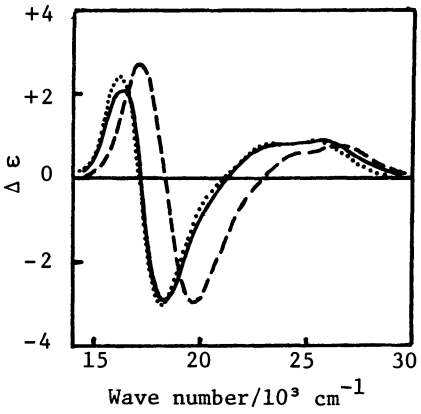

Fig. 3. CD Spectra of the $(-)_{589}$-u-fac-$[Co(mida)_2]^-$ (——), $(-)_{589}$-u-fac-$[Co(eida)_2]^-$ (.....), and $(-)_{589}$-u-fac-$[Co(ida)_2]^-$ (----).

The u-fac-$[Co(mida)_2]^-$ decomposed in basic aqueous solution (k' (pseudo-first-order rate constant) = 7.0 X 10^{-2} min^{-1}; pH 10; 25°C), accompanying the decomposition of ligand and the reduction of Co(III) to Co(II). The rate of this decomposition is equal to the rate of loss of the CD intensities, and these rates are proportional to the concentration of OH^- ion. These rates are about thirty times larger than that of the isomerization of the u-fac-$[Co(ida)_2]^-$ which will be mentioned later. The large steric compression may be closely related to the rapid decomposition of the u-fac-$[Co(mida)_2]^-$. The conventional preparation of the $[Co(mida)_2]^-$ complex had been made under basic condition, compared with the present preparation used acidic condition. Accordingly, it is probable that the u-fac-$[Co(mida)_2]^-$ was not obtained by the former method becase of the rapid decomposition.

After the decomposed solution of the u-fac-$[Co(mida)_2]^-$ was acidified with HCl, the solution was adsorbed on a Dowex 50W X 8 (H^+ form) column and developed with 0.2 mol dm^{-3} HCl. In the earlier eluted part, sar (Hsar = sarcosine) and mida were found and the ratio of the sar/mida was about 1/3. The decompositon reaction will be described in the following foformula.

$$2\ [Co(mida)_2]^- + OH^- \longrightarrow 3\ mida^{2-} + sar^- + HCHO + CO_2 + 2\ Co^{2+}$$

In the decomposed solution of u-fac-$[Co(eida)_2]^-$ (in basic aqueous solution), N-ethylglycine and eida were detected.

The absorption spectra of the s-fac and mer isomers of $[Co(mida)_2]^-$ have no

change for several hours in the solution of pH 10.

The u-fac- and s-fac-$[Co(ida)_2]^-$ isomerized to each other. The isomerization (u-fac $\rightleftharpoons$ s-fac) did not accompany decomposition or another isomerization (u-fac or s-fac $\longrightarrow$ mer). The rates of the isomerization (u-fac $\rightleftharpoons$ s-fac) were proportional to the concentration of the OH^- ion. The rate of the isomerization of the s-fac isomer (s-fac $\longrightarrow$ u-fac; $k' = 1.8 \times 10^{-3}$ min^{-1}; pH 10; 30°C) is about 1/2.5 of the u-fac isomer (u-fac $\longrightarrow$ s-fac; $k' = 4.6 \times 10^{-3}$ min^{-1}; pH 10; 30°C). The rate of loss of the CD intensity for the optically active u-fac-$[Co(ida)_2]^-$ is about twenty times larger than the rate of the u-fac $\longrightarrow$ s-fac isomerization. The mer-$[Co(ida)_2]^-$ [12] isomerized to the u-fac and s-fac isomers, while the mer-$[Co(mida)_2]^-$ did not indicate any isomerization at pH 10. The rate of the isomerization of the mer-$[Co(ida)_2]^-$ is rapid in basic aqueous solution and the ratio of the u-fac/s-fac in the equilibrated solution is about two.

Comparing the reactions in the $[Co(mida)_2]^-$ isomers with those in the $[Co(ida)_2]^-$ isomers, the following factors may be taken into account. The first is the steric compression of the inter-ligands (between the ligands in a complex ion). The second is difference of the strain energy between the ligand of the facial form and that of the meridional form. It is pointed out that the facial form of the terdentately coordinated ida and mida is less strained than the meridional form.[2, 3] The third is difference in the nature between the secondary nitrogen of the ida and the tertiary nitrogen of the mida. The proton attaching to the secondary nitrogen is released easily in basic solution, but the methyl group attaching to the tertiary nitrogen is not. The result that the u-fac-$[Co(mida)_2]^-$ decomposed more rapidly than the u-fac-$[Co(ida)_2]^-$ can be related intimately to the first factor. The rapid isomerization of mer-$[Co(ida)_2]^-$ will be related to the second and third factors, and the facts that the s-fac- and u-fac-$[Co(ida)_2]^-$ isomerized will be related to the third factor.

We are performing the study to obtain more detailed data of the rates of the reactions mentioned above, which will clarify the mechanisms and kinetics of the reactions.

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