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THE β-CIS ISOMER OF ETHYLENEDIAMINE-N,N'-DIACETATO(DIAMMINE)COBALT(III) AND SOME RELATED COMPLEXES

Kashiro KURODA
Department of Chemistry, Faculty of Science,
Ehime University, Matsuyama, Ehime

The β-cis isomer of ethylenediamine-N,N'-diacetato(diammine)-cobalt(III) perchlorate, β-cis-$[Co(EDDA)(NH_3)_2]ClO_4 \cdot H_2O$, and the corresponding ethylenediamine complex have been prepared by the reaction between $[Co(EDDA)(H_2O)_2]ClO_4$ and ammonia or ethylenediamine at 100°C. The β-cis configuration of the isomers has been identified by the electronic absorption spectra and PMR spectra.

Ethylenediamine-N,N'-diacetate (EDDA), a flexible chain tetradentate, may coordinate in three different modes (α-cis, β-cis, and trans) in octahedral complexes. Concerning the Co(III)-EDDA complexes, the experimental results so far appear to suggest that the α-cis configuration is preferred to the others. Although the β-cis isomers have been obtained in several [Co(EDDA)(AA)]-type species (AA = ethylenediamine[1], 1,10-phenanthroline[2], 2,2'-dipyridyl[2], oxalate[3] or malonate[3]), no β-cis isomer has been isolated which contains two unidentates as the additional ligand. In our previous study on $[Co(EDDA)(phen)]^+$ and $[Co(EDDA)(dipy)]^+$[2], we observed that in the reaction between $[Co(EDDA)(H_2O)_2]^+$ and the bidentate, the β-cis isomer occurred at high temperature whereas the α-cis isomer at low temperature. In the light of such coordination tendency, the reaction between the diaquo complex and ammonia or ethylenediamine was examined and the β-cis isomers were obtained easily. The diammine complex is the first example of the β-cis isomer which belongs to the $[Co(EDDA)a_2]$-type.

Preparations. In a small beaker, one milliliter of 6N ammonia was mixed with a solution of $[Co(EDDA)(H_2O)_2]ClO_4$ (0.5 g) in 3 ml of water. The red-violet solution of the diaquo complex turned to blue and a blue precipitate appeared. This phenomenon is probably owing to the formation of the hydroxo

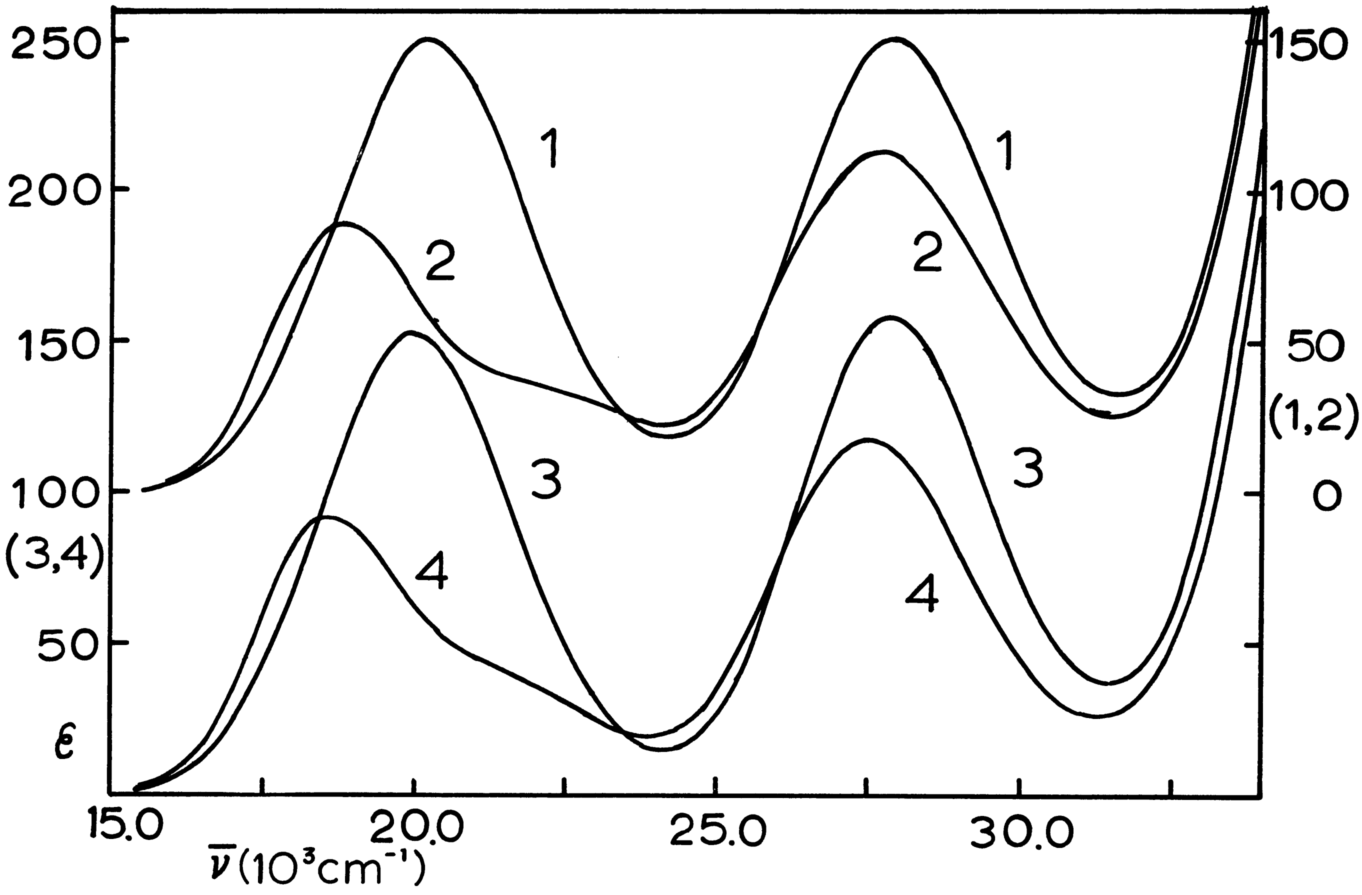

Fig. 1. Absorption Spectra.

1, β-cis-[Co(EDDA)(en)]ClO_4 2, α-cis-[Co(EDDA)(en)]ClO_4

3, β-cis-[Co(EDDA)$(NH_3)_2$]ClO_4 4, α-cis-[Co(EDDA)$(NH_3)_2$]ClO_4

complexes such as [Co(EDDA)(OH)(H_2O)] and $[Co(EDDA)(OH)_2]^-$ by the action of ammonia. The bottom of the beaker was immersed in boiling water, and the mixture was concentrated nearly to dryness with stirring. During this process, the precipitate disappeared soon and the color turned to red. After cooling, when the tarry product was stirred with a glass rod, crystals appeared suddenly and the whole solidified. The product, after washing with methanol, was dissolved in 3 ml of warm (~50°C) water and then the solution was filtered and cooled. A few drops of 6N $HClO_4$ was added for precipitation. Bright red crystals came out after a while. The product was washed with methanol and ether. Yield, 0.3 g. Found: C, 18.75; H, 4.60; N, 14.67 %.4) Calcd for [Co(EDDA)$(NH_3)_2$]$ClO_4 \cdot H_2O$ = $CoC_6H_{18}O_9N_4Cl$ (384.62): C, 18.74; H, 4.72; N, 14.57 %.

The β-cis isomer of [Co(EDDA)(en)]ClO_4 was prepared from 0.5 g of the diaquo complex and 0.1 g of ethylenediamine hydrate by the similar procedure. The

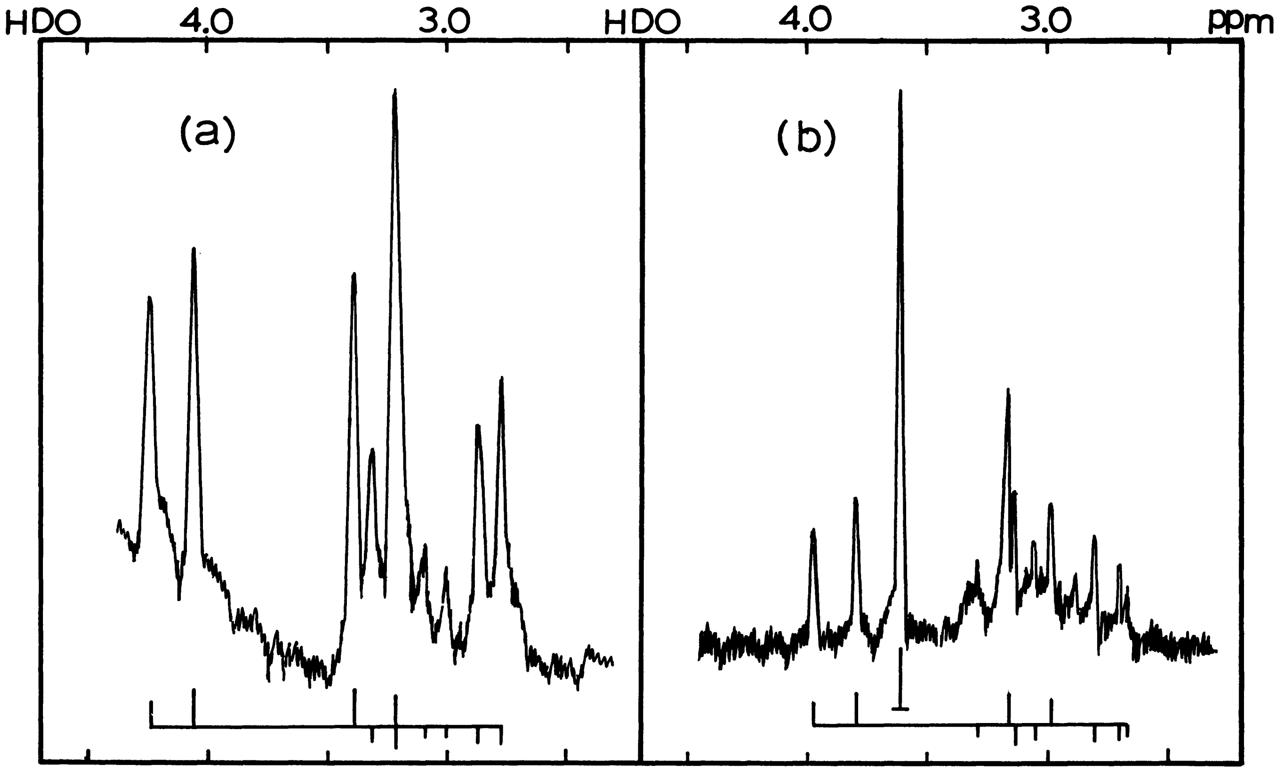

Fig. 2. NMR Spectra of $[Co(EDDA)(NH_3)_2]ClO_4$ in D_2O.
(a) α-cis isomer, (b) β-cis isomer

tarry evaporation product was extracted with 5 ml of water, and the orange extract, after the addition of a few drops of 6N $HClO_4$, was placed in a refrigerator overnight. The deposit was recrystallized from 3 ml of water, and washed with methanol and ether. Yield, 0.2 g. The less soluble reddish pink residue in the extraction consists of the α-cis isomer. By the recrystallization from 20 ml of water it can be purified easily. Yield, 0.2 g.

Identification. Among the species of the complexes in this communication, the α-cis and the β-cis isomers of the ethylenediamine complex and the α-cis isomer of the diammine complex have already been isolated and identified. As in the previous reports on these isomers[1-3], the visible and ultraviolet absorption spectra and the proton NMR spectra clearly indicated the configuration of the new diammine complex. The spectra are shown in Figs. 1 and 2. As may be seen in Fig. 1, the red-violet isomer of the diammine complex and the red-pink isomer of the ethylenediamine complex show a largely split first band, which indicates trans configuration with respect to O (the α-cis configuration). On the other hand, the other isomers (the red isomers) show an intense first band with no observable split, which indicates the cis configuration with respect to O (the β-cis configuration). Thus, the β-cis isomer of the diammine complex show a spectrum in good similitude with the known β-cis ethylenediamine complex. The numerical values of the absorption maxima of the β-cis diammine complex are: $\bar{\nu}_1 = 20.04$ kK ($\varepsilon_1 = 153.2$), $\bar{\nu}_2 = 27.93$ kK ($\varepsilon_2 = 159.4$). These agree with the values, $\bar{\nu}_1 = 20.00$ kK and $\bar{\nu}_2 = 27.93$ kK, measured qualitatively by Legg and Cooke[1]. (They obtained the isomer in solution by means of the ion-exchange chromatography, but could not isolate as solid.)

The PMR spectra also indicate the configuration of the isomers. As seen in Fig. 2, the red-violet isomer of the diammine complex shows the single AB quartet pattern which originates from the two equivalent glycinates in the α-cis configuration. The other absorptions, which are symmetrical in feature, come from the ethylene backbone protons of EDDA. The red isomer, in contrast, shows an intense absorption as well as the AB quartet assigned to the out-of-plane glycinate protons. The intense absorption has been observed in β-cis-$[\mathrm{Co(EDDA)(en)}]^+$ and β-cis-$[\mathrm{Co(EDDA)(ox\ or\ mal)}]^-$ by Legg et al[1,3], and they discussed that the protons in the in-plane glycinate of the β-cis configuration are located at magnetically very similar situations. The spectrum of the red isomer of the diammine complex is, thus, analogous to those of the known β-cis isomers.

According to the previous studies[1], the β-cis isomers of the Co(III)-EDDA complexes were difficult to prepare in comparison with the α-cis isomers. They were separated by means of the ion-exchange chromatography with taking a long time. By the new preparation method of this report which pays attention to the reaction temperature, they can be obtained easily as in the cases of β-cis-$[\mathrm{Co(EDDA)(phen\ or\ dipy)}]\mathrm{ClO_4}$ which were previously reported by us.

References and Footnote:

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