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PREPARATION OF OPTICALLY ACTIVE *MER* ISOMERS OF BIS(METHYLIMINODIACETATO)-COBALTATE(III) AND (METHYLIMINODIACETATO)(DIETHYLENETRIAMINE)COBALT(III) IONS

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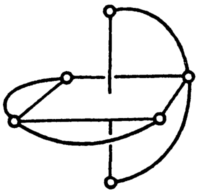
The preparation and optical resolution of a new complex, *mer*-$[Co(mida)_2]^-$(mida = methyliminodiacetate) were achieved together with the optical resolution of *mer*-$[Co(mida)(dien)]^+$(dien = diethylenetriamine). The d→d absorption and circular dichroism spectra, and some properties of these complexes are reported.

Octahedral complexes(I) coordinating meridionally two symmetrical terdentate ligands such as mida and dien, exist in a pair of enantiomers because of the non-coplanarity of coordinated ligands. So far optically active complexes of this type have been known only for the *mer*-$[Co(dien)_2]^{3+}$ complex[1)] and its analog.[2)] The optical activity of such a complex is never considered to arise from the configurational, conformational or vicinal effect, but from a unique one due to a chiral disposition of the two non-coplanar ligands.[3)] The present communication completes a series of optically active complexes *mer*-$[Co(mida)_n(dien)_{2-n}]^{3-2n}$(n = 0, 1, and 2).



(I)

The cobalt(III) complexes with mida adopt preferably the facial coordination than the meridional one,[4,5)] and the latter has been found only in a few mixed complexes with another ligand which prefers the meridional coordination such as dien[4)] and glycylglycinate.[6)] In the present study, *mer*-$K[Co(mida)_2]$ was prepared by isomerization from *sym-fac*-$Li[Co(mida)_2]\cdot 2H_2O$(*Anal.* Found: C, 30.55; H, 4.49; N, 7.12 %. Calcd: C, 30.62; H, 4.64; N, 7.14 %) which had been prepared by a similar method to that for the corresponding *(S)*-alaninate-*N*-monoacetato complex.[7)] To a solution of *sym-fac*-$Li[Co(mida)_2]\cdot 2H_2O$(100 g) in water(280 cm^3, 70 °C) was added active charcoal(5 g) and the mixture was stirred at 70 °C for 1 h and filtered to remove the charcoal. The filtrate was concentrated until a large amount of *sym-fac* isomer appeared as prismatic crystals. The crystals were removed by filtration after addition of an appropriate amount of methanol. By repeating this operation, the *sym-fac* isomer(96 g in total) was removed as much as possible and the fianl filtrate was concentrated to syrup. The syrup was diluted with water and the solution was poured into a column containing a cation-exchange resin(Dowex 50W-X8, K^+ form) and the column was eluted with water. The colored eluates were collected and concentrated to a few milliliters and the sparingly soluble potassium salt of *sym-fac* isomer was filtered off. A small amount of ethanol was added to the filtrate and the crude desired complex deposited was filtered off and recrystallized from water by adding ethanol; yield 0.68 g. *Anal.* Found: C, 29.47; H, 3.85; N, 6.90 %. Calcd for *mer*-K[Co(mida)$_2$]$\cdot$H$_2$O: C, 29.56; H, 3.98; N, 6.90 %. To a solution of *mer*-K[Co(mida)$_2$]$\cdot$H$_2$O(1.63 g, 4 mmol) in water(5 cm^3) was added a solution of silver nitrate(0.82 g, 4.8 mmol) in water(3 cm^3) and the silver salt deposited was collected by filtration; yield 1.7 g. *Anal.* Found: C, 26.71; H, 3.03; N, 6.43 %. Calcd for *mer*-Ag[Co(mida)$_2$]: C, 26.28; H, 3.09; N, 6.13 %.

To a suspension of *mer*-Ag[Co(mida)$_2$](0.91 g, 2 mmol) in water(2 cm^3) was added (+)$_D$-[Co(CO$_3$)(en)$_2$]I(0.73 g, 2 mmol) and the silver iodide precipitated was filtered off. To the filtrate was added ethanol until the solution became just cloudy and, after standing about 3 h, the less soluble diastereomer deposited was filtered off. The diastereomer was recrystallized from water by adding ethanol; yield 0.3 g. *Anal.* Found: C, 27.13; H, 5.67; N, 12.64 %. Calcd for (+)$_D$-[Co(CO$_3$)(en)$_2$]$\cdot$(-)$_D$-*mer*-[Co(mida)$_2$]$\cdot$4H$_2$O: C, 27.20; H, 5.80; N, 12.73 %. The diastereomer was converted to the potassium salt by using a cation-exchange resin(Dowex 50W-X8, K$^+$ form). *Anal.* Found: C, 28.99; H, 3.98; N, 6.74 %. Calcd for (-)$_D$-*mer*-K[Co(mida)$_2$]$\cdot$1.5H$_2$O: C, 28.92; H, 4.13; N, 6.75 %.

The *mer*-[Co(mida)(dien)]Cl complex was prepared by the method of Legg and Cooke[4)] with some modifications. To a suspension of *mer*-[CoCl$_3$(dien)][8)](2.69 g, 10 mmol) in water(18 cm^3) was added a solution of H$_2$mida(1.47 g, 10 mmol) in 4 mol dm^{-3} potassium hydroxide(5 cm^3, 20 mmol) and the mixture was stirred at 60 °C for 10 min. The solution was poured into a column containing a cation-exchange resin(Dowex 50W-X8, K$^+$ form) and the column was washed with water and the adsorbed band was eluted with 0.027 mol dm^{-3} aqueous potassium chloride. The first eluates containing the pure *mer* isomer were collected(76 % yield was estimated by absorption measurement) and, by concentration, the contaminated potassium chloride was removed as much as possible. To the final filtrate was added an appropriate amount of methanol and the complex deposited was filtered off and recrystallized from water by adding methanol; yield 2.3 g. *Anal.* Found: C, 25.99; H, 6.43; N, 13.41 %. Calcd for *mer*-[Co(mida)(dien)]Cl$\cdot$4H$_2$O: C, 26.06; H, 6.82; N, 13.51 %.

A solution of *mer*-[Co(mida)(dien)]Cl$\cdot$4H$_2$O(2.07 g, 50 mmol) in water(14 cm^3) was added to a solution of (+)$_D$-K[Co(edta)]$\cdot$2H$_2$O(2.11 g, 50 mmol) in water(5 cm^3), and then methanol(12 cm^3) was added to the resulting solution. The less soluble diastereomer deposited was filtered off and recrystallized twice from 0.01 mol dm^{-3} HCl by adding methanol; yield 2.5 g(corresponding to 152 % based on one of the enantiomers used). *Anal.* Found: C, 32.89; H, 5.09; N, 12.16 %. Calcd for (+)$_D$-*mer*-[Co(mida)(dien)]$\cdot$(+)$_D$-[Co(edta)]$\cdot$2H$_2$O: C, 33.05; H, 5.27; N, 12.17 %. The diastereomer was converted to the chloride by using an anion-exchange resin(Dowex 1-X8, Cl$^-$ form), where 0.01 mol dm^{-3} HCl was used as the solvent and eluent. *Anal.* Found: C, 25.96; H, 6.32; N, 13.50 %. Calcd for (+)$_D$-*mer*-[Co(mida)(dien)]Cl$\cdot$4H$_2$O: C, 26.06; H, 6.82; N, 13.51 %.

For the [Co(mida)$_2$]$^-$ complex, three geometrical isomers, *mer*, *sym-fac*, and *unsym-fac*, are theoretically possible.[5)] The absorption spectrum of the present isomer is shown in Figure 1 {$\sigma_{max}(\varepsilon)$: 19140 cm^{-1}(325) and 25640 cm^{-1}(241)}, exhibiting a shoulder at the lower energy side of the major peak in the first absorption band. This indicates that the isomer is of a *trans*-CoN_2O_4 type, *i.e.*, either *mer* or *sym-fac* one. Since the *sym-fac* isomer, which was used as the starting material of present preparation, has been fully characterized based on the absorption and ^1H NMR spectra,5) the isomerized complex is assigned to the *mer* isomer. The isolation of its silver salt as anhydrous crystals(*vide supra*) confirms that the complex has the desired octahedral structure. The ^1H and ^{13}C NMR spectra of the complex indicate that the complex is isomerically pure. As expected from the predominance of facial coordination of mida, the *mer* isomer was contained in a portion less than 1 % of the *sym-fac* one in the equilibrium mixture on active charcoal. The *mer* complex changes very gradually in an aqueous solution, but shows no measurable change in the absorption and CD spectra for at least 12 h at room temperature.

The racemic *mer*-$[Co(mida)(dien)]^+$ has already been prepared and characterized by Legg and Cooke,4) but our data of the molar absorption coefficients ε(161 at 19530 cm^{-1} and 213 at 27250 cm^{-1}) differ from those in the literature(129 and 173 respectively). In the present preparation method, the *mer* isomer was obtained almost selectively and in a high yield. The optically active complex racemizes with a half-life of *ca*. 25 min at room temperature($\approx$20 °C), owing to the inversion of the coordinated secondary amine of dien as observed for *mer*-$[Co(dien)_2]^{3+}$.1) This behavior explains the fact that in the optical resolution the less soluble diastereomer was obtained more than the theoretical yield.

It is worthwhile to note that the molar absorption coefficient(325) of the first absorption band of the *mer*-$[Co(mida)_2]^-$ complex is unusually large compared with those of most of the cobalt(III) complexes($\sim$200). Such a large coefficient ($>$200) has been observed specially for the complex with two terdentate ligands coordinated meridionally.6,9) In the $[Co(ida)(dien)]^+$ complex, the coefficient of *mer* isomer is larger than those of the *fac* isomers.4) Similar relation has been found for a number of complexes with one or two terdentate ligands.2,4,10,11)

The optical activity of the two *mer* complexes arises from an "NR chiral effect" which has been proposed for the *mer*-$[Co(dien)_2]^{3+}$ as a new source of chirality.3) The CD spectra of the *mer* complexes in the d→d absorption region are shown in Figure 1. In each of the *mer* complexes, the spectrum shows three components in the first absorption band region, corresponding to the actual symmetry, C_2 and C_1 for the *mer*-$[Co(mida)_2]^-$ and *mer*-$[Co(mida)(dien)]^+$ respectively. The splitting of absorption spectrum in the first absorption band can be explained well

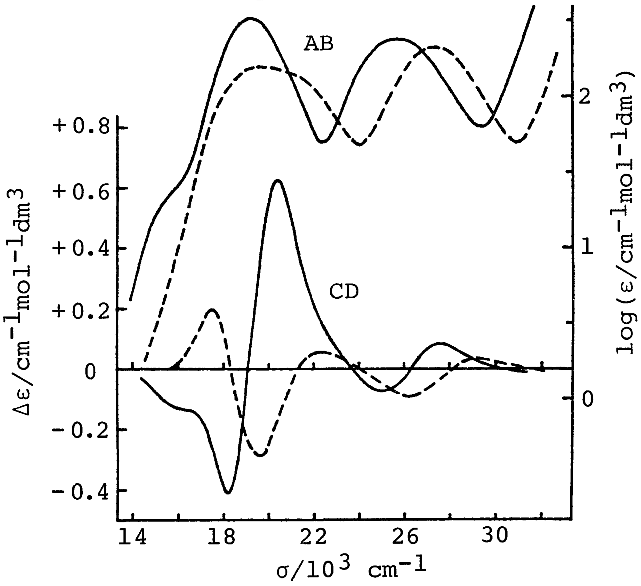


Fig. 1. Absorption(AB) and CD spectra of $(-)_D$-*mer*-$[Co(mida)_2]^-$ in water(——) and $(+)_D$-*mer*-$[Co(mida)(dien)]^+$ in 0.01 mol dm^{-3} HCl(---).

in terms of the holohedrized tetragonal symmetry, D_{4h}, of the *mer* complexes in which only the relative ligand-field strengths of the coordinated atoms are considered,[12] that is, the shoulders at *ca.* 16000 cm^{-1} for *mer*-$[Co(mida)_2]^-$ and at *ca.* 21500 cm^{-1} for *mer*-$[Co(mida)(dien)]^+$ are assigned to $A \rightarrow A_2(D_{4h})$ transition and the major peaks to the $A \rightarrow E(D_{4h})$ one. The CD component of the weakest intensity well corresponds to the $A \rightarrow A_2$ transition of the absorption band and the two components of opposite signs with comparable intensities to the $A \rightarrow E$ one. Recently, the relation between the CD sign and the absolute configuration of the *mer*-$[Co(dien)_2]^{3+}$ complex was established by an X-ray crystal structure analysis.[13] However, it will be premature to assign the absolute configurations of the present complexes from the signs of CD components. Indeed, the CD spectrum of the optically active *mer*-[Co{*(R,S)*-alamip}-(dien)]$^+${*(R,S)*-alamip = *(R,S)*-alaninate-*N*-monoisopropionate} of which the optical activity also arise only from the NR chiral effect, has the same CD pattern as the *mer*-$[Co(mida)(dien)]^+$ in the first absorption band region, but the main component of the *(R,S)*-alamip complex is at the lowest energy unlike the mida complex.[14] It is noted also that the CD intensity of main component in the series of *mer*-$[Co(mida)_n(dien)_{2-n}]^{3-2n}$ increases with the increase of n($\Delta\varepsilon$ = -0.18 at 21900 cm^{-1} for $(+)_D$-*mer*-$[Co(dien)_2]^{3+}$ [2])).

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