1354 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (5), 1354—1357 (1978) [Vol. 51, No. 5

Preparation and Isomerization of Three Isomers of L-Histidinatoiminodiacetatocobalt(III) Complex

Masatoshi WATABE, Masayuki ZAMA, and Sadao YOSHIKAWA*
General Education Department of Kogakuin University, Hachioji, Tokyo 193
**Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyoku, Tokyo 113*

(Received July 6, 1977)

Three isomers of L-histidinatoiminodiacetatocobalt(III) complex have been prepared and characterized on the basis of their absorption, circular dichroism and proton magnetic resonance spectra. These isomers isomerized mutually in water at 80 °C. The equilibrium mole fractions of these isomers in water were found for *cisN*, *transN* and *fac* to be 0.91, 0.04, and 0.05, respectively.

In previous papers,[1,2] the preparation and the isomer distribution at equilibrium in water in the presence of active carbon were studied for the mixed cobalt(III) complexes with D-aspartate and L-2,4-diaminobutyrate ions. The distribution in favor of one isomer was found. In the present paper, the preparation of mixed cobalt(III) complexes containing iminodiacetate (=ida) and L-histidinate (=his) ions will be reported. Their absorption, PMR, and CD spectra are discussed. These isomers were found to isomerize in water in the absence of active carbon as in the case of [Co(L-prolinato)$_3$].[3] The relative rate constants for the isomerizations were determined by using a network analysis.[4]

Experimental

Preparations. Iminodiacetic acid (1.33 g) and L-histidine (1.55 g) were dissolved in 15 cm^3 of water. To this solution was added 1M-sodium hydroxide until the pH of the solution became *ca.* 9. To this mixture was added a solution (20 cm^3) of $CoCl_2\cdot6H_2O$ (2.38 g) containing 5 cm^3 of 10% H_2O_2. The mixture was stirred at 80 °C for 30 min and filtered to remove the small amount of precipitate. The filtrate was passed through a colum (30×500 mm) containing strong cation exchange resin, Dowex 50WX8 (100—200 mesh, sodium form). Elution with water produced a violet band followed by a red band. The violet eluate was condensed to about 10 cm^3 and allowed to stand at room temperature for one week. Violet crystals (M1) and a gray violet powder (M2) appeared and were separated by a spatula. The product in the third red eluate isomerized with ease at room temperature, and consequently was kept in a refrigerator. Only a small amount of crystals were obtained (M3). Found M1: C, 34.82; H, 3.72; N, 16.10%. Calcd for $CoC_{10}H_{13}N_4O_6$: C, 34.95; H, 3.81; N, 16.30%. Found M2: C, 33.85; H, 3.89; N, 15.72%. Calcd for $CoC_{10}H_{13}N_4O_6\cdot0.5H_2O$: C, 34.06; H, 4.00; N, 15.89%. Found M3: C, 33.33; H, 4.00; N, 15.41%. Calcd for $CoC_{10}H_{13}N_4O_6\cdot H_2O$: C, 33.21; H, 4.18; N, 15.49%.

Isomerization. A solution containing one isomer was stirred and maintained at 80 °C in a temperature-controlled reaction vessel. The concentrations of M1, M2, and M3 were determined as follows. Initially, the concentrations of the M3 isomer (*fac*) was determined using high speed liquid chromatography and optical density. The concentrations of the M1 and M2 isomers could not be determined by chromatography since their bands overlaped. These were determined by measuring molar rotations $[\phi]$ at 454 and 500 nm. The values of the isomers are as follows.

	454 nm	500 nm
M1	4706	0
M2	0	−3029
M3	2066	3214

The concentrations of the M1 and M2 isomers were calculated using the following equation

$$[\phi]_{M1}x+[\phi]_{M2}y+[\phi]_{M3}(1-x-y)=\alpha[\text{molecular weight}]/cl,$$

where $[\phi]_{M1}$, $[\phi]_{M2}$, and $[\phi]_{M3}$ are the molar rotations, x and y are the concentrations of the M1 and M2 isomers, respectively. c is the initial concentration of the isomer, α the observed rotation expressed in degrees, and l the cell length. Since the concentration loss of the complexes due to reactions other than the isomerization was less than 2 percent, the concentration of the complex was assumed to be constant throughout the experiment. The isomerization of M3 was not attempted because of its insufficient yield.

Measurements. The electronic absorption spectra and optical rotatory dispersion curves were measured with a JASCO ORD-UV-5 spectrometer. The CD spectra were measured with a JASCO J-20 spectrometer, and the PMR spectra (60 MHz) in D_2O with a JEOL MH-60 spectrometer using sodium 2,3-dimethyl-2-silapentane-5-sulfonate as an internal reference.

Results and Discussion

Figure 1 shows the possible isomers of [Co(ida)(L-his)]. The two meridional isomers (a and b) are denoted by *cisN* and *transN* (the nitrogen atom of ida is cis or trans to the amine nitrogen atom of L-his). Figure 2 shows the absorption spectra of the three isomers of [Co(ida)(L-his)] and the numerical data are listed in Table 1. Zompa assigned the configurations of the three isomers of [Co(L-his)$_2$]$^+$ [5] by comparing their absorption spectra with those of the three isomers of [Co(L-2,4-dba)$_2$]$^+$ [6] (dba=diaminobutyrate ion). From previous spectroscopic studies,[7] it appears that the nitrogen atom of imidazole and that of ammine occupy nearly the same positions in the spectrochemical series. Since the nitrogen atom of amine lies at a higher position in the spectrochemical series than that of ammine, the nitrogen (Nα) attached to the α-carbon atom of L-his lies at a higher position than that of the imidazole ring (Ni). Yamatera's parameters[8] concerning the first band were estimated from the absorption maxima of the $[Co(NH_3)_6]^{3+}$,[9] $[Co(ox)_3]^{3-}$ [10] and *trans*(*N*)-K[Co(ida)$_2$]$^-$,[11] complexes ($\delta(NH_3\text{-ox})=4500$ and $\delta(N\alpha\text{-ox})=7400$ cm^{-1}). The estimated positions

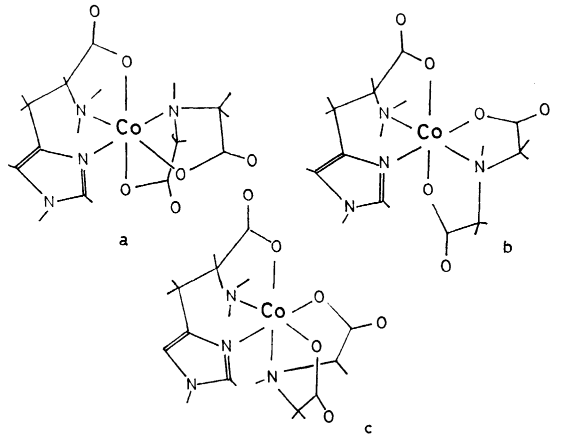

Fig. 1. The three possible geometrical isomers of the [Co(ida)(L-his)] complexes, a: *mer-cisN*, b: *mer-transN*, c: *fac*. The isomers are named by considering 5-membered N and O atoms.

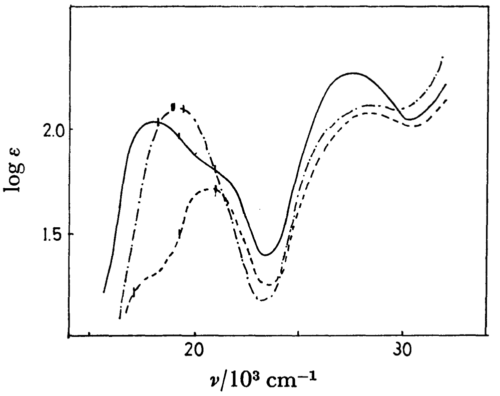

Fig. 2. Visible absorption spectra of [Co(ida)(L-his)]. *cisN* (——) *transN* (- - -), and *fac* (—·—·).

of the first absorption bands of the isomers are illustrated in Fig. 2. The isomer(M1) having a shoulder at the highest wave number in the first absorption band region can be assigned to the *cisN* isomer and one(M2) having a shoulder at the lowest wave number to the *transN* isomer.

PMR Spectra. Figure 3 shows the PMR spectra of [Co(ida)(L-his)]. We have reported that when X is an oxygen atom in the moity $-CH-NH_2-Co(III)-X$ (X is trans to NH_2), the methine proton signals appear at a slightly higher magnetic field strength than in the case when X is a nitrogen atom. The sharp peaks in the low magnetic field region may be due to the imidazole protons attached to the 2-carbon (Fig. 3). This assings the *cisN* isomer for M1 and the *transN* for M2, since the sharp peak for M1 is located in a lower magnetic field than those for M2 and M3.

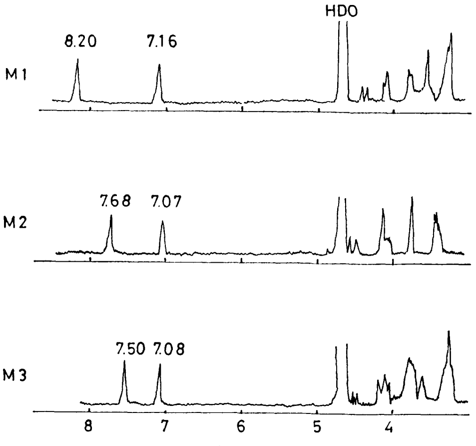

Fig. 3. PMR spectra of M1 (*cisN*), M2 (*transN*), and M3 (*fac*).

CD Spectra. Figure 4 shows the CD spectra of the isomers of [Co(ida)(L-his)]. The configurational effect of the complexes having one or two optically active tridentate ligands can not be well classified in terms of Δ and Λ chirality. These are for example $[Co(L\text{-}asp)_2]^-$,[12] *mer*-$[Co(dien)_2]^{3+}$,[13] (dien=diethylenetriamine), $[Co(L\text{-}2,4\text{-}dba)_2]^+$,[6] $[Co(L\text{-}2,3\text{-}dpa)_2]^+$[14] (dpa = diaminopropionate ion), and $[Co(ida)(L\text{-}asp)]^-$.[15] The complication of their CD spectra may be chiefly attributed to the vicinal effect due to the branch from the α-carbon atom. If such a vicinal effect can be eliminated from the CD curves, the calculated CD spectra may be compared with those of the known simple complexes. The assumption that the vicinal and the configurational effects is additive leads to the following additivity formulae:

$$\Delta\varepsilon(\mathrm{M1})=\Delta(5\text{—}5)+\Lambda(5\text{—}5)+\Lambda(5\text{—}6)+\mathrm{L}$$

$$\Delta\varepsilon(\mathrm{M2})=\Lambda(5\text{—}5)+\Delta(5\text{—}6)+\mathrm{L}$$

$$\Delta\varepsilon(\mathrm{M3})=\Delta(5\text{—}5)+\Delta(5\text{—}6)+\Lambda(5\text{—}6)+\mathrm{L}$$

Table 1. Absorption and CD data of [Co(ida)(L-his)]

Complex	I band				II band			
	Aasorption		CD		Absorption		CD	
	$\tilde{\nu}$ max[a)]	log ε	$\tilde{\nu}$ max	Δε	$\tilde{\nu}$ max	log ε	$\tilde{\nu}$ max	Δε
M1 (*cisN*)	18.0	2.05	17.2	0.69	27.0	2.28	27.0	0.73
	20.8	1.81	20.2	−1.02				
M2 (*transN*)	17.7	1.28	17.2	1.08	28.2	2.09	27.0	0.50
	20.6	1.72	20.4	−0.70				
M3 (*fac*)	19.1	2.12	17.9	−0.95	28.2	2.11	27.8	−0.13
			20.0	0.48				

a) Wave numbers are given in 10³ cm⁻¹.

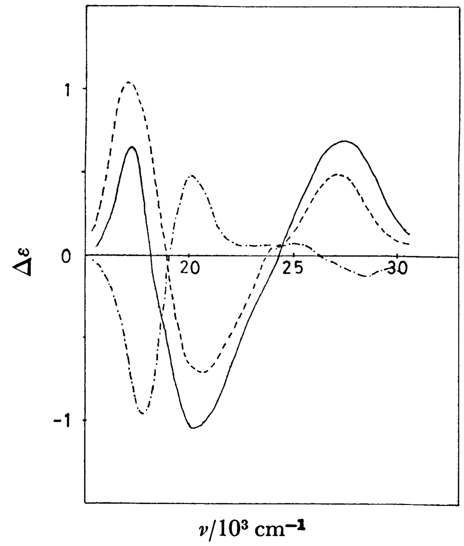

Fig. 4. CD spectra of three isomers of [Co(ida)(L-his)]. *cisN* (——), *transN* (- - -), and *fac* (—·—·).

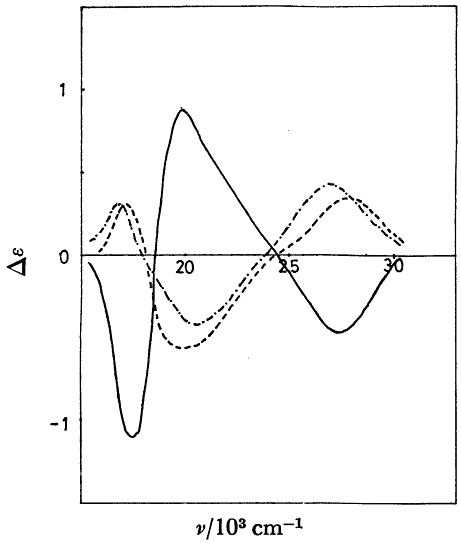

Fig. 5. Curve analysis of [Co(ida)(L-his)]. L(—·—·), Δ(5—5) (——), and Λ(5—6) (- - -).

where Δ(5—5) means the configurational effect between 5- and 5-membered chelate rings and L the vicinal effect due to L-his. It is reasonably assumed that $\Delta(5—5)+\Lambda(5—5)=0$ and $\Delta(5—6)+\Lambda(5—6)=0$. Then $\Delta(5—5)=\Delta\varepsilon(\mathrm{M3})-\mathrm{L}$, $\Lambda(5—6)=\Delta\varepsilon(\mathrm{M1})-\mathrm{L}$. The calculated curves of Δ(5—5) and Λ(5—6) are shown in Fig. 5. The sign of Δ(5—5) in the lower wave number side of the first absorption band is negative and that of Λ(5—6) positive. The intensity of the Δ(5—6) ($=-\Lambda$(5—6)) is smaller than that of Δ(5—5). The decrease in the intensity appears to correspond to the change in the CD intensity between $[\mathrm{Co(en)_3}]^{3+}$ and $[\mathrm{Co(tn)_3}]^{3+}$[16] (tn=trimethylenediamine). The configurational curve, Δ(5—5) compare favorably with those for Δ-*cis*(*N*)-$[\mathrm{Co(ida)_2}]^-$[17] and Δ-*cis*(*N*)-$[\mathrm{Co(L\text{-}alama)_2}]^-$[18] (alama=alanine-*N*-acetate ion) though its intensity is small. The above results show that the structures of all the isomers may be assigned on the basis of their CD spectra.

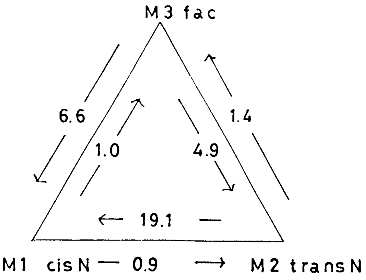

Fig. 6. The network of the isomerzation system.

Isomerization. The three isomers of [Co(ida)(L-his)] isomerized in water without any catalysis. The mole fractions of these three isomers at equilibrium were 0.91 for *cisN*, 0.04 for *transN*, and 0.05 for *fac*. Such a distribution in favor of the *cisN* isomer is remarkable. The free energy differences at 25 °C are as follows; $\Delta G_{12}=G(\mathrm{M1})-G(\mathrm{M2})=-RT\ln(91/4)=-7.7\mathrm{kJ}$ and $\Delta G_{13}=-7.2\mathrm{kJ}$. Figure 6 shows the relative rate constants calculated by means of the same method as that in the previous paper.[2] The molecular model concept suggests that the five-membered chelate rings of the coordinated ida can twist to some extent. The nearest atoms between the two coordinated ligands are the 2-proton of the imidazole and one of the methylene protons of ida for *cisN*, and the 2-proton of the imidazole and the imino proton of ida for *transN*. However, these distances do not appear to cause steric hindrance. In the case of the *fac* isomer, the distance between the one proton of L-his and the imino proton of ida is nearly 2.3—2.5 Å. This may cause some steric hindrance between these two ligands. However, the large free energy differences obtained are not reasonably accounted for by steric hindrance only. The electronic effect which is transmitted through the bonds may explain this distribution although this can not be deduced from the data.

References

1) M. Watabe, K. Onuki, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **48**, 687 (1975).
2) M. Watabe, S. Kawaai, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **49**, 1845 (1976).
3) R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1965).
4) M. Boudart, "Kinetics of Chemical Processes," Prentice Hall, In., Englewood Clifts, Newjersey (1968).
5) L. J. Zompa, *Chem. Commun.*, **1969**, 783.
6) W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **9**, 1191 (1970).
7) W. Eilbeck, F. Holmes, A. Underhill, *J. Chem. Soc., A*, **1967**, 757.
8) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).
9) H. Siebert, C. Siebert, and K. Wieghardt, *Z. Anorg. Allg. Chem.*, **380**, 30 (1971).
10) *Inorg. Synth.* **1**, 37.
11) J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **35**, 567 (1962).

12) S. Yamada, J. Hidaka, and B. E. Douglas, *Inorg. Chem.*, **10**, 2187 (1971).
13) Y. Yoshikawa and K. Yamasaki, *Bull. Chem. Soc. Jpn.*, **45**, 179 (1972).
14) W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7**, 764 (1968).
15) J. Hidaka, S. Yamada, and B. E. Douglas, *J. Coord. Chem.*, **2**, 123 (1972).
16) P. G. Beddoe and S. F. Mason, *Inorg. Nucl. Chem. Lett.*, **4**, 433 (1968).
17) C. W. Van Saun and D. W. Cooke, *Inorg. Chem.*, **8**, 1145 (1969).
18) K. Okamoto, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **44**, 1601 (1971).