The Preparation and Characterization of Isomers of (Amino acidato)-(iminodiacetato)nitrocobaltate(III)(1−) Complexes

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Three geometrical isomers of *fac(ida)*-$[Co(NO_2)(gly)(ida)]^-$ have been prepared and optically resolved (gly=glycinato(1−) and ida=iminodiacetato(2−) ligand), and their configurations were determined from the visible and ultraviolet absorption, and circular dichroism spectra. A diastereomeric pair was obtained for the corresponding L-alaninato, L-serinato, or L-prolinato complex.

There have been studied several types of cobalt(III) complexes with each one of uni-, bi-, and linear terdentate ligand. Those prepared previously include [CoX(N–N) (N–N–N)],[1) [CoX(N–N) (O–N–O)],[2) [CoX(N–O) (N–N–N)],[3) [CoX(O–O) (N–N–N)],[2,4) and [CoX(O–O) (O–N–O)][4) types: X=unidentate ligand, N–N and N–O=bidentate ligands, N–N–N and O–N–O=linear terdentate ligands, where N and O denote the coordinating atoms. In the present paper, the $[Co(NO_2)(am)(ida)]^-$ complexes belonging to a new type, [CoX(N–O) (O–N–O)], will be reported, where am stands for an amino acidato(1−) ligand such as gly (glycinato), L-ala (L-alaninato), L-ser (L-serinato), or L-pro (L-prolinato), and ida an iminodiacetato(2−) ligand.

Experimental

Preparation and Resolution. 1) Isomers of $Na[Co(NO_2)(gly)(ida)]$: Three grams (0.04 mol) of glycine and 6.80 g of potassium nitrite were dissolved in an aqueous solution (60 cm^3) containing 4.48 g (0.08 mol) of potassium hydroxide and 5.32 g (0.04 mol) of H_2ida. To this mixture was added 9.52 g (0.04 mol) of cobalt(II) chloride hexahydrate in 20 cm^3 of water at 45 °C. The dark red solution resulted was oxidized by adding 5.0 g of 30% hydrogen peroxide and stirring mechanically for about two hours. The deep red reaction mixture was poured into a column (45×750 mm) of a strong base anion-exchange resin (Dowex 1-X8, 200—400 mesh, chloride form). A reddish violet solution was swept out with water. The adsorbed band was eluted with a 0.07 M aqueous solution of sodium chloride. Five colored bands, a red one (i), a violet one (ii), a pinkish red one (iii), and two yellow ones (iv), (v) were eluted in this order. The amounts of the eluates (i) and (iii) were much larger than those of the (ii), (iv) and (v) eluates. The eluate (i) was condensed to a small volume with a vacuum rotary evaporator below 40 °C and the sodium chloride deposited was removed. To the filtrate a small amount of methanol was added and the sodium chloride deposited was removed again. After repeating this procedure, the filtrate was allowed to stand overnight in a refrigerator. Deep red prismatic crystals (isomer A) were obtained. They were filtered and washed with methanol-water(1:1), methanol and ether and then air-dried. Recrystallization was carried out from warm water.

The isolation of crystals from the eluate(iii) was performed by the same method; then violet prismatic fine crystals (isomer B) were obtained and recrystallized from warm water.

To the filtrate from the isomer B were added a mixture of water, methanol, ethanol and acetone (1:1:1:1). After allowing to stand for a long period at room temperature, a mixture of the violet and pinkish red crystals was obtained. The two kinds of crystals were separated by hand. The violet crystals were confirmed to be isomer B, while the pinkish red ones were found to be a new isomer (isomer C).

The eluate (ii) was confirmed to be *cis(N)*-$[Co(ida)_2]^-$ by the measurement of visible to near ultraviolet absorption spectra and elemental analysis. The absorption spectra of the eluate (iv) showed peaks at 21050 and 30030 cm^{-1} and that of the eluate (v) at 21370 and 30030 cm^{-1}. By comparing the absorption data with those reported by Ćelap *et al.*[5), these two complexes seem to correspond to the isomers of $[Co(NO_2)_2(gly)_2]^-$. The elemental analysis of crystals from the eluate (iv) showed the chemical composition of $Na[Co(NO_2)_2(gly)_2]\cdot 1.5H_2O$, but pure crystals were not obtained from the eluate (v).

2) Optical Resolution of the Isomers A, B and C: A suspension of 0.3 g of $(+)_{589}$-$[Co(ox)(en)_2]I$ and 0.13 g of silver acetate in 5 cm^3 of water was ground in a mortar for about 5 minutes. The silver iodide precipitated was filtered off and washed with a small amount of water. To the combined filtrate and washings was added 0.56 g of isomer A. The solution was kept in a refrigerator for a week; then the deep red diastereomer deposited was filtered. The less soluble diastereomer was recrystallized several times to show constant rotation ($[\alpha]_{589}=775°$) from warm water. The diastereomer was converted to the sodium salt by using a cation exchange resin of sodium form (Dowex 50W-X8, 200—400 mesh): $[\alpha]_{589}=-791°$.

The optical resolution of the isomers B and C was carried out by the same method as that of the isomer A: $[\alpha]_{589}=$ 611° and 397° for the less soluble diastereomers of the isomers B and C, respectively; $[\alpha]_{589}=194°$ and $-142°$ for the sodium salts, respectively.

3) L-Amino Acidato Complexes: The complex with an L-alaninato, L-serinato, or L-prolinato ligand was prepared by the same method as that of the glycinato complex. In these cases, only one diastereomeric pair (corresponding to the isomer A) was isolated. On the column chromatography (Dowex 1-X8, 200—400 mesh, chloride form, eluting by 0.07 M KCl aqueous solution) of the L-alaninato or L-prolinato complex, two earlier eluted red bands showed the similar absorption bands to the isomer A of glycinato complex. The major CD bands of the two eluates had the opposite signs in the first d-d absorption band region, *i, e.*, (−) for the first eluate (A-1) and (+) for the second eluate (A-2). In the case of L-serinato complex, the separation of isomers on the column chromatography was poor, and these were separated into two parts with opposite rotations at 589 nm by using a fraction collector. The major CD band of the faster eluting part (A-1) had (−) sign and that of the later one (A-2) (+) sign. The crystallizations of these red isomers were made by the same method as that for glycinato isomers. The faster eluted isomer of the L-alaninato complex was not obtained in pure solid. Thus, the absorption and CD measurements of this isomer (A-1) were made in an aqueous eluate purified on a QAE-sephadex column chromatography; the molar absorptivity is assumed to be the same as that of the isomer A-2.

4) Other Complexes: The complex $Na_2[Co(NO_2)(edta)]\cdot 3H_2O$ was prepared and resolved following the directions of Dwyer and Garvan[6] (edta = ethylenediaminetetraacetato (4−)). The complex $Na[Co(NO_2)(ed3a)]\cdot H_2O$ was prepared by the method of Blackmer *et al.*[7] and resolved by the method of Maricondi and Maricondi[8] (ed3a = ethylenediaminetriacetato(3−)).

Measurements. The visible and ultraviolet absorption spectra were obtained with a Shimadzu UV-200 spectrophotometer. The CD spectra were recorded on a Jasco MOE-1 spectropolarimeter. A Jasco DIP-4 digital polarimeter was used to check optical rotations. Proton magnetic resonance spectra were recorded on a Varian XL-100 spectrometer at about 36 °C, the internal temperature of the probe. A granule of DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) was added to serve as an internal reference. Two drops of 1M-DCl was added to the solvent, D_2O.

Results and Discussion

The analytical data of the complexes obtained are presented in Table 1. For the complex $[Co(NO_2)(gly)(ida)]^-$ five geometrical isomers are possible as is shown in Fig. 1. Three of them (I, II, and III) have a facially coordinating ida ligand and are optically resolvable, while the other two (IV and V) have a meridionally coordinating ida ligand and are optically unresolvable. In the glycinato complex, three optically resolvable geometrical isomers were obtained; thus they should take *fac(ida)* structures, I, II, and III. The fact that the remaining two *mer(ida)* isomers were not obtained is compatible with the previous recognition that the ida ligand can take a *meridional* coordination only with much difficulty.[9] The visible and ultraviolet absorption spectra of the three isomers are shown in Fig. 2. The absorption spectra resemble each other in the charge transfer region, while they are distinguished in the first d-d absorption band region. The three *fac(ida)* isomers belong to a CoN_3O_3 chromophore, and are classified into the *mer(O)* (I and II) and the

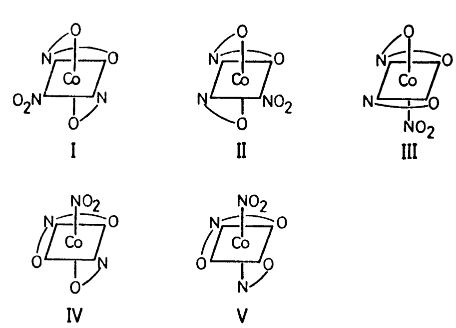

Fig. 1. Five possible geometrical isomers of $[Co(NO_2)(gly)(ida)]^-$. Upper three: *fac(ida)* type; (I) *mer(O)trans(N)*, (II) *mer(O)cis(N)*, and (III) *fac(O)*. Lower two: *mer(ida)* type; (IV) *mer(O)trans(N)* and (V) *mer(O)cis(N)*.

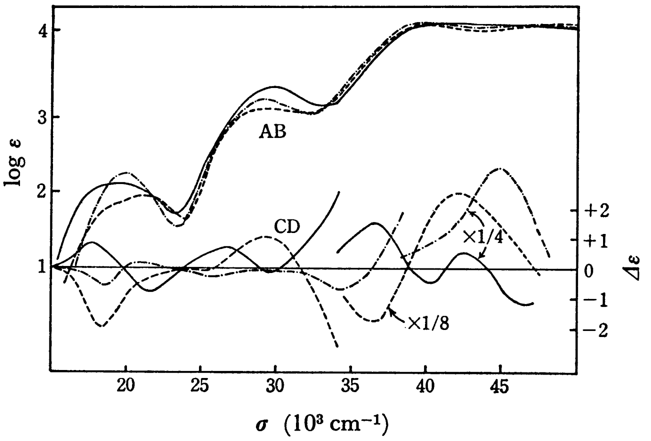

Fig. 2. Absorption (AB) and CD curves of three isomers of *fac(ida)*-$[Co(NO_2)(gly)(ida)]^-$: (----), $(-)_{589}$-A (I); (——) $(+)_{589}$-B (II); (-·-·-), $(-)_{589}$-C (III).

Table 1. Analytical data of the complexes (%)

Label	Complex	C Found	C Calcd	H Found	H Calcd	N Found	N Calcd
Gly (unresolved)							
A	$Na[Co(NO_2)(gly)(ida)]\cdot 2H_2O$	19.24	19.52	3.57	3.56	11.52	11.39
B	$Na[Co(NO_2)(gly)(ida)]\cdot 2H_2O$	19.59	19.52	3.50	3.56	11.79	11.39
C	$Na[Co(NO_2)(gly)(ida)]\cdot H_2O$	20.12	20.52	3.28	3.16	12.02	11.97
Gly (resolved)							
A	$(-)$-$Na[Co(NO_2)(gly)(ida)]\cdot 2H_2O$	19.69	19.52	3.74	3.56	11.67	11.39
B	$(+)$-$Na[Co(NO_2)(gly)(ida)]\cdot 2H_2O$	19.28	19.52	3.61	3.56	11.08	11.39
C	$(-)$-$Na[Co(NO_2)(gly)(ida)]\cdot 2H_2O$	19.27	19.52	3.52	3.56	11.66	11.39
L-Ser							
A-1	$(-)$-$Na[Co(NO_2)(L\text{-}ser)(ida)]\cdot 3H_2O$	19.87	20.15	3.96	4.11	10.05	10.07
A-2	$(+)$-$Na[Co(NO_2)(L\text{-}ser)(ida)]$	23.00	23.16	3.14	3.05	11.31	11.57
L-Pro							
A-1	$(-)$-$K[Co(NO_2)(L\text{-}pro)(ida)]\cdot 1.5H_2O$	25.84	25.96	3.91	3.88	10.20	10.10
A-2	$(+)$-$K[Co(NO_2)(L\text{-}pro)(ida)]\cdot 1.5H_2O\cdot 0.2KCl$	24.64	25.07	3.82	3.75	9.90	9.75
L-Ala							
A-2	$(+)$-$K[Co(NO_2)(L\text{-}ala)(ida)]\cdot 2H_2O$	20.94	21.06	3.78	3.79	10.64	10.53

The signs of the optical rotation, (+) or (−), at 589 nm are shown.

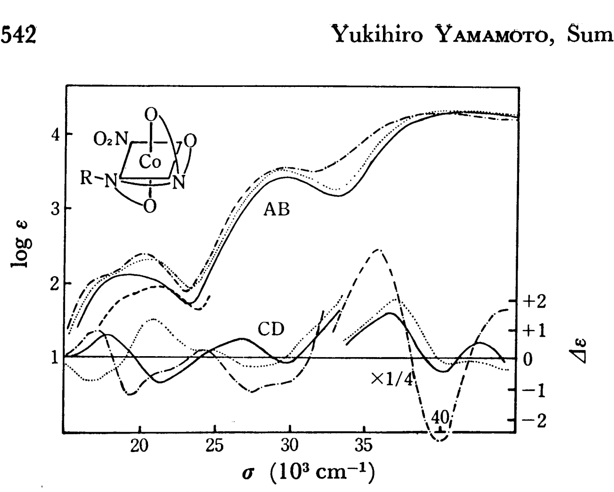

Fig. 3. Absorption (AB) and CD curves of (——), $(+)_{589}$-B; (–·–·–), $(-)_{546}$-$[\mathrm{Co(NO_2)(edta)}]^{2-}$; (····), $(+)_{546}$-$[\mathrm{Co(NO_2)(ed3a)}]^-$; and absorption curve of (----) the isomer A. The absolute configuration of $(-)_{546}$-$[\mathrm{Co(NO_2)(edta)}]^{2-}$ ($R=\mathrm{CH_2COO^-}$) and $(+)_{546}$-$[\mathrm{Co(NO_2)(ed3a)}]^-$ ($R=H$), is shown in the left upper corner.

fac(O) (III) types. The first d-d absorption bands of isomers A and B are broad and that of isomer C sharp as in Fig. 2. According to a semi-empirical rule,[10,11] the former two are assigned to the *mer(O)* configuration and the latter to the *fac(O)*. The geometrical configuration II of the *mer(O)* is similar to that of the $[\mathrm{Co(NO_2)(edta)}]^{2-}$[12] and $[\mathrm{Co(NO_2)(ed3a)}]^-$[7] complexes, except for the chelate ring connecting two donor nitrogens in the latter two complexes. As is shown in Fig. 3, the first absorption band of the isomer B is closer to those of the $[\mathrm{Co(NO_2)(edta)}]^{2-}$ and $[\mathrm{Co(NO_2)(ed3a)}]^-$ complexes. Moreover, Yamatera's rule[11] predicts, by taking a zero point at the first band position of $[\mathrm{Co(en)_3}]^{3+}$ and using parameter values, $\delta(\mathrm{N})=0$, $\delta(\mathrm{O})=-4730$ cm^{-1} (estimated from $[\mathrm{Co(ox)_3}]^{3-}$), and $\delta(\mathrm{NO_2})=4000$ cm^{-1} (estimated from *mer*-$[\mathrm{Co(NH_3)_3(NO_2)_3}]$ and *cis*-$[\mathrm{Co(NH_3)_4(NO_2)_2}]^{+}$[13]), that the first band splitting components locate at 18700, 18900, and 21100 cm^{-1} for the structure I, 17760, 19920, and 21100 cm^{-1} for II, and 18900, 19920, and 19920 cm^{-1} for III. The lowest energy component of the structure II is expected to lie at lower energy side than that of the structure I, and this is in accord with the observation that the first absorption band of the isomer B extends to the lower energy side. Thus the isomers A, B, and C are assigned to the structure I (*mer(O)trans(N)*), II (*mer(O)cis(N)*), and III (*fac(O)*), respectively.

The CD curves of $(+)_{589}$-B isomer, $(+)_{546}$-$[\mathrm{Co(NO_2)(ed3a)}]^-$ and $(-)_{546}$-$[\mathrm{Co(NO_2)(edta)}]^{2-}$ are shown in Fig. 3. It has been determined that the latter two complexes take the absolute configuration shown in Fig. 3 on the comparison of their CD spectra with those of the stereospecifically formed $(+)_{546}$-$[\mathrm{Co(NO_2)((\mathit{R})\text{-}pdta)}]^{2-}$[14] and $(-)_{546}$-$[\mathrm{Co(NO_2)((\mathit{R})\text{-}pd3a)}]^-$,[15] respectively. Three complexes in Fig. 3 give the resembling CD pattern in the charge transfer band region; *i.e.*, (+) at about 36000 cm^{-1} and (−) at about 40000 cm^{-1}. Therefore, it may be concluded that the $(+)_{589}$-B isomer has the same absolute configuration of the arrangement of donor atoms as the $(+)_{546}$-$[\mathrm{Co(NO_2)(ed3a)}]^-$ and $(-)_{546}$-$[\mathrm{Co(NO_2)(edta)}]^{2-}$ complexes. The fact that the CD curves of the $(+)_{589}$-B isomer and $(+)_{546}$-$[\mathrm{Co(NO_2)(ed3a)}]^-$ are enantiomeric to each other in the first d-d absorption band region suggests that the vicinal effect due to the asymmetric nitrogen atom of $(+)_{546}$-$[\mathrm{Co(NO_2)(ed3a)}]^-$ is large enough to invert the CD sign as pointed out by Maricondi and Maricondi.[8] It seems that the CD in the charge transfer region is ascribed mainly to the configurational chirality due to the arrangement of donor atoms. The absolute configuration of the isomer B cannot be named by the current IUPAC rule,[16] because two chiralities due to the arrangement of chelate rings are cancelled by each other such as $\Delta\Lambda$. On the other hand, the IUPAC rule is applicable to the other two isomers, A and C.

The $(-)_{589}$-A and $(-)_{589}$-C isomers give a negative major CD band in the first d-d absorption band region. Thus, the $(-)_{589}$-A and $(-)_{589}$-C isomers may be assigned tentatively to the Δ configurations. These two complexes show the similar CD pattern in the charge transfer region also as in Fig. 2.

By applying the additivity rule[17] of the configurational and vicinal effects to the CD curves of A-1 and A-2 diastereomeric isomers with L-ala, L-ser or L-pro, the configurational and vicinal CD contributions can be separated. All the calculated configurational CD curves of the A-1 isomers agree with the observed CD curve of the $(-)_{589}$-A isomer of glycinato complex as in Fig. 4. It was concluded, therefore, that the first eluted A-1 diastereomers with L-amino acidato ligand take the absolute configuration Δ same as the $(-)_{589}$-A glycinato complex. The vicinal CD curves of these isomers are different from each other as in Fig. 4.

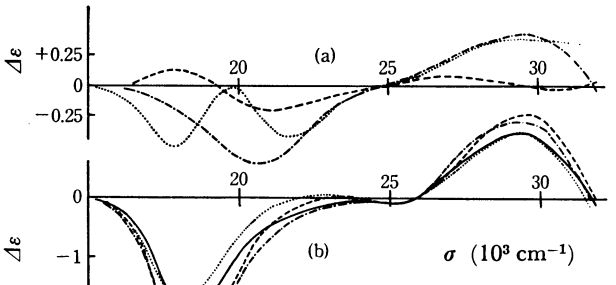

Fig. 4. Calculated vicinal effect (2L) curves (a) and caluculated configurational effect curves (b) of (----), L-alaninato; (–·–·–), L-serinato; and (····), L-prolinato complexes (A-1 series). Observed CD curve of $(-)_{589}$-A glycinato isomer (——) is also shown in (b).

In the pmr spectra of the L-prolinato diastereomers, it is predicted that the magnetic anisotropy of two carbon-oxygen single bonds[18] of the ida ligand plays the most influensive part for the NH proton chemical shift of the coordinated prolinato ligand, and that the NH proton of the Δ isomer resonates at the higher magnetic field than that of the Λ isomer. In fact, the isomer A-1 resonated at 7.19 ppm and the A-2 at 7.41

ppm. Thus it is confirmed that the A-1 series has the Δ absolute configuration and the A-2 Λ, and hence that the $(-)_{589}$-A isomer of glycinato complex has the Δ absolute configuration.

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