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Preparation and Circular Dichroism of *trans(N)*- and *cis(N)*-Isomers of (Ammoniatriacetato)(amino-acidato)cobalt(III) Complexes

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Eleven new complexes, *trans(N)*- or *cis(N)*-isomers of (ammoniatriacetato)(amino-acidato)-cobalt(III) ions, have been synthesized as their potassium salts, where the amino acids are glycine, β-alanine, γ-aminobutyric acid, sarcosine, L-alanine, L-serine, L-valine and L-proline. The geometrical isomers have been separated by ion-exchange column chromatography and their structures determined on the basis of their absorption spectra and proton magnetic resonance spectra. Stereoselectivity about the formation of the *trans* and *cis* isomers was found. The circular dichroism of the complexes containing optically active amino acidato ligands has been measured and discussed in relation to so-called vicinal contribution by the optically active ligands.

It has been recognized that the transition metal complexes, in which the configuration around the central metal ion is not chiral but the ligand coordinated has a kind of chiral configuration, show markedly the cotton effect in the d→d absorption bands of the central metal ion by so-called vicinal effect.[1] It has been pointed out that the CD curve due to the vicinal effect shows the split components of the d→d absorption bands more clearly than that of the configurational effect which arises from a chiral configuration near around the central metal ion.[2] These investigations have been achieved on the basis of the fact that the vicinal and the configurational contributions to the CD are separable and additive.[3,4] In these circumstances, it is thought to be desirable to study more in detail the vicinal contribution for various kinds of metal complexes. Two geometrical isomers, *trans(N)* and *cis(N)*, are possible for the (ammoniatriacetato)(L-amino-acidato)cobalt(III) ion, $[Co(ata)(L\text{-}am)]^-$, where the ata and the L-am are coordinated as a tetradentate and a bidentate ligand respectively.*1 Both the isomers of this complex have no chiral configuration near around the central cobalt(III) ion in a first approximation but have the vicinal CD contribution mainly due to an asymmetric carbon atom of the ligand amino acid ion.

The present study is concerned with the preparation, the d→d absorption spectra and CD spectra of the *trans(N)*- and *cis(N)*-K[Co(ata)(am)] complexes including both optically active and non-active amino acid ions as the bidentate ligand am. Only one complex, *cis(N)*-K[Co(ata)(gly)]·$2H_2O$,

1) For the octahedral cobalt(III) complexes: Y. Shimura, This Bulletin, **31**, 315 (1958); J. Fujita, T. Yasui and Y. Shimura, *ibid.*, **38**, 654 (1965); T. Yasui, J. Hidaka and Y. Shimura, *ibid.*, **39**, 2417 (1966).

2) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

3) B. E. Douglas and S. Yamada, *ibid.*, **4**, 1561 (1965). B. E. Douglas, *ibid.*, **4**, 1813 (1965); J. I. Legg, D. W. Cooke and B. E. Douglas, *ibid.*, **6**, 700 (1967); M. Shibata, H. Nishikawa and Y. Nishida, *ibid.*, **7**, 9 (1968); K. Yamasaki, J. Hidaka and Y. Shimura, This Bulletin, **42**, 119 (1969).

4) D. A. Buckingham, S. F. Mason, A. M. Sargeson and K. R. Turnbull, *Inorg. Chem.*, **5**, 1649 (1966).

*1 The abbreviation "ata" represents a tervalent ammoniatriacetate ion, $N(CH_2COO)_3^{3-}$ and "am" a univalent amino acid ion in general, and "gly" glycinate, "β-ala" β-alaninate, "γ-ambut" γ-aminobutyrate, "sar" sarcosinate, "L-ala" L-alaninate, "L-ser" L-serinate, "L-val" L-valinate, and "L-pro" L-prolinate ion.

has been known[5] in this group.

Experimental

Preparation of Potassium (Ammoniatriacetato)-(amino-acidato)cobaltate(III): K[Co(ata)(am)]·n-H_2O. A solution of 10.2 g of cobalt(II) acetate tetrahydrate in 20 m*l* of water was added to a solution containing 8.0 g of $ataH_3$ in 15 m*l* of 2 N potassium hydroxide. To this 6.0 g of lead dioxide was added and the resulting mixture was mechanically stirred at 60°C for about 30 min. The color of the solution changed from dark red to blue violet. After the mixture had been cooled to room temperature, an excess of lead dioxide was filtered off. To the filtrate a calculated amount of the amino acid concerned was added and the solution was mechanically stirred at 60°C until its color changed to reddish violet. The solution was cooled in an ice bath for one hour and a small quantity of insoluble material precipitated was filtered off. The reddish violet filtrate was treated as follows; as in (1) for the glycinato, sarcosinato and L-serinato complexes and as in (2) for the other amino acidato complexes. (1): A large amount of ethanol was added to the filtrate. The reddish violet deposit was filtered and washed with methanol and ether, and then dried in a vacuum desiccator. The yield was approximately 14 g. (2): In order to remove the lead(II) ion, 3.7 g of potassium sulfate was added to the filtrate and the mixed solution was thoroughly stirred at 60°C. After the resulting solution had been cooled to room temperature, the lead sulfate precipitated was filtered off. The filtrate was concentrated to the syrup on a vacuum evaporator. This syrup was diluted by adding an appropriate amount of methanol and then the insoluble by-products were filtered off. It was confirmed, by the column chromatographic method, that the by-products were not the complex desired. A large amount of ethanol-ether mixture (1 : 1) was added to the filtrate. The reddish violet product deposited was filtered and washed with methanol-ether mixture and ether, and then dried in a vacuum desiccator. The yield was approximately 7 g.

Separation of *trans*(*N*)- and *cis*(*N*)-K[Co(ata)·(am)]·$n$$H_2O$. Each of the products obtained in (1) or (2) was separated into the *trans*(*N*) and *cis*(*N*) isomers by the column chromatographic method. Namely, about 7 g of the crude product was dissolved in water and passed through a column (30 mm×500 mm) containing strong anion exchange resin (Dowex 1X-8, 100—200 mesh, chloride form). After the column had been swept with water, the adsorbed band was eluted with 0.07 N aqueous solution of potassium chloride at a rate of about 2.5 m*l* per min. By elution with 0.07 N potassium chloride, two colored bands, a reddish purple one and a violet one, were eluted in this order and completely separated from each other. The earlier fraction was confirmed to be the *trans*(*N*) isomer and the one eluted later to be the *cis*(*N*) isomer by the measurement of their absorption spectra.[5,6]

Each of the eluates was concentrated to dryness on a vacuum evaporator. The resulting crude complexes, which were contaminated with a small amount of potassium chloride, were treated as follows. In the case of the *trans*(*N*) isomers of the glycinato, sarcosinato and L-serinato complexes and of all the *cis* isomers, the crude complex was dissolved in a least amount of water as possible and less soluble potassium chloride was filtered off. The complex desired was obtained by adding methanol, little by little, to the filtrate. It was then recrystallized from water by adding methanol, washed with a water-methanol, methanol and then ether, and dried in air.

On the other hand, each of the *trans*(*N*) complexes other than the glycinato, sarcosinato and L-serinato ones was dissolved in methanol at 50°C. After the potassium chloride remaining in solid had been filtered off, the filtrate was kept in a refrigerator overnight. The complex deposited was gathered by filtration and washed with a small amount of methanol and ether, and then dried in air. The complex was recrystallized from hot methanol containing a small amount of water.

The *cis* isomers of the β-alaninato, γ-aminobutyrato and sarcosinato complexes could not be isolated because of their negligible yields. In the elution of L-prolinato

Table 1. Analytical results (amounts in %)

Complex	C		H		N	
	Found	Calcd	Found	Calcd	Found	Calcd
trans(*N*)-K[Co(ata)(gly)]·$2H_2O$	24.45	24.25	3.10	3.57	7.04	7.07
cis(*N*)-K[Co(ata)(gly)]·$2H_2O$	24.35	24.25	3.36	3.57	7.12	7.07
trans(*N*)-K[Co(ata)(β-ala)]·$2H_2O$	26.01	26.34	3.98	3.94	6.79	6.83
trans(*N*)-K[Co(ata)(γ-ambut)]·$3H_2O$	27.22	27.15	4.31	4.57	6.22	6.33
trans(*N*)-K[Co(ata)(sar)]·H_2O	27.83	27.55	3.44	3.61	7.05	7.14
trans(*N*)-K[Co(ata)(L-ala)]·$2.5H_2O$	25.77	25.78	4.05	4.09	6.59	6.68
cis(*N*)-K[Co(ata)(L-ala)]·$3H_2O$	25.41	25.24	3.91	4.24	6.46	6.54
trans(*N*)-K[Co(ata)(L-ser)]·H_2O	26.40	26.48	3.41	3.46	6.84	6.86
cis(*N*)-K[Co(ata)(L-ser)]·$2H_2O$	25.09	25.36	3.81	3.79	6.54	6.57
trans(*N*)-K[Co(ata)(L-val)]·$3H_2O$	28.80	28.95	4.70	4.87	6.08	6.14
cis(*N*)-K[Co(ata)(L-val)]·$4H_2O$	28.02	27.85	4.63	5.11	5.91	5.91
trans(*N*)-K[Co(ata)(L-pro)]·$3H_2O$	29.21	29.08	4.27	4.45	6.10	6.17

5) J. Hidaka, Y. Shimura and R. Tsuchida, This Bulletin, **35**, 567 (1962).

6) N. Matsuoka, J. Hidaka and Y. Shimura, This Bulletin, **40**, 1868 (1967).

complex, the violet band (*cis* isomer) was not observed; only the *trans*(*N*) isomer (reddish purple band) was isolated.

All of the complexes reported here are soluble in water. Of these complexes the *trans* isomers are soluble in methanol except those of the glycinato, sarcosinato and L-serinato complexes, which are sparingly soluble, while all the *cis* isomers are insoluble in methanol.

The results of the chemical analyses for all the complexes prepared are shown in Table 1.

Measurements. The electronic absorption spectra of the complexes were measured by a Beckman DU spectrophotometer. The CD spectra were recorded with a Roussel-Jouan dichrograph and the RD curves with a Yanagimoto recording spectropolarimeter model-185. All the measurements were made in aqueous solutions at room temperature.

The proton magnetic resonance (PMR) spectra of the complexes were obtained on a Japan Electron Optics JNM-4H-100 spectrometer operating at 100 Mc/sec, in deuterium oxide with NaTMS (sodium trimethylsilylpropanesulfonate) as an internal standard. The acidic solution (pH: about 0.6) was prepared by adding concentrated hydrochloric acid to the deuterium oxide solution.

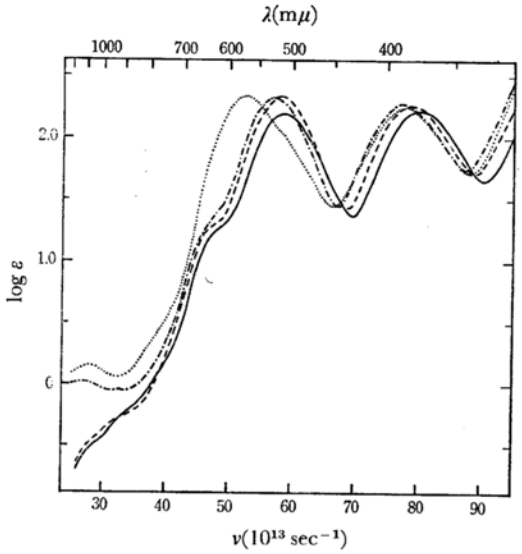

Fig. 1. Absorption curves of *trans*(*N*)-K[Co(ata)(am)]: (——) gly, (----) β-ala and (-·-·-) γ-ambut, and (·····) *cis*(*N*)-K[Co(ata)(L-ala)].

Results and Discussion

Stereoselectivity. As described in Experimental section, the column chromatographic investigation shows that the *trans*(*N*) isomer of L-prolinato complex is stereospecifically formed. This coincides with the consideration derived from the construction of molecular models. Namely, the stereospecificity of L-prolinato complex is attributed to the fact that the steric hindrance is remarkable between a pyrrolidine ring of the coordinated L-prolinate and one of the three acetate groups of ata in the *cis*(*N*) isomer. This consideration is also available in the case of *cis*(*N*) sarcosinato complex. A similar unbalanced formation is also observed in the case of β-alaninato or γ-aminobutyrato complex. Considering the formation of a trace amount of the *cis* isomer, it seems likely that the unbalance depends on the crowding of $-NH_2$ protons of the amino acid ion with the protons of the two acetate groups of ata in the *cis* isomers. This kind of crowding is expected to exist also in the *cis* isomers of glycinato or other L-aminoacidato complexes: so the pronounced unbalance in the case of the β-alaninato and γ-aminobutyrato complexes is mainly due to the instability of the six or seven membered chelate ring as compared with the five membered chelate ring.

Absorption Spectra. The absorption data of $[Co(ata)(am)]^-$ complex ions are summarized in Table 2 and their representative curves are shown in Fig. 1. It has been well known that *trans*-$[Co(O)_4(N)_2]$-type complexes show more remarkable splitting than *cis* isomers in their first absorption bands.[6-8] The first absorption bands of the reddish purple complexes obtained in the present study show quite similar splitting patterns, and this absorption behavior points out that the reddish purple complexes have the *trans*(*N*) structure (Fig. 1). In the first band of *trans*-$[Co(O)_4(N)_2]$-type complexes, it may be of interest that the ratio, $\{\log \varepsilon_{max}(\text{sub.})/\log \varepsilon_{max}(\text{major})\}$, of a sub- and a major-band for the complexes with tridentate ligand is smaller than those for the complexes with bidentate ligand.[5,9,10] This situation also stands for the present *trans*(*N*) complexes.

In the absorption curves of the violet complexes, a vague shoulder is observed at the shorter wavelength side of the major peak of the first absorption band (at *ca.* 570 mμ). This pattern shows that the violet complex is the *cis*(*N*) isomer.[6]

Proton Magnetic Resonance Spectra. In order to confirm the structure of the complexes, the PMR spectra of *cis*(*N*)-$[Co(ata)(gly)]^-$ and *trans*(*N*)-$[Co(ata)(L\text{-}ala)]^-$ ions were measured in deuterium oxide (Fig. 2) and in acidic deuterium oxide solution. Recently, Smith and Sawyer[10] discussed the PMR spectra of the ata complexes, $[Co(ata)(OH)(OH_2)]^-$ and *trans*(*N*)-$[Co(ataH)_2]^-$ and it has been shown that the methylene protons of the acetate groups of the complexes exhibit one symmetrical AB pattern and one singlet in the region of 4.6—3.7 ppm from NaTMS and that the chemical shift on the singlet, which was assigned to

7) J. Hidaka and Y. Shimura, This Bulletin, **40**, 2312 (1967).

8) H. Yamatera, *ibid.*, **31**, 95 (1958).

9) Unpublished results concerning bis(L-aspartato)-cobalt(III) complex.

10) B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, **7**, 922 (1968).

TABLE 2. ABSORPTION MAXIMA OF [Co(ata)(am)]$^-$ IONS

Complex ion	I Band		II Band	
	ν_{max}	($\log \varepsilon_{max}$)	ν_{max}	($\log \varepsilon_{max}$)
trans(*N*)-[Co(ata)(gly)]$^-$	*ca.* 48	(1.3)	80.1	(2.22)
	58.7	(2.20)		
trans(*N*)-[Co(ata)(β-ala)]$^-$	*ca.* 48	(1.3)	79.0	(2.26)
	58.2	(2.33)		
trans(*N*)-[Co(ata)(γ-ambut)]$^-$	*ca.* 47	(1.3)	77.9	(2.26)
	57.0	(2.31)		
trans(*N*)-[Co(ata)(sar)]$^-$	*ca.* 48	(1.3)	80.2	(2.27)
	58.5	(2.23)		
trans(*N*)-[Co(ata)(L-ala)]$^-$	*ca.* 48	(1.3)	80.5	(2.24)
	58.7	(2.21)		
trans(*N*)-[Co(ata)(L-ser)]$^-$	*ca.* 48	(1.3)	80.4	(2.24)
	58.6	(2.23)		
trans(*N*)-[Co(ata)(L-val)]$^-$	*ca.* 48	(1.3)	80.7	(2.24)
	58.6	(2.21)		
trans(*N*)-[Co(ata)(L-pro)]$^-$	*ca.* 48	(1.3)	80.0	(2.28)
	58.5	(2.23)		
cis(*N*)-[Co(ata)(gly)]$^-$	52.8	(2.34)	78.0	(2.23)
cis(*N*)-[Co(ata)(L-ala)]$^-$	52.6	(2.33)	78.1	(2.23)
cis(*N*)-[Co(ata)(L-ser)]$^-$	52.4	(2.32)	78.1	(2.22)
cis(*N*)-[Co(ata)(L-val)]$^-$	52.3	(2.32)	77.9	(2.22)

The frequencies are given in 10^{13} sec^{-1}.

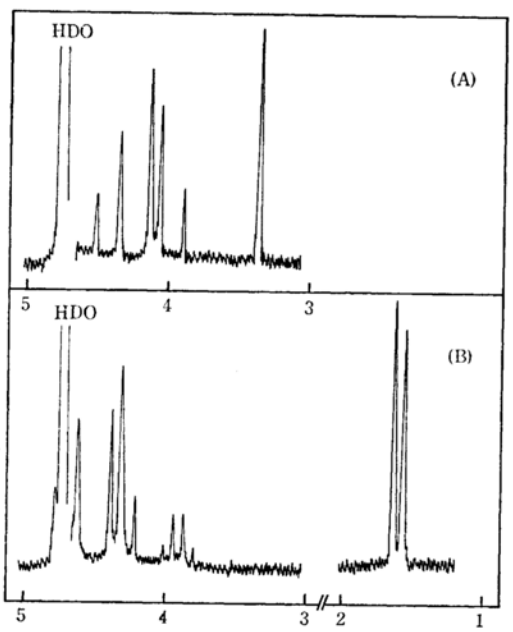

Fig. 2. PMR spectra in deuterium oxide: (A) *cis*(*N*)-K[Co(ata)(gly)] and (B) *trans*(*N*)-K[Co(ata)(L-ala)].

the protons of the uncoordinated acetate group of the latter complex, is much affected by the pH variation of the solution.

In the corresponding field, the spectra for the acetate protons of ata of the present complexes are quite similar to those reported by Smith and Sawyer, and all the peaks can be assigned as follows. For the glycinato complex (Fig. 2A), the AB pattern with centers at 4.41 and 3.99 ppm (J_{AB}= 17 cps) is assigned to the nonequivalent coupled acetate protons of two chelate rings of the ata, which are not co-planar with the glycinate ring, and the singlet at 4.12 ppm to the acetate protons of the third chelate ring of the ata, which is co-planar with the glycinate ring. The spectra of glycinato and L-alaninato complexes resemble each other, though a more complicated spectrum may be expected for the L-alaninato complex because all the acetate protons of ata have different environments. The AB pattern at 4.68 and 4.30 ppm (J_{AB}=17 cps) and the singlet at 4.30 ppm are assigned to the coordinated ata (Fig. 2B).

In acidic deuterium oxide solution (pH: about 0.6), no variation is observed in chemical shifts for all the peaks except the lowest field peak of AB pattern of the L-alaninato complex, which is overlapped by the HDO peak and shifts to down-field in acidic solution. These observations confirm that the ata functions as a tetradentate ligand.

The singlet at 3.35 ppm for the glycinato complex is assigned to the methylene protons of the glycinate chelate ring. For the L-alaninato complex, the AX_3 quartet at 3.90 ppm and the AX_3 doublet at 1.59 ppm, each with a coupling constant of 7 cps, are assigned to the methine proton and methyl protons of the L-alaninate chelate ring respectively.

These results agree with those reported by Buckingham and co-workers for several glycinato and L-alaninato complexes.[4,11]

Circular Dichroism. The CD or RD curves of the *trans*(*N*) ata complexes are quite similar to each other (Fig. 3), and the same relationship is also true for the CD or RD curves of the *cis*(*N*) ata complexes (Fig. 4).

As mentioned above, Liu and Douglas[2] pointed out that the existence of absorption components of the visible d→d transition band is shown more clearly through the CD due to the vicinal contribution than that due to the configurational one. Considering the symmetry of the *trans*(*N*) ata

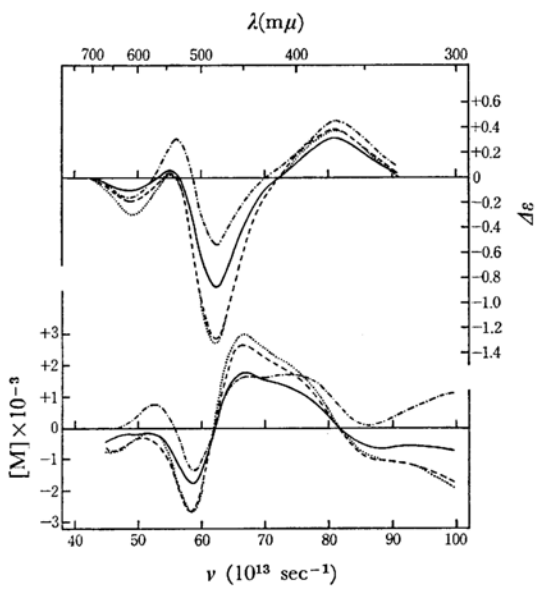

Fig. 3. CD (upper) and RD (lower) curves of *trans*(*N*)-K[Co(ata)(L-am)]: (——) L-ala, (----) L-ser, (·····) L-val and (-·-·-) L-pro.

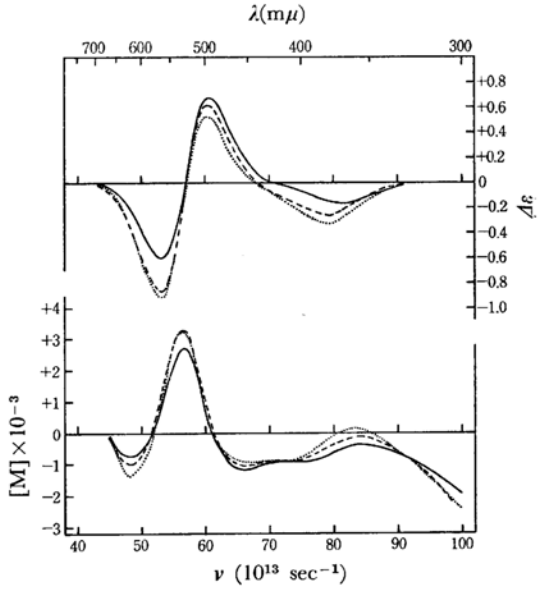

Fig. 4. CD (upper) and RD (lower) curves of *cis*(*N*)-K[Co(ata)(L-am)]: (——) L-ala, (----) L-ser and (·····) L-val.

TABLE 3. CD DATA OF [Co(ata)(L-am)]⁻ IONS

Complex ion	I Band		II Band	
	ν_{ext}	$(\Delta\varepsilon_{ext})$	ν_{ext}	$(\Delta\varepsilon_{ext})$
trans(*N*)-[Co(ata)(L-ala)]⁻	48.2	(−0.10)	81.5	(+0.30)
	55.3	(+0.06)		
	62.4	(−0.87)		
trans(*N*)-[Co(ata)(L-ser)]⁻	48.6	(−0.19)	81.1	(+0.38)
	55.2	(+0.04)		
	62.1	(−1.29)		
trans(*N*)-[Co(ata)(L-val)]⁻	48.8	(−0.29)	81.3	(+0.37)
	55.5	(+0.02)		
	62.1	(−1.32)		
trans(*N*)-[Co(ata)(L-pro)]⁻	48.5	(−0.16)	81.7	(+0.45)
	56.3	(+0.31)		
	62.2	(−0.54)		
cis(*N*)-[Co(ata)(L-ala)]⁻	53.1	(−0.60)	81.5	(−0.17)
	60.6	(+0.68)		
cis(*N*)-[Co(ata)(L-ser)]⁻	52.9	(−0.87)	79.7	(−0.26)
	60.4	(+0.61)		
cis(*N*)-[Co(ata)(L-val)]⁻	53.2	(−0.91)	78.9	(−0.33)
	60.2	(+0.53)		

The frequencies are given in 10^{13} sec^{-1}.

11) D. A. Buckingham, L. Durham and A. M. Sargeson, *Australian J. Chem.*, **20**, 257 (1967).

complex ion, the CD curves of the *trans*(N) complexes may be expected to split into three components.[2,7] In fact, the CD curves show the three components, a negative, a positive and a negative ones, listing from the longer wavelength side; on the contrary the absorption band splits into only two components in appearance (Figs. 1 and 3). This behavior resembles that of $[Co(ox)(\beta\text{-ala})_2]^-$ ion rather than that of $[Co(ox)(gly)_2]^-$ ion.[7]

The first absorption bands of *cis*(N) ata complexes split into two components as mentioned before. In the corresponding region, their CD curves show two components (a negative one and a positive one), as may be seen in Fig. 4.

From these facts, it may be concluded that the CD curve due to only the vicinal effect points out more clearly the absorption components than that due to the configurational chirality.

As shown in Table 3, the CD peaks are more intense for the ata complexes than those of the other optically active complexes which have only the so-called vicinal effect due to the optically active ligand.[1] Similar behavior was observed between the CD curves of triethylenetetramine and ethylenediamine complexes, and it was assumed that the fixed conformation of triethylenetetramine causes a greater effect than the rather mobile conformation of ethylenediamine.[12] Similar consideration may also be available for the present case.

12) C.-Y. Lin and B. E. Douglas, *Inorg. Nucl. Chem. Letters*, **4**, 15 (1968).