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Preparation and Circular Dichroism of *trans*(*N*) and *cis*(*N*) Isomers of (L- or D-Alaninate-*N*,*N*-diacetato) (amino-acidato)-cobaltate(III) Complexes

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Eight new complexes, *trans*(*N*) or *cis*(*N*) isomers of (L- or D-alaninate-*N*,*N*-diacetato) (amino-acidato)cobaltate(III) ions, have been synthesized as their potassium salts, where the amino acids are glycine, L-alanine and L-proline. Stereoselective formation of a limited number of the isomers with respect to the geometrical arrangement of the coordinated nitrogen and oxygen atoms and with respect to the position of the chelate ring containing the methyl group of the coodinated alaninate-*N*,*N*-diacetate ion, were confirmd from the results of the studies by ion-exchange column chromatography, proton magnetic resonance and circular dichroism spectra. The additivity of vicinal circular dichroism contributions from the two different optically active ligands in a complex has been discussed for the complexes without the configurational chirality.

There have been many studies[1,2] concerning the so-called vicinal contribution to circular dichroism (CD) spectra of Co(III) complexes containing optically active ligands; in most of these complexes,[1] however, the "vicinal" effect is combined with the "configurational" CD contribution due to a chiral configuration around the central Co(III) ion. Therefore, it was inevitable to separate the two kinds of contribution from each other on the CD curves. In a previous paper,[3] we reported the CD spectra of *trans*(*N*)- and *cis*(*N*)-(ammoniatriacetato)(L-amino-acidato)cobaltate(III) ions, [Co(ata)(L-am)]$^-$, in which the configuration around the central Co(III) ion is not chiral, and the coordinated chelate ligand has a chiral configuration. In the present paper,*[1] the preparation and the CD curves of *trans*(*N*)- and *cis*(*N*)-(L- or D-alaninate-*N*,*N*-diacetato) (L-amino-acidato) cobaltate(III), [Co(L- or D-alada)(L-am)]$^-$, will be reported. These have no chiral configuration around the central Co(III) ion in a first approximation but have two kinds of optically active ligand in their coordination sphere, the one being bidentate and the other quadridentate. The electronic absorption spectra, CD and PMR spectra of these complexes will be discussed mainly in relation to their geometrical structures.

Experimental

Preparation of L- or D-Alanine-*N*,*N*-diacetic Acid. To a solution of 8.9 g of L- or D-alanine in 25 m*l* of 4N lithium hydroxide, a solution of 20.8 g of monochloroacetic acid in 30 m*l* of 4N lithium hydroxide and 80 m*l* of 4N lithium hydroxide were added simultaneously over a period of about 2 hr with vigorous stirring at 70°C, the pH of the reaction mixture being adjusted in a range of 9—10 all over the reaction time. At the end of the reaction, the mixture was heated at 90°C for about 10 min. After the reaction mixture had been cooled to room temperature, 25 m*l* of concentrated hydrochloric acid was added to it. The solution was concentrated as far as possible in a vacuum evaporator. When about 300 m*l* of absolute ethanol was added to the residue, insoluble crystals separated out, which were collected by filtration and then washed well warm ethanol. The white crystals were lithium salt of the desired acid, which was contaminated with a small amount of lithium chloride. It was recrystallized from 35 m*l* of 2N hydrochloric acid and then from 50 m*l* of 0.2N hydrochloric acid. The yield was approximately 10 g. L-aladaH$_3$: mp 199—200°C (decomp.), $[\alpha]_D^{25}$ −41.5° (*c* 4.0, water).

Found: C, 40.66; H, 5.42; N, 6.71%. Calcd for $C_7H_{11}O_6N$: C, 40.97; H, 5.41; N, 6.83%. D-aladaH$_3$:

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[1] C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); B. E. Douglas and S. Yamada, *ibid.*, **4**, 1561 (1965); S. K. Hall and B. E. Douglas, *ibid.*, **8**, 372 (1969); K. Yamasaki, J. Hidaka and Y. Shimura, This Bulletin, **42**, 119 (1969); N. Matsuoka, J. Hidaka and Y. Shimura, *Inorg. Chem.*, **9**, 719 (1970).

[2] T. Yasui, J. Hidaka and Y. Shimura, This Bulletin, **39**, 2417 (1966); T. Yasui, J. Fujita and Y. Shimura, *ibid.*, **42**, 2081 (1969).

[3] N. Koine, N. Sakota, J. Hidaka and Y. Shimura, *ibid.*, **42**, 1583 (1969).

*[1] The following abbreviations are used for the ligands: "gly" for glycinate ion, "L-ala" L-alaninate, "L-pro" L-prolinate, "ata" ammoniatriacetate and "L- or D-alada" L- or D-alaninate-*N*,*N*-diacetate ion.

TABLE 1. ANALYTICAL RESULTS (amounts in %)

Complex	C Found	C Calcd	H Found	H Calcd	N Found	N Calcd
trans(*N*)-K[Co(L-alada)(gly)]·H_2O	27.76	27.55	3.50	3.60	7.06	7.14
trans(*N*)-K[Co(L-alada)(L-ala)]·$2H_2O$	28.52	28.30	4.24	4.28	6.91	6.60
trans(*N*)-K[Co(D-alada)(L-ala)]·$2H_2O$	28.00	28.30	4.50	4.28	6.84	6.60
trans(*N*)-K[Co(L-alada)(L-pro)]·H_2O	33.30	33.33	4.37	4.20	6.29	6.48
trans(*N*)-K[Co(D-alada)(L-pro)]·$2H_2O$	31.89	32.00	4.63	4.49	6.08	6.22
cis(*N*)-K[Co(L-alada)(gly)]·$3H_2O$	25.12	25.24	4.23	4.24	6.48	6.54
cis(*N*)-K[Co(L-alada)(L-ala)]·$3H_2O$	27.34	27.15	4.55	4.57	6.37	6.33
cis(*N*)-K[Co(D-alada)(L-ala)]·$3H_2O$	27.60	27.15	4.48	4.57	6.34	6.33

mp 198—199°C (decomp.), $[\alpha]_D^{25}$ +41.4° (*c* 4.0, water). Found: C, 40.53; H, 5.42; N, 6.74%.

Preparation and Separation of Potassium (L- or D-Alaninate-*N*,*N*-diacetato)(amino-acidato)-cobaltate(III). *1) Trans(N)- and cis(N)-K[Co(L-alada)(gly)].* A solution of 7.5 g of cobalt(II) acetate tetrahydrate in 20 m*l* of water was added to a solution containing 6.2 g of L-aladaH$_3$ in 15 m*l* of 2N potassium hydroxide. To this solution was added gradually 4.0 g of lead dioxide and the mixture was warmed at 60°C on a water bath for about 40 min. After the mixture had been filtered, 2.3 g of glycine was dissolved in the blue-violet filtrate. When the solution was concentrated almost to dryness at 60°C on a water bath, the color of the reaction mixture changed from blue-violet to red-violet. To the residue was added a saturated aqueous solution of 2.6 g of potassium sulfate in order to eliminate the lead ion. The precipitate was filtered off. The filtrate was evaporated in a vacuum evaporator to a fourth of its original volume. When about 30 m*l* of methanol was added to the concentrated solution, the crude *trans*(*N*) isomer crystallized out. After cooling in an ice bath, the crude product was filtered out and recrystallized from water-methanol (1 : 2) mixture. This isomer was confirmed to be pure *trans*(*N*) isomer by ion-exchange column chromatography.[3] To the filtrate was added a large amount of ethanol and ether. The precipitated crude *cis*(*N*) isomer was filtered off and purified by ion-exchange column chromatographic method.[3] Recrystallization was achieved from water-methanol (1 : 1).

2) Trans(N)- and cis(N)-K[Co(L- or D-alada)(L-ala)]. The L-alada complexes were prepared and separated by a similar procedure to that of the corresponding glycinato complexes, using L-alanine instead of glycine. The D-alada complexes were prepared by the same way as that of L-alada complexes, using D-alada instead of L-alada.

In preparation 1) and 2), the *trans*(*N*) isomer can be also easily separated and purified from the original reaction mixture by ion-exchange column chromatography as in preparation 3) of L-prolinato complex.

3) Trans(N)-K[Co(L-alada)(L-pro)]·H$_2$O. To a solution containing 8.2 g of L-aladaH$_3$ in 20 m*l* of 2N potassium hydroxide was added a solution of 10.0 g of cobalt(II) acetate tetrahydrate in 30 m*l* of water. To the solution 5.3 g of lead dioxide was gradually added and the resulting mixture was warmed at 60°C on a water bath for 40 min. After the insoluble materials had been filtered off, 4.6 g of L-proline was dissolved in the filtrate and the solution was added to a saturated aqueous solution containing 3.5 g of potassium sulfate and the resulting precipitate was filtered off. A large amount of ethanol and ether was added to the filtrate. The crude product precipitated was purified by ion-exchange column chromatographic method.[3] The complex was recrystallized from water-methanol (1 : 5). The column chromatographic investigation indicated that no *cis*(*N*) isomer arose in this preparation.

4) Trans(N)-K[Co(D-alada)(L-pro)]·2H$_2$O. This complex was prepared and separated in a similar way to that of L-alada complex, using D-alada instead of L-alada. The *cis*(*N*) isomer was not formed in this preparation. Recrystallization was achieved from methanol containing a small amount of water.

In the preparation of each isomer, the solid complex finally isolated was more than 80% of the isomer separated by column chromatography.

The results of the chemical analysis for the complexes obtained are shown in Table 1.

Measurements. The electronic absorption spectra of the complexes were measured with a Shimadzu QV-50 spectrophotometer. The CD spectra were recorded with a Rousel-Jouan dichrograph. All the measurements were made in aqueous solution at room temperature.

The proton magnetic resonance (PMR) spectra of the complexes were recorded with a Japan Electron Optics JNM-4H-100 spectrometer operating at 100 MHz, in D$_2$O solutions. The spectra for the *trans*(*N*) complexes were measured after adding a few drops of 20% DCl to the D$_2$O solution to avoid the overlap of the signals of the complex and of HOD. No significant variation of the general pattern on the spectra was observed by the addition of the acid. Measurements were carried out using *t*-butanol as an internal standard. All the signals lie at a lower field than that of the standard. The chemical shifts are referred to NaTMS (sodium trimethylsilylpropanesulfonate) as zero; *t*-butanol resonates at 1.234 ppm downfield of NaTMS.

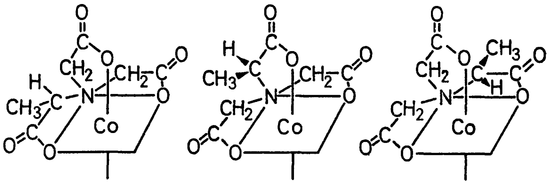

Fig. 1. Three geometrical isomers with respect to the methyl group of the coordinated L-alada.

Results and Discussion

Stereoselectivity. Complete stereoselective formation of the *trans*(*N*) isomer was observed in the preparation of (L- or D-alanine-*N*,*N*-diacetato)(L-prolinato)cobaltate(III) ion as in the case of (ammoniatriacetato)(L-prolinato)cobaltate(III) ion.[3] On the column chromatographic investigation of the reacted solutions, it was confirmed that for all of the present complexes the *trans*(*N*) isomers are dominantly formed in comparison with the corresponding *cis*(*N*) ones. This fact coincides with the results of the corresponding ata complexes.[3]

In the case of L- or D-alada complexes, three geometrical isomers due to the difference in the position of the chelate ring containing a methyl group are possible for each of the *trans*(*N*) and *cis*(*N*) isomer as shown in Fig. 1. It is reasonable to expect that these isomers concerning the methyl group are separable by ion-exchange column chromatographic method. For each of the present complexes, however, all the fractions by solubility difference or by ion-exchange chromatography showed a constant CD spectrum. All the *trans*(*N*) and *cis*(*N*) isomers were obtained in good isolation yields (more than 80% of the yields estimated by absorbance measurements). These results suggest that each of the complexes obtained is not a mixture of the isomers concerning the methyl group but only one type of isomer, and that the present complexes were stereoselectively formed. This consideration is strongly supported from the results of PMR and CD spectra of the complexes.

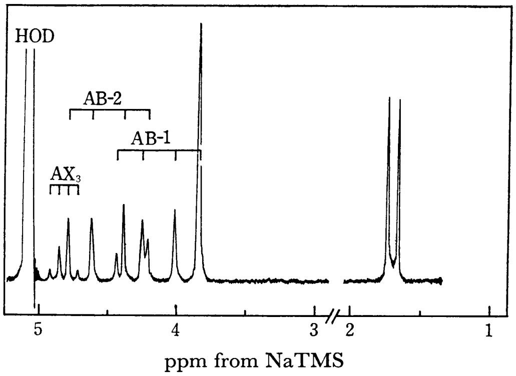

Fig. 2. PMR spectrum of *trans*(*N*)-K[Co(L-alada)(gly)]·H_2O in acid D_2O solution.

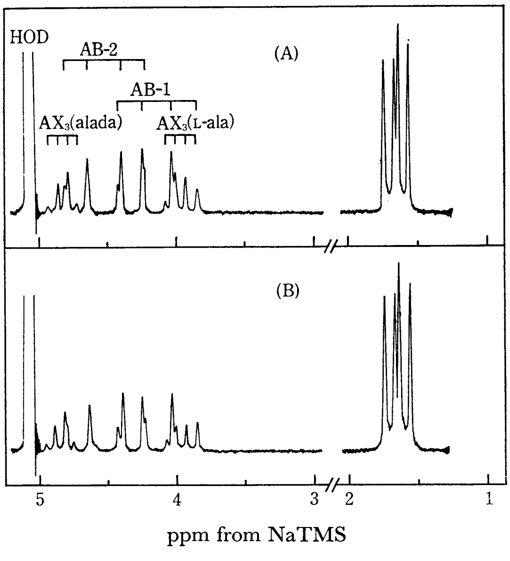

Fig. 3. PMR spectra of (A) *trans*(*N*)-K[Co(L-alada)(L-ala)]·$2H_2O$ and (B) *trans*(*N*)-K[Co(D-alada)(L-ala)]·$2H_2O$ in acid D_2O solution.

Proton Magnetic Resonance Spectra. It can

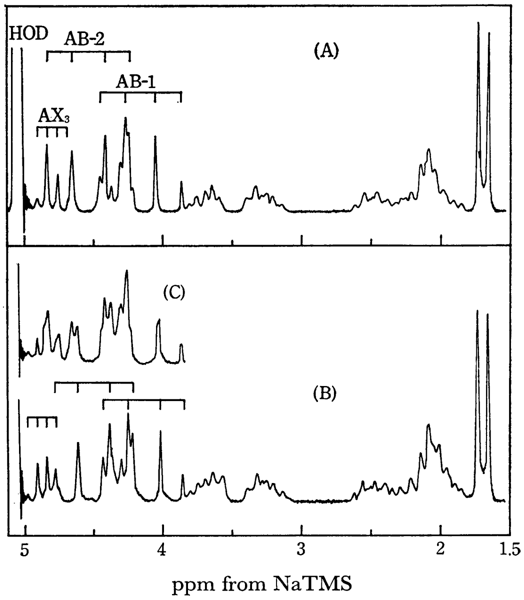

Fig. 4. PMR spectra of (A) *trans*(*N*)-K[Co(L-alada)(L-pro)]·H_2O, (B) *trans*(*N*)-K[Co(D-alada)(L-pro)]·$2H_2O$ and (C) *trans*(*N*)-K[Co(DL-alada)(L-pro)][*2] in acid D_2O solution.

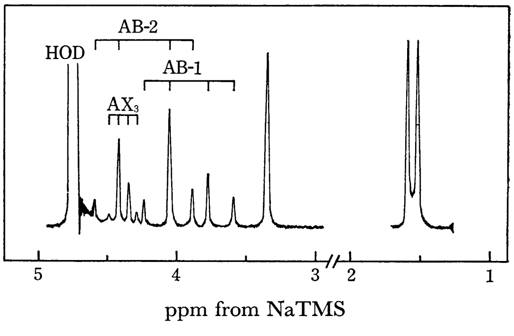

Fig. 5. PMR spectrum of *cis*(*N*)-K[Co(L-alada)(gly)]·$3H_2O$ in D_2O solution.

[*2] This complex was prepared by mixing equivalent amounts of (L-alada)- and (D-alada)-complexes.

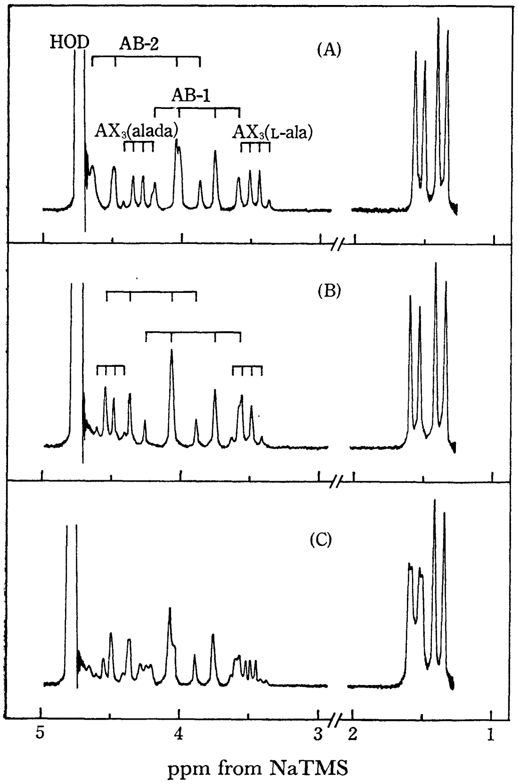

Fig. 6 PMR spectra of (A) *cis*(*N*)-K[Co(L-alada)(L-ala)]·$3H_2O$, (B) *cis*(*N*)-K[Co(D-alada)(L-ala)]·$3H_2O$ and (C) *cis*(*N*)-K[Co(DL-alada)(L-ala)]*[2] in D_2O solution.

be expected that the three geometrical isomers concerning the methyl group show a difference in their PMR spectra due to the protons of the coordinated alada or amino acid.

The PMR spectra of the complexes are shown in Figs. 2—6 and the assignments of the signals are summarized in Tables 2 and 3 with the coupling constants. For all the complexes, the signals for the protons of the alada consist of one AX_3 pattern due to the $>$CH–CH_3 and two AB pattern (AB-1 and AB-2) of equal intensities due to the two –CH_2– groups. The molecular model indicates that the two –CH_2– groups of the alada are in different environments; furthermore, the geminate protons in each the group are also in different environments. The appearance of two AB patterns due to the protons of L-alada coincides well with this topological consideration. This result indicates that the complexes obtained here are just one of the three isomers concerning the methyl group of alada.

The spectra of the alada complexes with L-alaninate exhibit another AX_3 pattern due to the metal-L-alaninate ring protons; the doublet and the quartet are at a fairly higher field than that of the protons of alada (Tables 2 and 3). This is justified by the chemical shifts of the corresponding ata complexes. Namely, the chemical shifts of the signals assigned to AX_3 pattern of L-alaninate protons in *trans*(*N*)-[Co(L- or D-alada)(L-ala)]$^-$ ion are quite similar to those (1.59 ppm for the doublet and 3.90 ppm for the quartet) of L-alaninate protons in *trans*(*N*)-[Co(ata)(L-ala)]$^-$ ion.*[3]

The complexes with L-prolinato ligand show very complicated spectra because of the many spin-spin couplings between the protons in pyrrolidine ring. Judging from the integrations and chemical shifts, however, it is possible to point out that the multiple signals at the region from 1.83—2.73 ppm are assigned to four ethylenic protons (–CH_2CH_2–) which are not adjacent to nitrogen atom and the

TABLE 2. PMR SPECTRAL DATA OF *trans*(*N*)-K[Co(L- or D-alada)(am)] COMPLEXES IN ACID D_2O SOLUTION

Assignment	Chemical shifts(ppm from NaTMS)					Coupling constant(Hz)*
	(L-alada)-(gly)	(L-alada)-(L-ala)	(D-alada)-(L-ala)	(L-alada)-(L-pro)	(D-alada)-(L-pro)	
gly, –CH_2–	3.83					
L-ala, –CH_3 (AX_3)		1.60	1.60			7
$>$CH–		3.96	3.96			
alada, –CH_3 (AX_3)	1.69	1.70	1.70	1.70	1.70	7
$>$CH–	4.81	4.82	4.86	4.80	4.87	
–CH_2–(AB-1)	3.94	3.95	3.96	3.97	3.96	18
	4.32	4.31	4.32	4.34	4.32	
–CH_2–(AB-2)	4.31	4.34	4.33	4.34	4.32	16
	4.68	4.71	4.72	4.73	4.68	

* The values are common for all of the complexes.

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*[3] Only one AB pattern and one singlet for the protons of the coordinated ata was observed in the spectrum of *trans*(*N*)-[Co(ata)(L-ala)]$^-$ ion.[3] From more detailed measurements, however, it was confirmed that the AB pattern splits into two as expected theoretically. Thus the two signals at the lower field in the AB quartet are somewhat broad, while each one at the higher field splits further into two signals of equal intensities separated by 1.0 Hz.

TABLE 3. PMR SPECTRAL DATA OF *cis*(N)-K[Co(L- or D-alada)(am)] COMPLEXES IN D_2O SOLUTION

Assignment	Chemical shifts (ppm from NaTMS) (L-alada)-(gly)	(L-alada)-(L-ala)	(D-alada)-(L-ala)	Coupling constant (Hz)*
gly, $-CH_2-$	3.35			
L-ala, $-CH_3$ (AX$_3$)		1.37	1.38	7
$>CH-$		3.68	3.52	
alada, $-CH_3$ (AX$_3$)	1.56	1.54	1.56	7
$>CH-$	4.38	4.31	4.51	
$-CH_2-$(AB-1)	3.70	3.69	3.68	18
	4.12	4.09	4.14	
$-CH_2-$(AB-2)	3.97	3.96	3.99	17
	4.49	4.56	4.44	

* The values are common for all of the complexes.

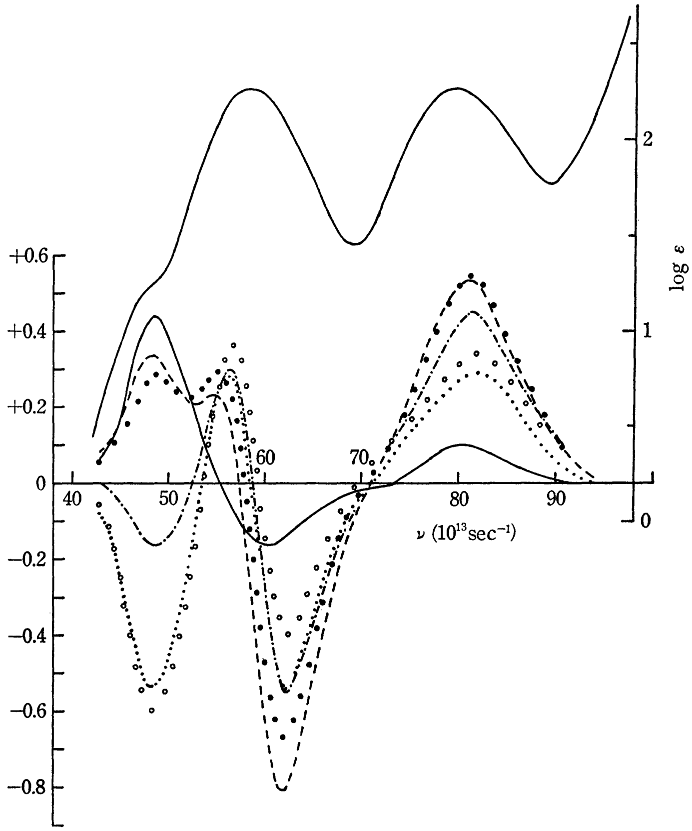

Fig. 7. Absorption and CD curves of *trans*(N)-[Co(O)$_4$(N)$_2$] type complexes.

Absorption curve: ——, [Co(L-alada)(L-pro)]$^-$, CD curves: (1) -·-·-, [Co(ata)(L-pro)]$^-$; (2) ——, [Co(L-alada)(gly)]$^-$; (3) ----, [Co(L-alada)(L-pro)]$^-$; (4) ····, [Co(D-alada)(L-pro)]$^-$; (5) ●●●●, calculated curve, (1)+(2); (6) oooo, calculated curve, (1)−(2).

TABLE 4. ABSORPTION MAXIMA OF $[Co(L\text{- or }D\text{-alada})(am)]^-$ IONS

Complex ion	I Band		II Band	
	ν_{max}	$(\log \varepsilon_{max})$	ν_{max}	$(\log \varepsilon_{max})$
trans(*N*)-$[Co(L\text{-alada})(gly)]^-$	*ca.* 48 58.9	(1.3) (2.26)	80.2	(2.23)
trans(*N*)-$[Co(L\text{-alada})(L\text{-ala})]^-$	*ca.* 48 58.9	(1.3) (2.27)	80.2	(2.23)
trans(*N*)-$[Co(D\text{-alada})(L\text{-ala})]^-$	*ca.* 48 58.9	(1.3) (2.27)	80.2	(2.23)
trans(*N*)-$[Co(L\text{-alada})(L\text{-pro})]^-$	*ca.* 48 58.6	(1.2) (2.26)	80.0	(2.26)
trans(*N*)-$[Co(D\text{-alada})(D\text{-pro})]^-$	*ca.* 48 58.6	(1.3) (2.25)	80.0	(2.25)
cis(*N*)-$[Co(L\text{-alada})(gly)]^-$	52.8	(2.37)	77.7	(2.24)
cis(*N*)-$[Co(L\text{-alada})(L\text{-ala})]^-$	52.8	(2.37)	77.9	(2.22)
cis(N)-$[Co(D\text{-alada})(L\text{-ala})]^-$	52.8	(2.36)	77.8	(2.23)

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

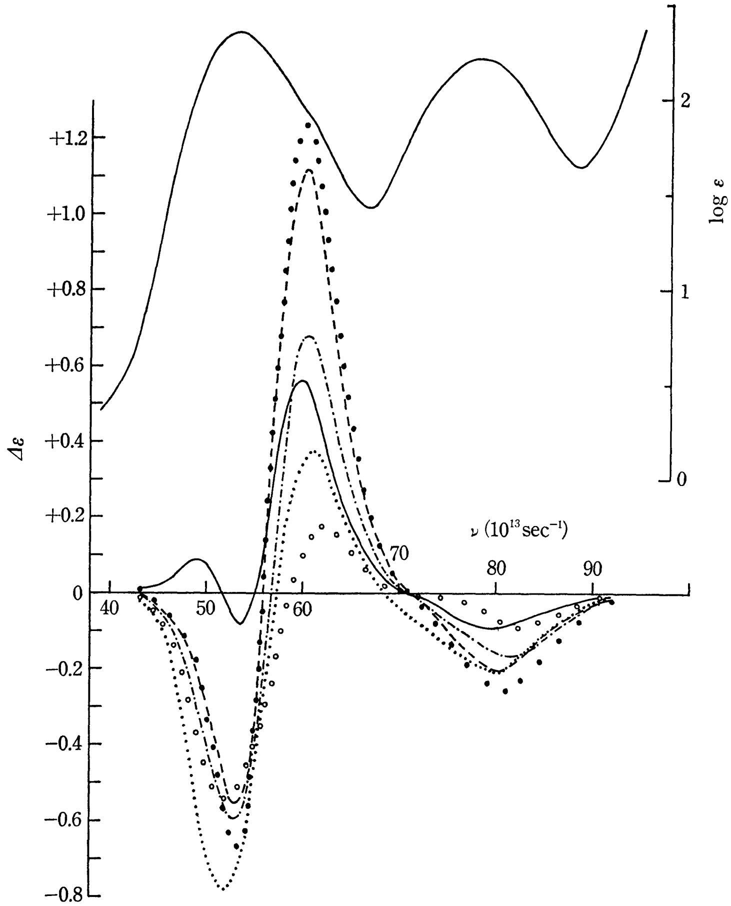

Fig. 8. Absorption and CD curves of *cis*(*N*)-$[Co(O)_4(N)_2]$ type complexes.

Absorption curve: ——, $[Co(D\text{-alada})(L\text{-ala})]^-$, CD curves: (1) –·–·–, $[Co(ata)(L\text{-ala})]^-$; (2) ——, $[Co(L\text{-alada})(gly)]^-$; (3) ----, $[Co(L\text{-alada})(L\text{-ala})]^-$; (4) ····, $[Co(D\text{-alada})(L\text{-ala})]^-$; (5) ••••, calculated curve, (1)+(2); (6) oooo, calculated curve, (1)−(2).

TABLE 5. CD DATA OF [Co(L- or D-alada)(am)]$^-$ IONS

Complex ion	I Band ν_{ext}	($\Delta\varepsilon_{ext}$)	II Band ν_{ext}	($\Delta\varepsilon_{ext}$)
trans(*N*)-[Co(L-alada)(gly)]$^-$	48.6	(+0.44)	81.3	(+0.10)
	60.1	(−0.16)		
trans(*N*)-[Co(L-alada)(L-ala)]$^-$	48.5	(+0.35)	81.3	(+0.44)
	61.7	(−1.00)		
trans(*N*)-[Co(D-alada)(L-ala)]$^-$	48.3	(−0.54)	81.7	(+0.20)
	56.3	(+0.12)		
	62.4	(−0.68)		
trans(*N*)-[Co(L-alada)(L-pro)]$^-$	48.3	(+0.34)	81.3	(+0.35)
	55.3	(+0.23)		
	62.0	(−0.81)		
trans(*N*)-[Co(D-alada)(L-pro)]$^-$	48.5	(−0.54)	82.2	(+0.29)
	56.5	(+0.28)		
	62.4	(−0.55)		
cis(*N*)-[Co(L-alada)(gly)]$^-$	49.2	(+0.09)	78.5	(−0.09)
	53.8	(−0.09)		
	60.0	(+0.57)		
cis(*N*)-[Co(L-alada)(L-ala)]$^-$	53.1	(−0.56)	78.1	(−0.20)
	60.5	(+1.12)		
cis(*N*)-[Co(D-alada)(L-ala)]$^-$	51.9	(−0.79)	79.6	(−0.26)
	61.0	(+0.37)		

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

signals at 3.03—3.93 ppm to the remaining two protons (-CH$_2$-). Consequently, the weak signals at 4.22, 4.30 and 4.37 ppm for the L-alada complex and the signals at 4.30 and 4.37 ppm for the D-alada complex will be assigned to the methine protons.

In conclusion, all the signals observed for each of the present complexes can be assigned without considering the existence of more than one isomer. Therefore, it is reasonable to consider that each of the complexes obtained consists of only one species of the three possible isomers concerning the methyl group of alada.

Circular Dichroism and Absorption Spectra. The visible absorption data of the complex ions are summarized in Table 4 and the representative curves are shown in Figs. 7 and 8. The absorption spectra are very similar to those of the corresponding ata complexes.[3)] The geometrical structures with respect to the two coordinated nitrogen atoms were confirmed from the splitting pattern of the so-called first absorption band and from the ion-exchange column chromatographic behavior.[3–5)] The CD data and curves of the complexes are shown in Table 5, and Figs. 7 and 8. The observed CD curve of the *trans*(*N*)-[Co(L-alada)(L-ala)]$^-$ and the *trans*(*N*)-[Co(D-alada)(L-ala)]$^-$ ion agrees quite well with the CD curve calculated from those of the *trans*(*N*)-[Co(ata)(L-ala)]$^-$ and *trans*(*N*)-[Co-(L-alada)(gly)]$^-$ ions, on the basis of the following additivity formulas;[4)]

$$\text{CD(L-alada, L-ala)} = \text{CD(L-alada, gly)} + \text{CD(ata, L-ala)} \qquad (1)$$

$$\begin{aligned}\text{CD(D-alada, L-ala)} &= \text{CD(D-alada, gly)} + \text{CD(ata, L-ala)} \\ &= -\text{CD(L-alada, gly)} + \text{CD(ata, L-ala)} \qquad (2)\end{aligned}$$

Similar good agreement of the observed CD curves with the calculated ones is also realized for the two *trans*(*N*) complexes with L-prolinate and for one of the two *cis*(*N*) complexes, *cis*(*N*)-[Co(L-alada)-(L-ala)]$^-$ (Figs. 7 and 8). These facts indicate that the additivity of the two vicinal contributions is perfect and each of the asymmetric carbon atoms of the two optically active ligands in a complex contribute independently to the optical activity of the complex ion. This agreement will show that the complexes obtained have commonly only one type of geometrical structure concerning the methyl group of the quadridentate ligand alada.

As an exception, the observed CD curve of *cis*(*N*)-[Co(D-alada)(L-ala)]$^-$ deviates considerably from the calculated one derived from the observed CD curves of *cis*(*N*)-[Co(L-alada)(gly)]$^-$ and *cis*(*N*)-[Co(ata)(L-ala)]$^-$ (Fig. 8). This deviation suggests that the position of the chelate ring containing the methyl group of the D-alada in this *cis*(*N*)-[Co(D-alada)(L-ala)]$^-$ complex obtained here differs from that of the other complexes, since from their PMR data we confirmed that the complex obtained is not a mixture of the possible isomers.

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4) N. Koine, N. Sakota, J. Hidaka and Y. Shimura, This Bulletin, **42**, 1779 (1969).

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