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Studies of Mixed Cyano Cobalt(III) Complexes. IV.[1] Preparation and Characterization of *trans*(O,X)-[Co(X)(aminoacidato)(diethylenetriamine)]$^+$ Complexes with X=CN$^-$, NO$_2^-$, or Cl$^-$

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A series of new kinds of mixed cobalt(III) complexes, *trans*(O,X)-[Co(X) (aminoacidato) (diethylenetriamine)]Y, have been prepared and characterized by visible and ultraviolet, circular dichroism, and proton magnetic resonance spectroscopy for X=CN$^-$, NO$_2^-$, and Cl$^-$; aminoacid=glycine, α-aminoisobutyric acid, L-alanine, L-valine, L-threonine, and L-proline; and Y=Br$^-$, Cl$^-$, or ClO$_4^-$. The proton magnetic resonance spectra of the cyano mixed complexes show the existence of new conformational isomers, *endo* and *exo* forms, which concern the ligand CN$^-$ and the hydrogen atom attached to the central nitrogen atom of the meridionally coordinated diethylenetriamine ligand.

In the course of preparative studies of mixed cyano cobalt(III) complexes,[1–3] we have obtained a group of new cyano-diethylenetriamine cobalt(III) complexes with various aminoacids, including optically active ones.[4] In order to characterize these complexes, we have also prepared analogous complexes in which cyanide ion is replaced by a chloride or a nitrite ion. This paper reports the preparation of such complexes and their structures as determined by visible and ultraviolet, circular dichroism, and proton magnetic resonance spectroscopy. A short communication was given on the existence of a couple of novel isomers of the new cyano-diethylenetriamine cobalt(III) complex ion.[5]

Experimental

Ligands and Starting Materials. Diethylenetriamine, glycine, α-aminoisobutyric acid, L-alanine, L-proline, L-valine, and L-threonine were obtained from Wako Pure Chemicals, and used without further purification.

[Co(NO$_2$)$_3$dien],[6] [CoCl$_3$dien],[6] and *trans*-[Co(CN)(SO$_3$)(NH$_3$)$_4$][7] were prepared according to the methods described in literature.

Preparation of the Complexes. All *trans*(O,X)-monoacido-aminoacidato-diethylenetriamine-cobalt(III) complexes (X=CN$^-$, NO$_2^-$, or Cl$^-$) were prepared as follows.

Method 1) *trans*-[Co(CN)(SO$_3$)(NH$_3$)$_4$] $\xrightarrow{\text{dien}}$ an intermediate complex (not isolated) $\xrightarrow{\text{concd. HBr}}$ Co(CN)(OH$_2$)(dien)Br$_2$ $\xrightarrow{\text{amH, NaOH}}$ *trans*(O, CN)-[Co(CN)(am)(dien)]$^+$ (in water)

Method 2) *trans*(O, Cl)-[Co(Cl)(am)(dien)]$^+$ $\xrightarrow{\text{KCN}}$ *trans*(O,CN)-[Co(CN)(am)(dien)]$^+$ (in DMSO)

Method 3) [CoCl$_3$dien] $\xrightarrow{\text{amH, NaOH}}$ *trans*(O, Cl)-[Co(Cl)-(am)(dien)]$^+$ (in water)

Method 4) [CoCl$_3$dien] $\xrightarrow{\text{amH, NaOH, NaNO}_2}$ *trans*(O, NO$_2$)-[Co(NO$_2$)(am)(dien)]$^+$ (in water)

Method 5) [Co(NO$_2$)$_3$dien] $\xrightarrow{\text{amH, NaOH}}$ *trans*(O, NO$_2$)-[Co(NO$_2$)(am)(dien)]$^+$ (in water)

trans(O,CN)-[Co(CN)(gly)(dien)]Br·3H$_2$O. *Method 1*: To a suspension of 35 g of *trans*-[Co(CN)(SO$_3$)(NH$_3$)$_4$]·2H$_2$O in 250 m*l* of water was added 15.5 g of diethylenetriamine. Upon heating at 70—80°C for 2 hr with occasional stirring, the starting complex dissolved nearly completely with evolution of ammonia gas. The resulting brown solution was filtered, and the filtrate was concentrated to about 60 m*l* at 60°C under reduced pressure. The sticky solution was treated wtih 100 m*l* of concd. hydrobromic acid, cooled in an ice bath overnight and filtered. The brown solution was warmed at 75°C for about 4 hr until the color turned deep red and was then filtered. To the filtrate was added 400 m*l* of water and an appropriate amount of methanol and acetone. A crude complex, precipitated on cooling was filtered off, washed with methanol, air-dried and recrystallized from water by adding methanol and acetone. Elemental analysis showed the composition Co(CN)(OH$_2$)-(dien)Br$_2$.

Found: C, 16.13; H, 4.81; N, 15.53%. Calcd for C$_5$H$_{15}$-N$_4$OCoBr$_2$: C, 16.41; H, 4.13; N, 15.31%. The complex turns from pale rose to testaceous by storing in a vacuum desiccator or by heating. Such a color change might be due to the dehydration of coordinated water followed by the anation of bromide ion. Further study was not made.

To a warm aqueous solution (50—60°C, 50 m*l*) containing 7.3 g of Co(CN)(OH$_2$)(dien)Br$_2$ was added slowly an aqueous solution (50 m*l*) containing 1.5 g of glycine and 0.56 g of sodium hydroxide. The solution was warmed at 75°C with occasional stirring until the color changed from dark red

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[1] Part III of this series: K. Ohkawa, J. Hidaka, and Y. Shimura, This Bulletin, **40**, 2830 (1967).

[2] K. Ohkawa, J. Fujita, and Y. Shimura, This Bulletin, **38**, 66 (1965).

[3] K. Ohkawa, J. Hidaka, and Y. Shimura, *ibid.*, **39**, 1715 (1966).

[4] Abbreviations: dien, diethylenetriamine: amH, aminoacid; gly, glycinate ion; L-ala, L-alaninate ion; L-pro, L-prolinate ion; L-val, L-valinate ion; L-thr, L-threoninate ion; α-aibut, α-aminoisobutyrate ion.

[5] K. Ohkawa, S. Yano, and J. Fujita, This Bulletin, **41**, 2224 (1968).

[6] B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, **19**, 2045 (1966); P. H. Crayton and T. A. Mattern, *J. Inorg. Nucl. Chem.*, **13**, 248 (1960); *Inorg. Synth.*, **7**, 207 (1963).

[7] H. Siebert, *Z. Anorg. Chem.*, **327**, 63 (1964).

to yellow brown, and then concentrated to about 15 m*l* at about 60°C and cooled. Orange yellow crystalline powder precipitated was filtered off, washed with methanol and air-dried. The aqueous solution of this product was passed through a column (3×30 cm) containing cation exchange resin Dowex 50W-X8 in hydrogen ion form. The column was washed with water and the adsorbed yellow band was eluted with 4% aqueous solution of lithium bromide. The desired complex was eluted first, followed by $[Co(CN)(glyH)_2(dien)]^{2+}$. Each fraction was checked by its visible absorption spectrum. The fractions containing the desired complex were collected and concentrated at 60°C under reduced pressure. A yellow complex, *trans*(O,CN)-$[Co(CN)(gly)(dien)]Br\cdot 3H_2O$ was precipitated by adding methanol, filtered off, washed with water-methanol and methanol and air-dried. The complex was recrystallized from water by adding methanol.

An orange complex $[Co(CN)(glyH)_2(dien)]Br_2\cdot 3H_2O$ was obtained from the fractions eluted later.

Found: C, 20.26; H, 5.46; N, 15.72%. Calcd for $C_9H_{29}N_6O_7CoBr_2$: C, 19.57; H, 5.29; N, 15.22%. The complex which contains two neutral unidentate glycine is less soluble in water than *trans*(O,CN)-$[Co(CN)(gly)(dien)]Br\cdot 3H_2O$.

Method 2: Four grams of *trans*(O,Cl)-$[Co(Cl)(gly)(dien)]ClO_4$ was ground thoroughly and suspended in 30 m*l* of dimethylsulfoxide (DMSO) with mechanical stirring, and 1 g of potassium cyanide was added. The color of the solution changed from reddish violet to orange and a yellowish orange product precipitated. This was filtered off as rapidly as possible and was dissolved in 0.47% hydrobromic acid. The solution was poured on a column containing cation exchange resin Dowex 50W-X8 in hydrogen ion form. The column was washed with water and the adsorbed band was eluted with an aqueous solution containing 20 m*l* of 47% hydrobromic acid and 30 g of lithium bromide in 1000 m*l* of water. A pure complex was obtained from the eluate by the same way as in Method 1.

trans*(O,CN)*-$[Co(CN)(am)(dien)]Br\cdot xH_2O$ (am=α-aibut, L-ala, L-pro, L-val, and L-thr)

The complexes were prepared by Method 1) as for the glycine complex using α-aibutH, L-alaH, L-proH, L-valH and L-thrH instead of glyH.

trans*(O,Cl)*-$[Co(Cl)(gly)(dien)]ClO_4$. *Method 3*: An aqueous solution (30 m*l*) containing 1.5 g of glycine and 0.56 g of sodium hydroxide was added to a suspension of 5.4 g of $[CoCl_3dien]$ in 30 m*l* of warm water (40°C) with mechanical stirring. This was warmed at 65°C until the $[CoCl_3dien]$ dissolved nearly completely, and then filtered. The filtrate was passed through a column containing the same kind of resin as in Method 1. By elution with 3% aqueous solution of sodium perchlorate, the column gave many bands with different colors. The desired complex was obtained from the brownish-violet band eluted first. The brownish-violet eluate was concentrated at 50°C under reduced pressure and cooled. Pure crystals precipitated were filtered off, washed with ice water, water-methanol and methanol, and air-dried.

trans*(O,Cl)*-$[Co(Cl)(am)(dien)]ClO_4\cdot xH_2O$ (am=L-ala, L-pro, L-val, and L-thr)

The complexes were obtained from $[CoCl_3dien]$ and L-alaH, L-proH, L-valH, and L-thrH by Method 3) as for the glycinato complex.

trans*(O,NO₂)*-$[Co(NO_2)(gly)(dien)]Cl\cdot H_2O$ *Method 4*: A mixture containing 5.4 g of $[CoCl_3dien]$, 1.5 g of glycine and 0.56 g of sodium hydroxide in 50 ml of water was warmed at 50°C for an hour, and filtered. 1.3 g of sodium nitrite was added to the filtrate and the resulting solution was concentrated to about 25 m*l* at 80°C, filtered and cooled. Brownish-yellow crystals were precipitated by adding 10 m*l* of concd. hydrochloric acid under cooling in an ice bath. They were filtered off, washed with ice water, water-methanol and methanol, and air-dried. The complex was recrystallized from hot water or water-methanol.

Method 5: The complex was also prepared from $[Co(NO_2)_3dien]$ (3.8 g), glycine (1.5 g), sodium hydroxide (0.56 g) and a small amount of activated charcoal, using a method similar to Method 4.

trans*(O,NO₂)*-$[Co(NO_2)(am)(dien)]Cl\cdot xH_2O$ (am=α-aibut, L-ala, L-val, L-pro, and L-thr)

The complexes were prepared from $[CoCl_3dien]$ or $[Co(NO_2)_3dien]$ and α-aibutH, L-alaH, L-proH, L-valH, and L-thrH according to the method for the glycinato complex.

Table 1. Chemical analysis of the complexes

Complexes	C, %		H, %		N, %	
	Found	Calcd	Found	Calcd	Found	Calcd
trans(O,CN)-$[Co(CN)(gly)(dien)]Br\cdot 3H_2O$[a]	21.18	21.22	5.61	5.85	17.94	17.68
trans(O,CN)-$[Co(CN)(gly)(dien)]Br\cdot 3H_2O$[b]	21.10	21.22	5.62	5.85	17.65	17.68
trans(O,CN)-$[Co(CN)(\alpha\text{-aibut})(dien])Br\cdot 2H_2O$[a]	26.41	26.61	6.18	6.20	17.31	17.24
trans(O,CN)-$[Co(CN)(\text{L-ala})(dien)]Br\cdot 2H_2O$[a]	24.49	24.50	5.68	5.91	17.66	17.86
trans(O,CN)-$[Co(CN)(\text{L-pro})(dien)]Br\cdot 2H_2O$[a]	28.38	28.72	6.01	6.03	16.71	16.75
trans(O,CN)-$[Co(CN)(\text{L-val})(dien)]Br$[a]	31.12	31.27	6.33	6.04	18.24	18.23
trans(O,CN)-$[Co(CN)(\text{L-thr})(dien)]Br\cdot 2H_2O$[a]	25.98	25.61	6.06	5.97	15.78	16.59
trans(O,NO₂)-$[Co(NO_2)(gly)(dien)]Cl\cdot H_2O$	21.46	21.47	5.77	5.71	20.75	20.87
trans(O,NO₂)-$[Co(NO_2)(\alpha\text{-aibut})(dien)]Cl\cdot 2H_2O$	25.10	25.17	6.37	6.60	18.28	18.35
trans(O,NO₂)-$[Co(NO_2)(\text{L-ala})(dien)]Cl\cdot H_2O$	24.19	24.05	6.46	6.05	19.83	20.03
trans(O,NO₂)-$[Co(NO_2)(\text{L-pro})(dien)]Cl\cdot H_2O$	28.62	28.77	6.08	6.17	18.58	18.64
trans(O,NO₂)-$[Co(NO_2)(\text{L-val})(dien)]Cl\cdot H_2O$	28.71	28.62	6.68	6.67	18.32	18.54
trans(O,NO₂)-$[Co(NO_2)(\text{L-thr})(dien)]Cl\cdot 2H_2O$	24.17	24.16	6.36	6.34	17.57	17.61
trans(O,Cl)-$[Co(Cl)(gly)(dien)]ClO_4$	19.42	19.42	4.64	4.62	15.08	15.10
trans(O,Cl)-$[Co(Cl)(\text{L-ala})(dien)]ClO_4\cdot H_2O$	20.82	20.86	5.29	5.25	14.09	13.90
trans(O,Cl)-$[Co(Cl)(\text{L-pro})(dien)]ClO_4$	26.25	26.29	5.12	5.15	13.79	13.63
trans(O,Cl)-$[Co(Cl)(\text{L-val})(dien)]ClO_4$	26.12	26.17	5.59	5.61	13.78	13.56
trans(O,Cl)-$[Co(Cl)(\text{L-thr})(dien)]ClO_4$	23.12	23.15	5.12	5.10	13.72	13.50

a) Prepared according to Method 1. b) Prepared according to Method 2.

Results of the chemical analyses of all the new complexes are given in Table 1.

Measurements. Visible and ultraviolet absorption spectra were obtained with a Beckman DU spectrophotometer and a Hitachi EPS-3 recording spectrophotometer. The circular dichroism (CD) curves were recorded with a Model ORD/UV-5 spectrophotometer of Japan Spectroscopic Co. Proton magnetic resonance (PMR) spectra were obtained with a Varian A-60 spectrometer in deuterium oxide, with sodium tetramethylsilane (NaTMS) as an internal reference. All spectral measurements were carried out at room tempertaure.

Results and Discussion

Configuration of the Complexes. As Fig. 1 shows, the first absorption bands of the cyano complexes exhibit no sign of splitting and the absorption curves have a pattern very similar to those of *trans*(O,CN)-[Co-$(OH_2)(CN)en_2]^{2+}$ and *trans*(O,CN)-[Co(OH)(CN)-$en_2]^+$ reported in the previous paper.[1] The chloro complexes, on the other hand, give the first absorption bands split into two components at *ca.* 18000 and *ca.* 22000 cm^{-1}. Such a splitting is expected for only the complex in which chloride ion takes the position *trans* to the oxygen atom of amino-acidato group. The *trans*(O,Cl) structure of the chloro complex has been confirmed by a recent X-ray analysis on the [Co(Cl)-(gly)(dien)]ClO_4.[8] We thus conclude that all the cyano and chloro complexes we prepared have the structure of *trans*(O,X) type (X=CN^- or Cl^-). The data of absorption spectra are summarized in Table 2.

The absorption spectra of the nitro complexes provide no definite information on the structure, but their CD curves are very similar to those of the cyano complexes as is seen in Fig. 2. Thus, it is concluded that the nitro complexes also take the *trans*(O,NO_2) structure. This conclusion has been confirmed by X-ray analysis on *trans*(O,NO_2)-$[Co(NO_2)(gly)(dien)]Cl\cdot H_2O$.[9]

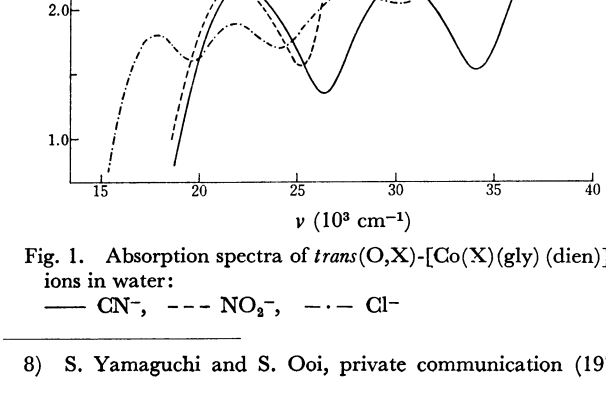

Fig. 1. Absorption spectra of *trans*(O,X)-[Co(X)(gly) (dien)]$^+$ ions in water:
—— CN^-, - - - NO_2^-, —·— Cl^-

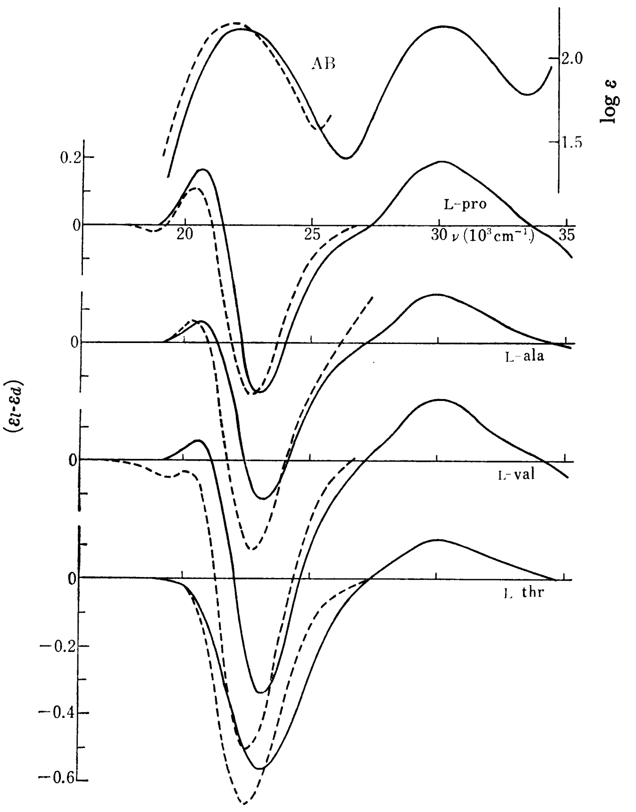

Fig. 2. Absorption(AB) and CD curves of *trans*(O,X)-[Co(X)-(L-am)(dien)]$^+$ ions in water:
—— CN^-, - - - NO_2^-.

PMR spectra of the complexes in deuterium oxide also support the *trans*(O,X) structure (X=CN^-, Cl^-, and NO_2^-). In the deuterium oxide solutions, hydrogen atoms of the amino groups were deuterated rapidly. Legg and Cooke[10] reported that the ethylene signals of dien coordinated meridionally in Co(III) complexes showed a rather sharp peak in the 181—187 cps region (60 MHz), while those of facially coordinated dien gave broad and complicated peaks in the 156—190 cps region. As Fig. 3 and Table 3 show, the present complexes exhibit sharp signals characteristic of the meridionally coordinated dien in the 179—186 cps region.

Further evidence for the *trans*(O,X) structure can be seen in the CD spectra of the complexes in the region of the first absorption band. Since the complex *trans*-(O,X)-[Co(X)(L-am)(dien)]$^+$, has no configurational chirality around the cobalt(III) ion, the CD in the region of the *d–d* transitions can be brought about by the vicinal effect of the coordinated L-amino-acidato group. Figure 2 shows the CD spectra of the cyano and nitro complexes in the region of the first and second absorption bands. The pattern and magnitude of these CD curves correspond to those of the complexes of the type $[Co(NH_3)_4(L\text{-}am)]^{2+}$,[11] indicating that the present dien complexes have no configurational chirality. This in turn suggests that the dien group in the

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[8] S. Yamaguchi and S. Ooi, private communication (1970).

[9] S. Yamaguchi and S. Ooi, private communication (1969).

[10] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

[11] T. Yasui, J. Hidaka, and Y. Shimura, This Bulletin, **39**, 2417 (1966).

TABLE 2. ABSORPTION AND CIRCULAR DICHROISM DATA OF *trans*(O,X)-[Co(X)(am)(dien)]$^+$ IONS IN THE *d-d* ABSORPTION BAND REGION[a]

Complexes	I-Band		II-Band	
	ν_{max}^{AB} (log ε)	ν_{ext}^{CD} ($\varepsilon_l-\varepsilon_d$)	ν_{max}^{AB} (log ε)	ν_{ext}^{CD} ($\varepsilon_l-\varepsilon_d$)
(CN)(L-ala)[c]	22.1 (2.15)	20.7 ($+0.06_4$) 23.2 (-0.47)	30.2 (2.16)	29.9 ($+0.14_6$)
(CN)(L-pro)[c]	22.1 (2.12)	20.6 ($+0.16_1$) 23.1 (-0.50)	30.1 (2.19)	30.1 ($+0.19$)
(CN)(L-val)[c]	22.2 (2.10)	20.6 ($+0.05_7$) 23.2 (-0.69_7)	30.1 (2.12)	30.1 ($+0.18_2$)
(CN)(L-thr)[c]	22.2 (2.16)	*ca.* 22 sh 23.2 (-0.55_5)	30.1 (2.19)	29.9 ($+0.13$)
(CN)(gly)[c]	22.2 (2.16)		30.2 (2.19)	
(CN)(gly)[d]	22.2 (2.16)		30.2 (2.19)	
(CN)(α-aibut)[c]	22.3 (2.15)		30.3 (2.17)	
(NO_2)(L-ala)	21.7 (2.20)	20.4 ($+0.07$) 22.7 (-0.51)		
(NO_2)(L-pro)	21.6 (2.21)	20.4 ($+0.10_2$) 22.7 (-0.50)		
(NO_2)(L-val)	21.7 (2.19)	19.4 (-0.04_8) 22.6 (-0.84_8)		
(NO_2)(L-thr)	21.9 (2.20)	*ca.* 22 sh 22.6 (-0.67)		
(NO_2)(gly)	21.7 (2.17)			
(NO_2)(α-aibut)	21.8 (2.20)			
(Cl)(L-ala)	18.0 (1.83) 21.9 (1.91)	17.3 ($+0.05_3$) 22.1 (-0.28_6)	27.8 (2.15)	28.0 (-0.14)
(Cl)(L-pro)	17.8 (1.79) 21.6 (1.93)	18.1 ($+0.54$) 21.9 (-0.44_2)	27.2 (2.17)	25.3 ($+0.13_7$) 28.0 (-0.18)
(Cl)(L-val)	18.1 (1.81) 21.9 (1.94)	16.9 (-0.03_8) 22.2 (-0.37_7)	28.2 (2.20)	27.9 (-0.12_7)
(Cl)(L-thr)	18.0 (1.79) 21.8 (1.93)	18.3 (-0.09_4) 22.2 (-0.27)	*ca.* 28 (2.25)	28.0 (-0.09_8)
(Cl)(gly)	17.9 (1.79) 21.8 (1.88)		27.7 (2.14)	

a) The frequencies are given in 10^3 cm^{-1}.
b) Complexes are abbreviated to (X) (am).
c) Prepared from [Co(CN)(SO_3)(NH_3)$_4$] according to Method 1.
d) Prepared from *trans*(O,Cl)-[Co(Cl)(gly)(dien)]$^+$ according to Method 2.

TABLE 3. RESONANCE FREQUENCY ASSIGNMENTS[a] AND INTEGRATION VALUES FROM THE PMR SPECTRA (60 MHz) OF *trans*(O,X)-[Co(X)(am)(dien)]$^+$ DISSOLVED IN D_2O

Complexes[d]	-CH_3		>$NCH_2CH_2NH_2$		-CH_2-	
	Res. freq. cps	No. of H's	Res. freq.[b] cps	No. of H's	Res. freq. cps	No. of H's
(CN)(gly)[e]			179.5	8.0	210.5 213.5	2.0
(CN)(gly)[f]			179	8.3	210.0	1.7
(Cl)(gly)			185	8.1	216.3	1.9
(NO_2)(gly)			186	8.1	213.4	1.9
(CN)(L-ala)[e]	86.5[c] 87.5[c]	3.2	180.0	7.8	221.0	1.0
(Cl)(L-ala)	85.0[c]	2.7	182.5	8.4	219.5	0.9
(NO_2)(L-ala)	87.5[c]	2.5	183.9	8.6	218.5	0.8
(CN)(α-aibut)[e]	84.2 86.0	5.7	179.2	8.3		
(NO_2)(α-aibut)	87.5	5.7	186	8.3		

a) All frequencies on low-field side of NaTMS (internal reference).
b) The center of rather broad peaks.
c) The center of -CH_3 doublet.
d) Complexes are abbreviated to (X) (am).
e) Prepared from [Co(CN)(SO_3)(NH_3)$_4$] according to Method 1.
f) Prepared from *trans* (O, Cl)-[Co(Cl)(gly)(dien)]$^+$ according to Method 2.

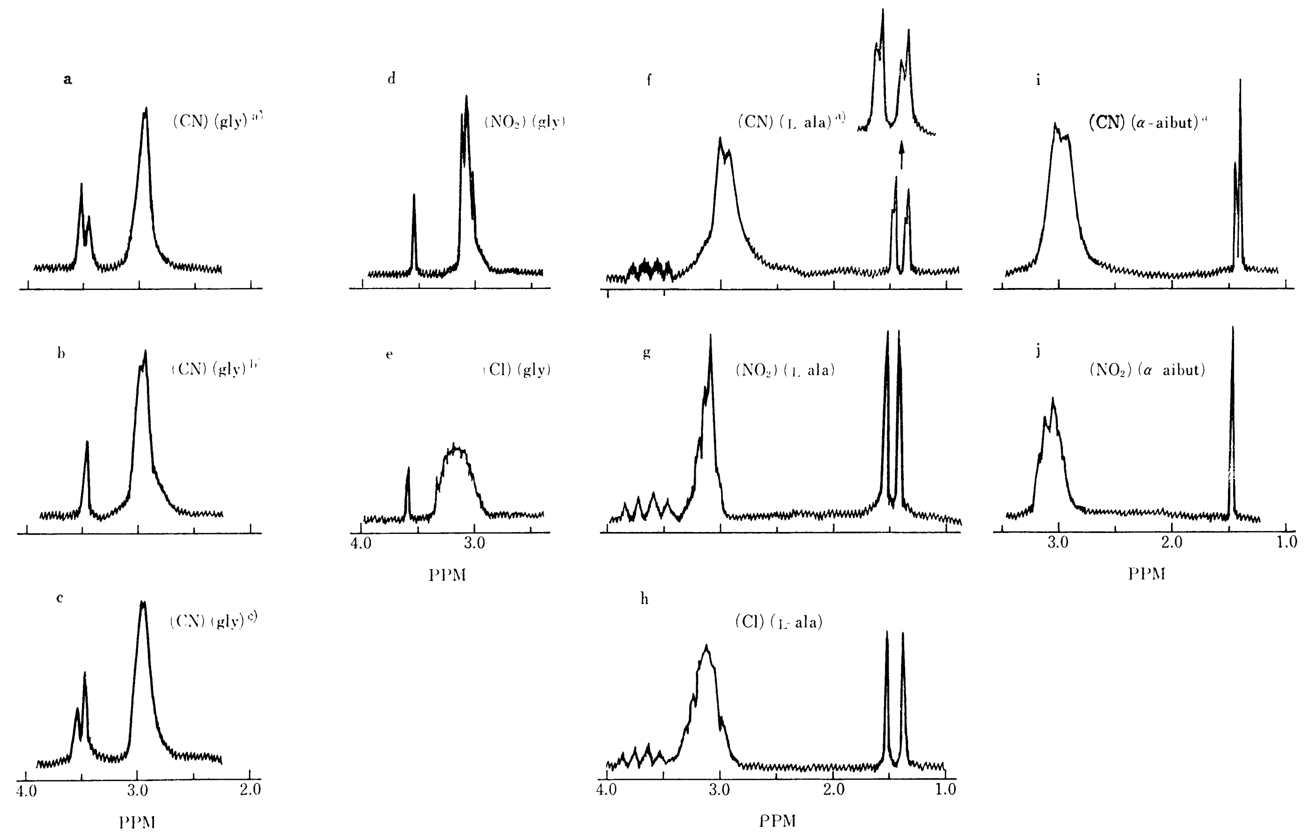


Fig. 3. The PMR spectra (60 MHz) of *trans*(O,X)-[Co(X)(am)(dien)]$^+$ in D_2O. NaTMS was used as an internal reference.
a) Samples prepared according to Method 1: Mixture of *endo* and *exo*(CN,NH) forms.
b) *endo* (CN,NH) form prepared from *endo*(Cl,NH) complex according to Method 2: see text.
c) Sample b isomerized to a mixture of *endo* and *exo*(CN,NH) forms: see text.

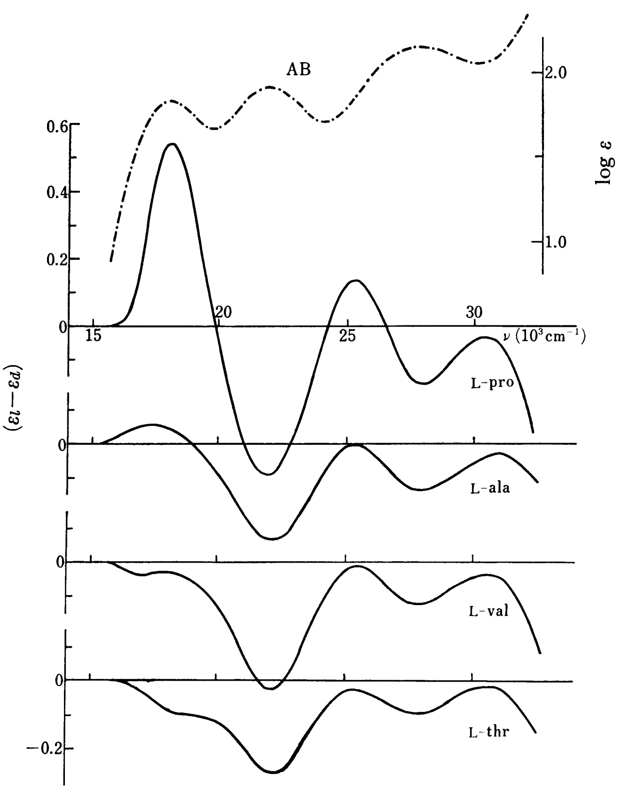


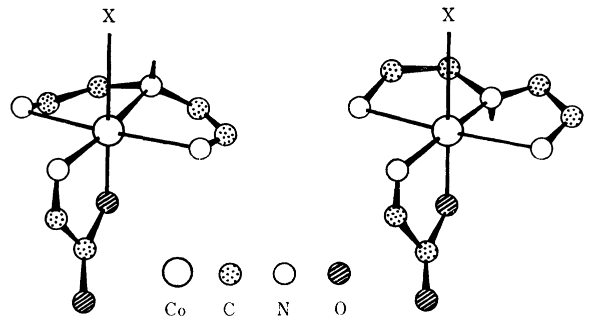
Fig. 4. Absorption (AB) and CD curves of *trans*(O,Cl)-[Co(Cl)(L-am)(dien)]$^+$ ions in water.

present complexes takes a meridional coordination.

Figure 4 shows that the chloro complexes give CD curves differing somewhat from those of the cyano or nitro complexes in the region of the *d–d* absorption bands. Such a difference may be attributed to the larger splitting of the first absorption band of the chloro complex than those of the cyano or nitro complex.[1]

Conformational Isomerism. As Fig. 3-a shows, *trans*(O,CN)-[Co(CN)(gly)(dien)]$^+$, prepared from [Co(CN)(SO_3)(NH_3)$_4$] by Method 1, gives two kinds of methylene signals due to the glycinato chelate at 210.5 and 213.5 cps. Similarly, *trans*(O,CN)-[Co(CN)(L-ala)(dien)]$^+$ and *trans*(O,CN)-[Co(CN)(α-aibut)(dien)]$^+$ show two kinds of methyl signals at 86.5 and 87.5, and at 84.2 and 86.0 cps, respectively (Fig. 3-f and 3-i). On the other hand, the corresponding chloro (Fig. 3-e) and nitro (Fig. 3-d) complexes show only one kind of methylene or methyl signal due to the amino-acidato chelate.

The appearance of the two kinds of methylene or methyl signals in the cyano-aminoacidato complexes can be attributed to the existence of two isomers such as shown in Fig. 5. We refer to them as *endo*(X,NH) form and *exo*(X,NH) form in this paper. Such an isomerism is originated from a puckering structure of the dien group and produces a remarkable difference in the direction of the hydrogen atom attached to the central nitrogen atom of dien. As Fig. 5 shows, the direction of this hydrogen atom of the *endo*(X,NH)



endo (X, NH) form *exo* (X, NH) form

Fig. 5. Two isomers of *trans*(O,X)-$[\mathrm{Co(X)(gly)(dien)}]^+$.

isomer is toward the ligand X, while that of the *exo*-(X,NH) isomer toward the oxygen atom of amino-acidato chelate.

In order to confirm the existence of such isomers, we prepared another sample of *trans*(O,CN)-$[\mathrm{Co(CN)(gly)(dien)}]^+$ from *trans*(O,Cl)-$[\mathrm{Co(Cl)(gly)(dien)}]^+$, which gave only one methylene signal in its PMR spectrum, according to Method 2. The cyano complex thus prepared gives an identical electronic absorption spectrum with that of the sample prepared from *trans*-$[\mathrm{Co(CN)(SO_3)(NH_3)_4}]$, but its PMR spectrum exhibits only one methylene signal. As Fig. 3-b shows, this signal coincides with one of the two signals observed for the sample prepared by Method 1. The result strongly supports the existence of two stable isomers of *endo* and *exo* forms, in the cyano complex. It is not possible to correlate the chemical shift of methylene or methyl signal with the structure of these isomers at present. However, the complexes *trans*(O,Cl)-$[\mathrm{Co(Cl)(gly)(dien)}]\mathrm{ClO_4}$[8] and *trans*(O,$\mathrm{NO_2}$)-$[\mathrm{Co(NO_2)(gly)(dien)}]\mathrm{Cl\cdot H_2O}$[9] were determined to have the *endo* form by X-ray analysis. Consequently, the *trans*-(O,CN)-$[\mathrm{Co(CN)(gly)(dien)}]^+$ prepared from the *trans*-(O,Cl)-$[\mathrm{Co(Cl)(gly)(dien)}]^+$ can be assigned to the *endo*(CN,NH) form, since complete isomerization to the *exo* form during synthesis from the *endo* form seems to be very unlikely. The methylene signal of this cyano complex coincides with the higher field component of the doublet observed for the mixture of two cyano isomers prepared from $[\mathrm{Co(CN)(SO_3)(NH_3)_4}]$.

The isomerization reaction between the *endo* and the *exo* isomers is expected to take place relatively easily in an alkaline solution, since the reaction may involve deprotonation of the secondary amine of the dien group. In fact, the *trans*(O,CN)-$[\mathrm{Co(CN)(gly)(dien)}]^+$ which gave only one methylene signal showed two kinds of methylene signals on being treated with aqueous hydroxide (pH 10, 60°C, 6 hr), as shown in Fig. 3-c.

The present isomerism would be attributed to the coordination of X on either of the non-equivalent sides of the $\mathrm{N_4}$ plane involving the puckered rings of dien.[5] Hence, this kind of isomerism can not be substantiated in such complexes as $[\mathrm{Co(NO_2)_3(dien)}]$,[12] in which both sides of the $\mathrm{N_4}$ plane are occupied by the same $\mathrm{NO_2}^-$ ions.

A similar isomerism was found by Gainsford and House[13] for $[\mathrm{Co(Cl)(en)(dien)}]^{2+}$ (en=ethylenediamine).

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