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Isomerism of the Metal Complexes Containing Multidentate Ligands. II. The Cobalt(III), Cobalt(II), and Nickel(II) Complexes of *N,N,N′,N′*-Tetrakis(2-aminoethyl)ethylenediamine and -1,2-propanediamine and Their Absolute Configurations

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The cobalt(III), cobalt(II), and nickel(II) complexes of *N,N,N′,N′*-tetrakis(2-aminoethyl)ethylenedianime and -1,2-propanediamine were prepared, and the cobalt(III) complex of the former ligand was resolved by fractional crystallization and column chromatography on SE-Sephadex. The absolute configurations of the cobalt(III) complexes were assigned on the basis of the stereospecificity of the latter ligand; they were later confirmed by the X-ray analysis. The electronic absorption, circular dichroism, and optical rotatory dispersion spectra of the complexes prepared were also measured.

The cobalt(III) complex of *N,N,N′,N′*-tetrakis(2-aminoethyl)-ethylenediamine (abbreviated as penten) was first prepared by Emmenegger and Schwarzenbach;[1] it has been characterized by infrared and electronic spectral measurements and by stability studies in an aqueous solution. The absolute configuration of the complex was assigned from its rotatory dispersion[1] and its circular dichroism spectrum.[2] We have prepared nickel(II) and cobalt(II) complexes of penten in addition to the cobalt(III) complexes, and assigned the absolute configuration of the latter using the stereospecificity of *N,N,N′,N′*-tetrakis(2-aminoethyl)-1,2-propanediamine (abbreviated as R-mepenten) and its cobalt(III) complex.

The absolute configuration thus tentatively assigned (Fig. 1) was enantiomeric to that of Emmenegger and Schwarzenbach,[1] and to that of Mason and Norman,[2]

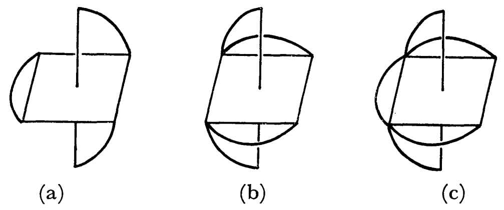

Fig. 1. Absolute configurations of (a): $(-)_{589}$-$[Co(en)_3]^{3+}$, (b): $(-)_{589}$-*u-facial*-$[Co(dien)_2]^{3+}$, and (c): $(-)_{589}$-$[Co(penten)]^{3+}$. The configurations are denoted by Δ, $\Delta\Lambda\Delta$, and $\Delta\Lambda\Delta$ respectively. By summing the contribution from each skew chelate pair, the net contribution of the latter two will become Δ.

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[1] E. P. Emmenegger and G. Schwarzenbach, *Helv. Chim. Acta*, **49**, 625 (1966).

[2] S. F. Mason and B. J. Norman, *Chem. Commun.*, **1965**, 73.

but the same as that of Gollogly and Hawkins.[3] The absolute configuration assigned by us was confirmed by the X-ray analysis of Saito *et al.*[4] Since only a brief preliminary report[5] has been published on these nickel and cobalt complexes of penten and R-mepenten, a detailed report will be published here.

Experimental

1. Ligands. The penten and laevorotatory R-mepenten were specially prepared by the Seikenkagaku Co., the latter being synthesized from R-propylenediamine. They were then further purified by vacuum distillation. Penten, bp 159—163°C (0.08—0.10 mmHg); R-mepenten, bp 147—153°C (0.10 mmHg).

2. Preparation of the Complexes. *2.1.* $[Co(penten)]Br_3\cdot 2H_2O$: *Method A*: One gram of penten and 2 g of finely ground $[CoBr(NH_3)_5]Br_2$ were mixed in a 100 m*l* round-bottomed flask; the flask was then gently heated over a flame until the color of the mixture became reddish-brown, ammonia having been evolved during the reaction. After the mixture had then been cooled to room temperature, a 2 m*l* portions of water was added and the unreacted $[CoBr(NH_3)_5]Br_2$ was filtered off. By adding ethanol to the filtrate, a red syrup was obtained; this syrup yielded red hexagonal crystals after repeated recrystallizations from water. Found: Co, 10.03; N, 14.14; C, 21.39; H, 5.44; Br, 42.56; H_2O, 6.39%. Calcd for $CoC_{10}H_{28}N_6Br_3\cdot 2H_2O$: Co, 10.39; N, 14.82; C, 21.18; H, 5.69; Br, 42.28; H_2O, 6.35%.

Method B: Two and half grams of $[CoBr(NH_3)_5]Br_2$, 1.3 g of penten, and 0.2 g of active charcoal were mixed with 30 m*l* of water, and the mixture was stirred for 11 hrs. After filtering off the charcoal, the filtrate was concentrated and the red syrup thus obtained was purified as Method A.

2.2. $(-)_{589}$-$[Co^{III}(\text{R-}mepenten)]I_3\cdot H_2O$: This complex was prepared in the same way as Method B. A hygroscopic reddish-brown powder obtained by adding ethanol to the reaction mixture was dissolved in water, and to this solution an aqueous solution of potassium hexacyanocobaltate(III) was added. The reddich-brown crystals of $(-)_{589}$-[Co(R-mepenten)]$[Co(CN)_6]\cdot 3H_2O$ thus precipitated were purified by recrystallization. These crystals were suspended in water together with the ion-exchange resin (Dowex 1-X8, 20—50 mesh) in the bromide form, and the mixture was stirred for several hours. The filtrate was evaporated, and by the subsequent addition of potassium iodide, red crystals of $(-)_{589}$-[Co(R-mepenten)]$I_3\cdot H_2O$ were obtained. Found: Co, 8.62; N, 12.23; C, 19.07; H, 4.48; I, 53.86; H_2O, 2.38%. Calcd for $CoC_{11}H_{30}N_6I_3\cdot H_2O$: Co, 8.37; N, 11.94; C, 18.77; H, 4.58; I, 54.07; H_2O, 2.56%.

The molar rotation of this complex iodide is $[M]_{545}=-5150°$, $[M]_{485}=+9980°$. The complex iodide was converted to the chloride by passing it through a column of Dowex 1-X8 in the chloride form. The molar rotation of the chloride is $[M]_{546}=-5200°$, and $[M]_{485}=+10220°$.

2.3. $[Ni(penten)](ClO_4)_2$: Two grams of nickel(II) perchlorate hexahydrate dissolved in 1 m*l* of water, and 1 g of penten dissolved in 1 m*l* of water were mixed; when the mixture was left standing, a reddish-violet syrup separated out. After the repeated recrystallization of this syrup from hot water, violet crystals were obtained. Found: Ni, 12.18; N, 17.09; C, 24.77; H, 5.85%. Calcd for $NiC_{10}H_{28}N_6O_8Cl_2$: Ni, 11.98; N, 17.15; C, 24.51; H, 5.76%.

2.4. $(+)_{589}$-$[Ni(\text{R-}mepenten)](ClO_4)_2\cdot 1/2H_2O$: Five grams of nickel(II) perchlorate hexahydrate and 4 g of R-mepenten were dissolved in 20 m*l* of water. On evaporating the solution, violet crystals were obtained, and they were purified by recrystallization from water. Found: Ni, 11.57; N, 16.14; H_2O, 1.78%. Calcd for $NiC_{11}H_{30}N_6O_8Cl_2\cdot 1/2H_2O$: Ni, 11.44; N, 16.38; H_2O, 1.76%. The molar rotation is $[M]_{494}=+520°$.

2.5. $[Co^{II}(penten)]^{2+}$ *and* $(+)_{589}$-$[Co^{II}(\text{R-}mepenten)]^{2+}$ *Ions*: These complexes were not isolated in solid states, but were prepared only in aqueous solutions under nitrogen, since they were oxidized in air. About 74 mg of R-mepenten was dissolved in a small amount of water. Nitrogen was bubbled through this solution and also the solution of the equivalent amount of cobalt(II) chloride, and then both solutions were mixed in a vessel filled with nitrogen and connected to a quartz cell 1 cm thick for the spectral measurements. All the measurements were carried out in nitrogen to prevent oxidation.

The concentration of the complex was determined by chelatometric titration using a 0.01M EDTA solution after decomposing the complex with a mixture of perchloric and sulfuric acids. The complex ion $[Co^{II}(penten)]^{2+}$ was prepared in a manner similar to that described above.

3. Resolution of the Cobalt(III) Penten Complex. *Method A*: As the resolving agent, $(-)_{589}$-$K_3[Co(C_2O_4)]_3$ was used. When 1 g of $[Co(penten)]Br_3\cdot 2H_2O$ dissolved in 8 m*l* of water and 0.5 g of the resolving agent dissolved in 4 m*l* of water were mixed, a sparingly soluble diastereoisomer of $(+)_{589}$-$[Co(penten)]^{3+}$ was precipitated. To this diastereoisomer suspended in water, barium iodide was added. After removing barium trisoxalatocobaltate(III) by filtration, the filtrate was evaporated; $(+)_{589}$-$[Co(penten)]I_3\cdot H_2O$ was thus obtained. Found: Co, 8.39; N, 12.04; C, 17.49; H, 4.19; I, 54.99; H_2O, 2.56%. Calcd for $CoC_{10}H_{28}N_6I_3\cdot H_2O$: Co, 8.54; N, 12.18; C, 17.41; H, 4.38; I, 55.17; H_2O, 2.61%.

The enantiomer, $(-)_{589}$-iodide, was obtained from the mother liquor as the dihydrate. The molar rotation is $[M]_{542}=+5700°$ and $[M]_{481}=-9810°$ for the $(+)_{589}$-iodide, and $[M]_{542}=-5640°$ and $[M]_{481}=+9660°$ for the $(-)_{589}$-iodide.

Method B: A column chromatographic method on SE-Sephadex was used to resolve the complex; the details have been described previously.[6] Both enantiomers were completely separated on the column by the use of 0.3M sodium antimony $(+)_{589}$-tartrate as the eluent. First the $(-)_{589}$-isomer and then the $(+)_{589}$-isomer were eluted. Each effluent was diluted four to five times, and then again adsorbed on a P-cellulose column.

After washing the column with a large amount of 0.01N HCl, each enantiomer was eluted with 0.5N HCl. The enantiomers were further purified through the hexacyanocobaltate(III), which was reconverted to the chloride by passing it through a column of Dowex 1-X8 in the chloride form. The molar rotation for the $(+)_{589}$-chloride is $(M]_{542}=$

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[3] J. R. Gollogly and C. J. Hawkins, *Chem. Commun.*, **1966**, 873; *Aust. J. Chem.*, **20**, 2395 (1967).

[4] A. Muto, F. Marumo, and Y. Saito, *Inorg. Nucl. Chem. Lett.*, **5**, 85 (1969); *Acta Crystallogr.*, **B26**, 226 (1970). The determination of the absolute configuration by X-rays was carried out for $(+)_{589}$-$[Co(penten)][Co(CN)_6]2H_2O$. The absolute configuration of the $(-)_{589}$-$[Co(\text{R-mepenten}]^{3+}$ ion was reported by Saito *et al.* (Proc. XII ICCC, Sydney, 1969, p. 90).

[5] Y. Yoshikawa, E. Fujii, and K. Yamasaki, *Proc. Japan Acad.*, **43**, 495 (1967).

[6] Y. Yoshikawa and K. Yamasaki, *Inorg. Nucl. Chem. Lett.*, **6**, 523 (1970); This Bulletin, **45**, 179 (1972). The absolute configuration of *u-facial*-$[Co(dien)_2]^{3+}$ assigned in these reports was later confirmed by the X-ray crystal analysis of Y. Saito *et al.* (Paper read at the annual meeting of the Chemical Society of Japan, April, 1972).

Table 1. Absorption and circular dichroism spectra

Complex	Absorption spectra		CD spectra	
	ν_{max}(cm^{-1})	ε_{max}	ν_{max}(cm^{-1})	$\Delta\varepsilon_{max}$
$(+)_{589}$-$[Co(penten)]Cl_3 \cdot H_2O$	20500	214	19600	+3.64
			22300	−0.49
	29200	166	29900	+1.06
	43700	19890	43900	−10.8
			50800	+4.6
$(-)_{589}$-$[Co(penten)]Cl_3 \cdot H_2O$	20500	214	19600	−3.61
			22300	+0.49
	29200	163	29900	−1.04
	43700	19440	43900	+10.9
			50800	−4.5
$(-)_{589}$-$[Co(R\text{-}mepenten)]Cl_3 \cdot 2H_2O$	20500	215	19570	−3.31
			22000	+0.79
	29200	170	29900	−1.05
	43500	19150	43700	+9.1
			50300	−4.6
$[Ni(penten)](ClO_4)_2$	10600	20.9		
	18500	12.3		
	27800	15.8		
$(+)_{589}$-$[Ni(R\text{-}mepenten)](ClO_4)_2 \cdot 1/2H_2O$	11000	16.6	9700a)	−0.130a)
			11500a)	−0.132a)
	18600	10.0	18800	−0.140
	28200	12.9	27600	−0.067
$[Co(penten)]^{2+}$	10700	4.5		
	17500	3.5		
	19900	8.5 sh		
	20800	10.5		
	21600	10.5		
$(+)_{589}$-$[Co(R\text{-}mepenten)]^{2+}$	11000	3.7	10700	−0.112
	14200	5.1		
	17600	12.3	16700	−0.136
			17400	−0.118 sh
	19800	19.1 sh	19700	−0.092
	20900	22.9		
	21600	21.9	21800	−0.085

sh: shoulder

a) These values were obtained for the more soluble chloride.

+5920° and $[M]_{481}=-10280°$, while that for the $(-)_{589}$-chloride is $[M]_{542}=-5910°$ and $[M]_{481}=+10280°$. The active isomers resolved by Method A were further subjected to the chromatographic resolution, but no further increase in rotation occurred, indicating the complete resolution by the crystallization of the diastereoisomers.

4. Measurements. The electronic absorption(AB), and optical rotatory dispersion(ORD) spectra of aqueous solutions of the complexes were measured at 25°C by the use of a JASCO ORD/UV-5 recording spectrometer, using quartz cells 1 and 10 mm thick. The circular dichroism(CD) spectrum in the region 190—700 nm was measured with the same apparatus, and that in the region 700—1200 nm with a Shimadzu QV-50 spectrophotometer equipped with a CD attachment.

Results and Discussion

1. Co(III) Complexes. Table 1 lists the data of the AB and CD spectra of the complexes studied, and in Fig. 2 the AB, CD, and ORD spectra of $(-)_{589}$-$[Co(penten)]^{3+}$ and the CD spectrum of $(-)_{589}$-$[Co(R\text{-}mepenten)]^{3+}$ are shown. These two complexes, which have the same absolute configuration, as determined by the X-ray crystal analysis,4) show almost the same AB and CD spectra.

Among the CoN_6-type complexes, $[Co(en)_3]^{3+}$ was most extensively studied for the AB, CD, and absolute configuration. It has been found that the sign of CD band at about 20000 cm^{-1}, which corresponds to the $^1A_1 \rightarrow {}^1E_a$ transition of the first *d-d* absorption band in the D_3 symmetry, depends on the chirality around the central cobalt atom; that is, the Δ configuration7) shows a minus sign and the Λ configuration, a plus sign.

When three complexes, $[Co(en)_3]^{3+}$,8) *u-facial*-$[Co(dien)_2]^{3+}$,6) and $[Co(penten)]^{3+}$,4) whose absolute configurations have been determined by X-ray crystal analysis, are compared (Fig. 1), the complexes with the Δ configuration always show the same minus sign

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7) *IUPAC Information Bull.*, No. 33, 68 (1968); *Inorg. Chem.*, **7**, 1 (1970).

8) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Acta Crystallogr.*, **8**, 729 (1955); This Bulletin, **30**, 158, 795 (1957).

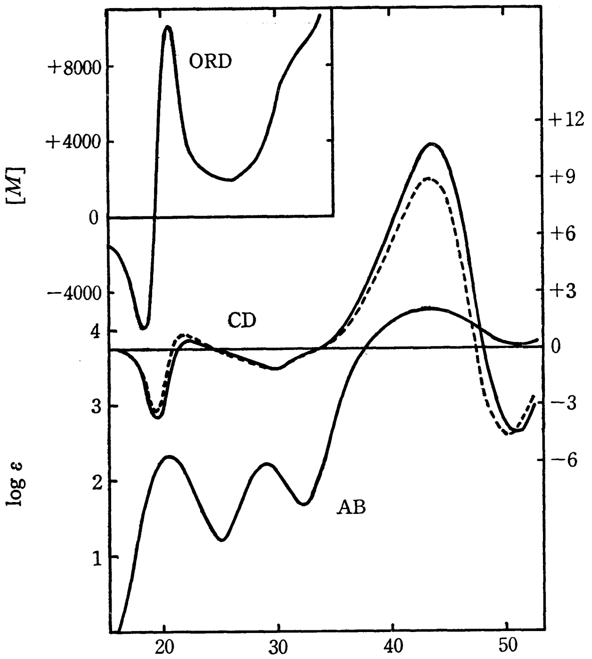

Fig. 2. The AB, CD, and ORD spectra of $(-)_{589}$-[Co(penten)]$Cl_3 \cdot H_2O$ (——) and the CD spectrum of $(-)_{589}$-[Co(R-mepenten)]$Cl_3 \cdot 2H_2O$ (----).

of the CD band at about 20000 cm^{-1}. Thus, for these complexes a close relationship exists between the absolute configuration and the sign of the CD band, and the absolute configuration tentatively assigned from the sign of the CD band is found to agree with those determined by the use of X-rays. In these three cases, the configurations derived from the octant rule[9] and the ring-pairing method[10] agree with those determined by the X-ray crystal analysis.

2. *Co(II) Complexes.* In Fig. 4, the AB, CD, and ORD spectra of $(+)_{589}$-[Co(R-mepenten)]$^{2+}$ and the AB spectrum of [Co(penten)]$^{2+}$ ions are shown. The first AB band of the former complex splits into two at 11000 and 14200 cm^{-1}; these bands may be assigned to the transition, $^4T_{1g}(^4F) \rightarrow {}^4T_{2g}(^4F)$ split in the lower symmetry. The signs of the CD bands are all minus.

3. *Ni(II) Complexes.* In Fig. 3, the AB, CD, and ORD spectra of $(+)_{589}$-[Ni(R-mepenten)]$(ClO_4)_2$ and the AB spectrum of [Ni(penten)]$(ClO_4)_2$ are shown. Three absorption bands of the former complex at 11000, 18600, and 28200 cm^{-1} are assigned to the transitions, $^3A_{2g}(^3F) \rightarrow {}^3T_{2g}(^3F)$, $^3A_{2g}(^3F) \rightarrow {}^3T_{1g}(^3F)$, and $^3A_{2g}(^3F) \rightarrow {}^3T_{1g}(^3P)$ respectively in the octahedral field. The signs of the CD bands are all minus.

4. *Absolute Configuration of the Co(II) and Ni(II) Complexes.* When R-mepenten coordinates to a metal in a six coordination, its methyl group takes an equatorial position, and the absolute configuration of the complex thus formed is stereospecifically determined. The configuration thus determined was confirmed by X-ray analysis of [Co(R-mepenten)]$^{3+}$. On the basis of the stereospecificity of R-mepenten thus confirmed it seems reasonable to assume that the cobalt(II) and nickel(II) complexes of R-mepenten have the same absolute configuration as the cobalt(III) complex of the same ligand.

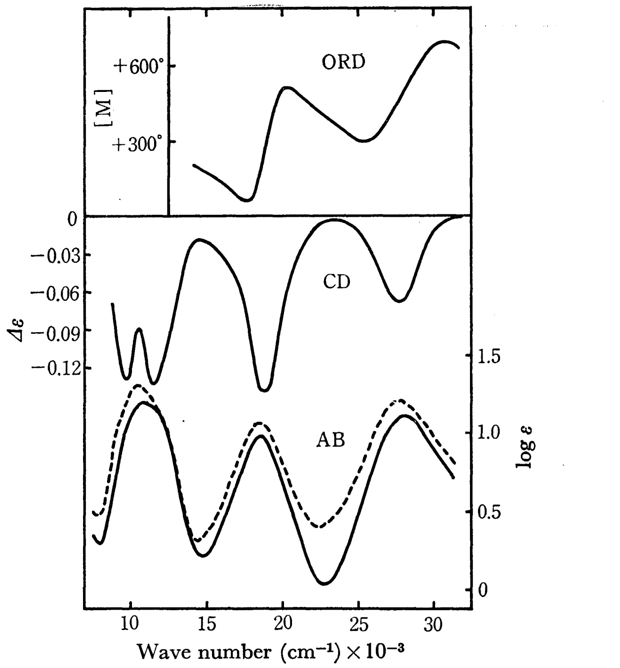

Fig. 3. The AB, CD, and ORD spectra of $(+)_{589}$- [Ni(R-mepenten)]$(ClO_4)_2$ (——) and the AB spectrum of [Ni(penten)]$(ClO_4)_2$ (----).

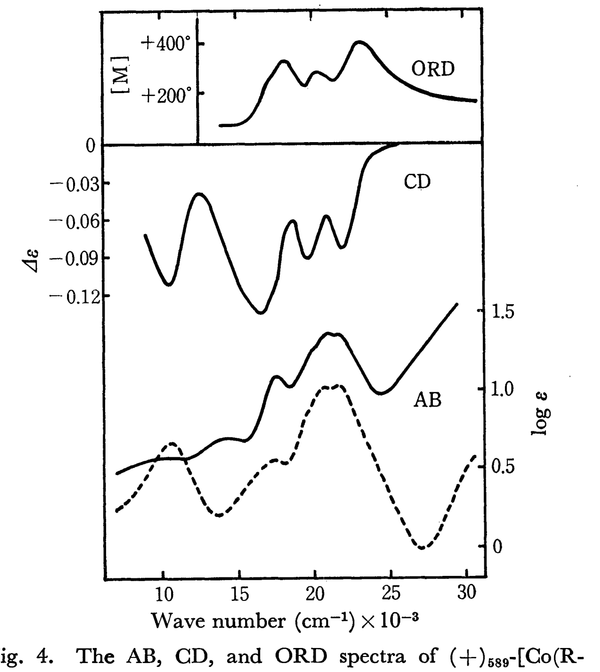

Fig. 4. The AB, CD, and ORD spectra of $(+)_{589}$-[Co(R-mepenten)]$^{2+}$ (——) and the AB spectrum of [Co(penten)]$^{2+}$ (----).

The transitions of the first *d-d* absorption band of the octahedral cobalt(III), cobalt(II), and nickel(II) complexes are all magnetically allowed. Although the complexes of R-mepenten are not strictly octahedral, the sign of the CD band corresponding to the first

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[9] C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 185 (1965).

[10] J. I. Legg and B. E. Douglas, *J. Amer. Chem. Soc.*, **88**, 2967 (1966).

absorption band is minus for $(+)_{589}$-[Co(R-mepenten)]$^{2+}$ and for [Ni(R-mepenten)]$^{2+}$, that of $(-)_{589}$-[Co(R-mepenten)]$^{3+}$, corresponding to the $^1A_1 \rightarrow {}^1E_a$ transition, is also minus, indicating a close relationship between these signs and their absolute configurations.

In addition to the cobalt(III), cobalt(II), and nickel(II) complexes, we have tried to prepare the copper complexes of penten and R-mepenten from copper(II) perchlorate and the ligands. For both ligands, complexes with the approximately 1:1 composition were obtained as blue powders, but it was not possible to isolate them in chromatographically pure states and to characterize them.

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