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The Isomerism of Metal Complexes Containing Multidentate Ligands. IV. The Cobalt(III) Complex of Linear Pentaethylenehexamine[1)]

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The cobalt(III) complex incorporating sexidentate linear pentaethylenehexamine(1,14-diamino-3,6,9,12-tetraazatetradecane) as the ligand was prepared by the reaction of the ligand with $[CoBr(NH_3)_5]Br_2$ at room temperature in the presence of active charcoal. The resulting solution was subjected to column chromatography on *SP*-Sephadex, geometrical and optical isomers with four different configurations were then separated and characterized by their electronic and infrared absorption, circular dichroism, and PMR spectra. They have the chemical composition of $[Co(C_{10}H_{28}N_6)]Cl_3 \cdot nH_2O$, n being 1.5—3.

Linear pentaethylenehexamine(abbreviated as linpen) is able to function as a sexidentate ligand of stereochemical importance, but so far no study has been published of its cobalt(III) complex. A few copper(II), lead(II), and cadmium(II) complexes have been studied polarographically,[2)] and one preliminary report[3)] on the isolation of the copper(II), nickel(II), zinc(II), and mercury(II) complexes has been published. We have now prepared the cobalt(III) complex of linpen and isolated all the geometrical and optical isomers by means of column chromatography on ion-exchange Sephadex.

Experimental

Ligands. The ligand, linpen, a product of the Tokyo Kasei Co., was first purified by fractional distillation, the fraction distilling at 165—170 °C(0.05 mmHg)being collected. The distillate was then converted to the hydrochloride and re-precipitated by adding hydrochloric acid to its concentrated aqueous solution. This precipitation procedure was repeated several times until a constant infrared spectrum of the hydrochloride was obtained. Found: C, 26.28; H, 7.63; N, 18.71; Cl, 46.69%. Calcd for $C_{10}H_{28}N_6 \cdot 6HCl$: C, 26.62; H, 7.60; N, 18.63; Cl, 47.15%.

Preparation of the Complex, $[Co(linpen)]Cl_3 \cdot nH_2O$. An aqueous solution of linpen hydrochloride(2.6 g) was neutralized with sodium hydroxide to pH 9.2. To this solution 2.0 g of $[CoBr(NH_3)_5]Br_2$ and 0.5 g of active charcoal were added, and then the mixture was stirred at 25 °C for 24 hr. After the charcoal had been removed, the filtrate was subjected to column chromatography to separate the isomers.

Separation of the Isomers. In the following chromatographic separation, a column of the size, $\phi 2.7 \times 140$ cm, of *SP*-Sephadex was always used; the absorbance of the eluate at 470 nm was plotted against V/V_0, the ratio of the eluate volume *versus* the void volume of the column.[4)] The symbols used in the present report, (+) and (−), denote the optical

Table 1. The water of crystallization and the assigned structures of the isomers

Isomer	Water of crystal-lization	Absolute config-uration	Structure (Fig. 2)
(+)-I	$2H_2O$	"Λ"[a)]	A
(+)-II	$2H_2O$	"Λ"	B-1 and B-2[b)]
(+)-III	$2H_2O$(rac.)[c)]	"Λ"	C-1 or C-2
(+)-IV	$1.5H_2O$	"Λ"	C-2 or C-1
(−)-V	$1.5H_2O$	"Δ"	D-1(SS)
(−)-VI	$3H_2O$	"Δ"	D-2(RS)
(−)-VII	$2H_2O$	"Δ"	D-3(RR)

a) *Cf.* Table 3.
b) Mixture of two conformational isomers, B-1 and B-2.
c) Analysis was done for the racemate.

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1) Parts I, II, and III were published in This Bulletin, **45**, 179, 3415 (1972), and **46**, 1687 (1973).

2) H. B. Jonassen, J. A. Bertrand, F. R. Groves, Jr., and R. I. Stearns, *J. Amer. Chem. Soc.*, **79**, 4279 (1957); E. Jacobsen and K. Schrøder, *Acta Chem. Scand.*, **16**, 1393 (1961).

3) G. G. Schlessinger, "Werner Centennial," American Chemical Society (1967), p. 565.

4) The void volume was measured by the elution of K[Co(edta)] with the same eluent, sodium (+)-tartrate. The value of V_0 is slightly different for each column.

rotation at 589 nm. The water of crystallization is different for each isomer, the numbers of which are listed in Table 1.

The I Isomer: The prepared complex was adsorbed on *SP*-Sephadex and eluted by means of a 0.18 M sodium (+)-tartrate solution; the elution curve was thus obtained (Fig. 1-a). The first four peaks were found to correspond to the two pairs of enantiomers; they were named (+)-I, (−)-I, (+)-II, and (−)-II respectively.

The fractions (V/V_0=3.3—4.0) corresponding to the (+)-I and (−)-I isomers were again adsorbed on *SP*-Sephadex after dilution and then eluted with a 1 M sodium chloride solution. By adding potassium hexacyanocobaltate(III) to this eluate, the hexacyanocobaltates of (+)-I and (−)-I were precipitated; they were then converted to the chlorides by stirring with an anion-exchange resin(Dowex 1-X8, 200—400 mesh) in the chloride form. On the evaporation of each filtrate, yellow crystals of the (+)-I and (−)-I, $[Co(linpen)]Cl_3 \cdot 2H_2O$, were obtained. Found: C, 27.80; H, 7.39; N, 19.23% for the (+)-I and C, 27.67; H, 7.40; N, 19.58% for the racemic I. Calcd. for $CoC_{10}H_{28}N_6Cl_3 \cdot 2H_2O$: C, 27.70; H, 7.44; N, 19.38%.

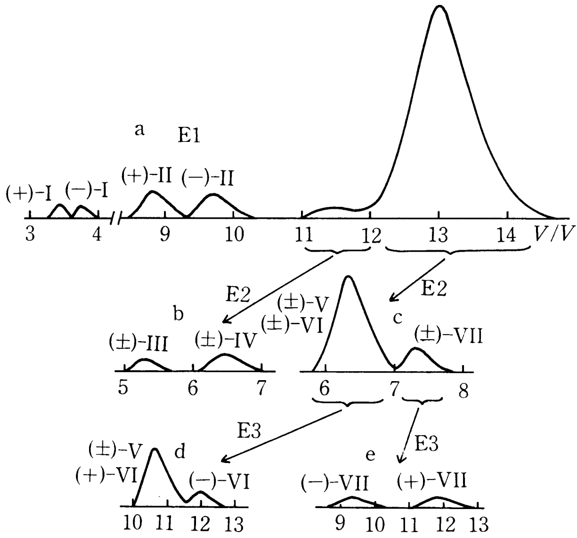

Fig. 1. Elution curves of the isomers of $[Co(linpen)]^{3+}$. The eluents E1, E2, and E3 are 0.18 M sodium (+)-tartrate, a mixture of 0.18 M sodium sulfate and 0.01 N hydrochloric acid, and 0.3 M sodium (+)-tartratoantimonate, respectively.

The II Isomer: The fractions V/V_0=8.4—10.3 (Fig. 1-a), when treated in the same way as above, yielded the (+)- and (−)-enantiomers of the II isomer. The (+)-enantiomer was further separated into two isomers by chromatography with a 0.18 M sodium sulfate solution containing 0.01 N HCl as the eluting agent, but these separated isomers were labile and isomerized into a mixture during separation on the column, so they could not be obtained in pure states. The (−)-II isomer behaved in the same way. Therefore, it may be concluded that the II isomer consists of a mixture of two conformational isomers which isomerize very quickly to each other.

The III and IV Isomers: The fractions V/V_0=11.0—12.0 (Fig. 1-a) were again adsorbed on *SP*-Sephadex and eluted with a 0.18 M sodium sulfate solution containing 0.01 N HCl. As is shown in Fig. 1-b two peaks of optically inactive isomers were obtained. The yellow, fast-moving isomer was named III, and the yellowish-brown, slow-moving one, IV. Since the complete resolution of these isomers, III and IV, into their enantiomers by chromatography was difficult, the optically-pure enantiomers of III and IV were obtained by the isomerization of the (+)-II and (−)-II isomers respectively. The (+)-II gave a mixture of the (−)-III and (−)-IV isomers which were then separated by elution with a 0.18 M sodium sulfate solution containing 0.01 N HCl. The (−)-II similarly gave a mixture of the (+)-III and (+)-IV isomers.

The V, VI, and VII Isomers: A large peak corresponding to the fractions V/V_0=12.6—14.5(Fig. 1-a) was further separated into two peaks by elution with a 0.18 M sodium sulfate solution containing 0.01 N HCl(Fig. 1-c). The large first peak at V/V_0=6—7 was further separated into two by elution with a 0.3 M sodium (+)-tartratoantimonate(III) solution (Fig. 1-d). From the first peak, the (±)-V isomer was precipitated as the hexacyanocobaltate, leaving the (+)-VI isomer in the mother liquor, from which it could not be isolated in a pure state. The fractions corresponding to the small second peak contained the pure (−)-VI(Fig. 1-d). This isomer, (−)-VI, readily isomerized in a neutral or alkaline solution into a mixture of the (−)-V, the (−)-VI, and a small amount of the (−)-VII isomers. By applying to this mixture the separation procedure shown in Figs. 1-c and d, pure (−)-V and (−)-VI were obtained.

The fractions corresponding to a small second peak in Fig. 1-c can be resolved into the (−)-VII and (+)-VII isomers by elution with a 0.3 M sodium (+)-tartratoantimonate(III) solution(Fig. 1-e). The VII isomer is labile and isomerizes readily in a neutral solution into a mixture of the V, VI, and VII isomers. Therefore, it should always be handled in an acid solution.

Measurements. The electronic absorption(AB), infrared, and circular dichroism(CD) spectra were measured at 25 °C with a Hitachi recording spectrophotometer 323, a JASCO-402G infrared spectrophotometer, and a JASCO J-20 spectrophotometer respectively. The NaCl disk was used for the infrared spectrum measurement. The PMR spectra in 0.1 N $DCl(D_2O)$ were measured by means of a JEOL model JNM-MH-100 spectrometer, with DSS as the internal standard. When the signals due to the amino-hydrogen atoms overlapped with those due to the hydrogen of HOD, an additional amount of concentrated DCl was used to shift the latter signals.

Results and Discussion

Isomerization Reaction. In a neutral solution without active charcoal the I and II isomers do not isomerize, while the III and IV isomers isomerize under the same conditions, to give their mixture; V, VI, and VII also give their mixture. In an alkaline solution of pH 12 without active charcoal, the (−)-II isomerizes partly into a mixture of (+)-III and (+)-IV; this specific isomerization reaction was used to prepare the optically pure III and IV as has been described above. In a borate buffer solution of pH 9.0 and in the presence of active charcoal, each of the I—VII isomers isomerizes to give a mixture of all the isomers at 60 °C after 2—8 hr.

The formation ratio found experimentally in the preparative work was I: II: III: IV: V: VI: VII= 9: 15: 1: 2: 47: 23: 3; it varies to some extent with the experimental conditions.

Number of Possible Isomers. When linpen is coordinated to cobalt(III) as a sexidentate ligand, four different configurational isomers, A, B, C, and D, can

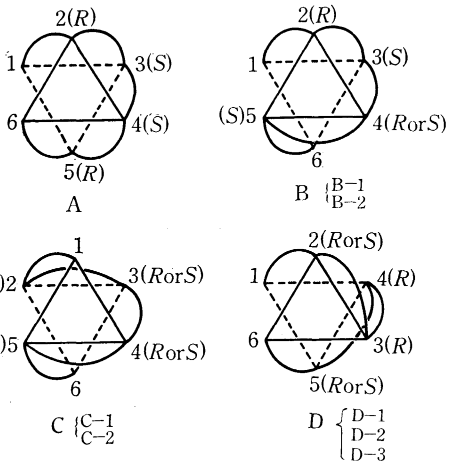

Fig. 2. Four geometric isomers of [Co(linpen)]$^{3+}$.

be expected (Fig. 2). If the absolute configurations around the secondary amine-N atoms are taken into account, the number of isomers increases. For the A structure, the absolute configurations of the nitrogen atoms are fixed; *R* for the N2 and N5, and *S* for the N3 and N4. Thus, only one isomer is possible. For the B structure, the absolute configuration of the N2 is fixed to *R*, and those of the N3 and N5, to *S*, whereas the N4 can take either the *R* or *S* configuration. Thus, two isomers are possible for the B structure. For the C structure, both the N2 and N5 are fixed to *S*. As the N2, N3, N4, and N5 are adjacent to each other on the same plane, their absolute configurations are not independent; both the N3 and N4 atoms should take the same configuration, that is, *RR* or *SS*. Therefore, two isomers are possible. For the D structure, the absolute configurations of the N3 and N4 are fixed to R, but the configuration of the N2 is independent of that of the N5. Consequently, three isomers are possible, isomers which have the *RR*, *RS*, and *SS* configurations for the N2 and N5 atoms. Thus, when the absolute configurations around the secondary amine-N atoms are taken into consideration, the symmetry of the A and C structures and two of the D structures is C_2, while that of the B structure is C_1; that of the third one of the D structures is also C_1. Consequently, the number of isomers is 1 for the A, 2 each for the B and C, and 3 for the D structure, making a total of 8. This number agrees with the number of isomers actually found.

If the conformation (δ or λ) of each chelate ring is further taken into account, the number of possible isomers increases much more. These conformational isomers, however, can not be separated under the present experimental conditions because of the rapid inversion of their conformations.

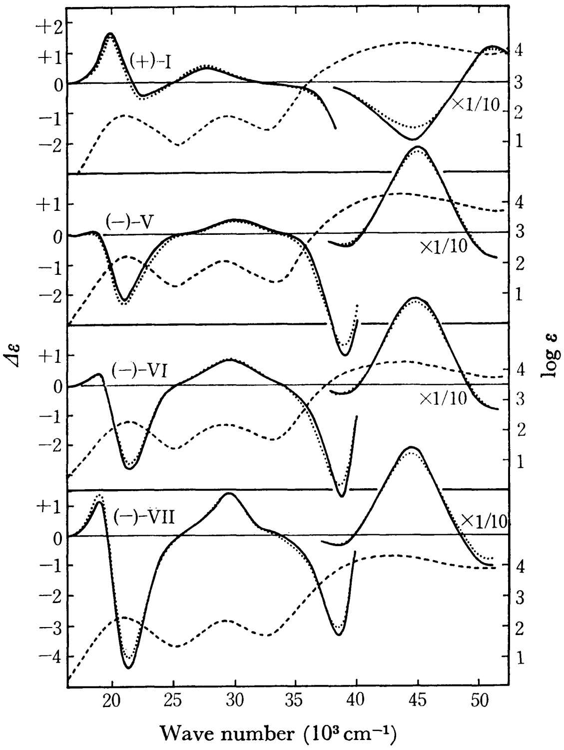

Fig. 3a. AB (-----) and CD (—— in water and ······ in 0.2 M Na_2SO_4) spectra of the (+)-I, (−)-V, (−)-VI, and (−)-VII isomers of [Co(linpen)]$^{3+}$.

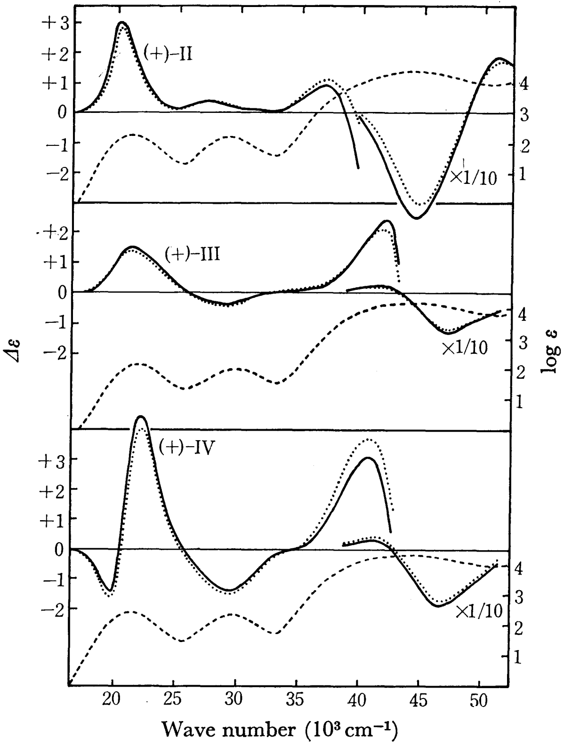

Fig. 3b. AB (-----) and CD (—— in water and ······ in 0.2 M Na_2SO_4) spectra of the (+)-II, (+)-III, and (+)-IV isomers of [Co(linpen)]$^{3+}$.

The AB and CD Spectra. The AB and CD spectra were measured in a 0.01N HCl solution except for the (+)-I and (+)-II isomers; the results are shown in Fig. 3 and Table 2. The absorption maxima are at 21600—20800 cm^{-1} (462—480 nm) for the first band, at 29500—29100 cm^{-1} (339—344 nm) for the second band, and at 44800—43100 cm^{-1} (223—232 nm) for the charge transfer band, indicating a 6N-type cobalt(III) complex. The CD spectrum of the (+)-I isomer (Fig. 3-a) closely resembles that of Λ-[Co(en)$_3$]$^{3+}$ and its absolute configuration is identified as "Λ" from the sign of the main CD component in the first absorption

Table 2. Absorption and circular dichroism spectra (in 10^3 cm^{-1})

Isomer	1st band				2nd band				CT band			
	AB		CD		AB		CD		AB		CD	
	ν_{max}	(ε_{max})	ν_{max}	($\Delta\varepsilon_{max}$)	ν_{max}	(ε_{max})	ν_{max}	($\Delta\varepsilon_{max}$)	ν_{max}	(ε_{max})	ν_{max}	($\Delta\varepsilon_{max}$)
(+)-I	21.2	(85.0)	19.9	(+1.68)	29.5	(77.4)	27.8	(+0.54)	44.8	(20360)	44.4	(−18.8)
			22.5	(−0.42)							51.0	(+11.6)
(+)-II	21.1	(168)	20.3	(+3.06)	29.15	(129)	27.2	(+0.44)	44.4	(20330)	37.5	(+0.86)
							30.3	(+0.11)			44.4	(−34.5)
											51.5	(+17.2)
(+)-III	21.65	(143)	21.0	(+1.58)	29.5	(101)	29.0	(−0.39)	44.1	(14760)	41.9	(+2.50)
											46.9	(−12.6)
(+)-IV	21.3	(212)	19.5	(−1.41)	29.3	(185)	29.5	(−1.44)	43.9	(17840)	40.8	(+3.13)
			22.0	(+4.49)							46.5	(−18.3)
(−)-V	21.15	(176)	18.3	(+0.02)	29.2	(120)	29.8	(+0.44)	43.7	(19240)	39.1	(−4.16)
			21.1	(−2.22)							44.9	(+28.8)
(−)-VI	21.0	(203)	18.7	(+0.31)	29.2	(151)	29.4	(+0.79)	43.5	(18660)	38.8	(−3.81)
			21.3	(−2.80)							44.8	(+27.6)
(−)-VII	20.8	(212)	18.8	(+1.15)	29.1	(152)	29.5	(+1.42)	43.1	(20810)	38.5	(−3.26)
			21.3	(−4.38)							44.4	(+28.7)

region.[5] The (+)-II isomer has only one positive CD peak in the first absorption region (Fig. 3-b); from its sign it is identified as having the "Λ" configuration also (*cf.* Table 3).

The (+)-III and (+)-IV isomers were obtained by the isomerization of the (−)-II isomer in an alkaline solution of pH 12 without any active charcoal. Since these two isomers have a main CD component with the plus sign in the first absorption region (Fig. 3-b), their absolute configurations were identified as "Λ". As the starting substance, (−)-II, has the "Δ" configuration, a complicated isomerization mechanism with a configuration inversion is suspected. Under the same experimental conditions the formation of the (+)-II isomer from the (−)-II isomer is less than 0.4% in amount.

All the CD spectra of the (−)-V, (−)-VI, and (−)-VII isomers (Fig. 3-b) have the main peak with the minus sign in the first absorption region; from the sign of the CD peak, these isomers were all determined to have the "Δ" configuration.

Summarizing the results shown in Figs. 3-a and 3-b, the (+)-I has a main plus peak on the longer wavelength side of the first absorption region, and a small minus peak on the shorter wavelength side. The (+)-II and (+)-III isomers both have only a plus peak, in the same region. The (+)-IV isomer shows a small plus peak and a large minus peak, whereas the (−)-V, (−)-VI, and (−)-VII isomers all have a small plus peak and a large minus peak, in the same region. In the present section, the relationship between the sign of the main CD peak and the absolute configuration of each isomer has been discussed.

There is a very weak CD peak for the (−)-V isomer at 17000 cm^{-1} (589 nm) ($\Delta\varepsilon = -0.02$) and for the (−)-VI isomer at 16200 cm^{-1} (616 nm) ($\Delta\varepsilon = -0.01$). The origin of this weak peak is not yet clear. One possibility is the spin-forbidden band which is similar to the $^3T_{2g} \leftarrow {}^1A_{1g}$ transition of $[Co(en)_3]^{3+}$.[6] Another possibility is a band remaining after the cancellation of two bands with opposite signs which are situated close to each other. The positions of these weak peaks are too low in frequency to be attributed to the first absorption band split by a low symmetry, like C_1 or C_2.

It is often assumed that the CD spectrum in the visible region is the sum of the hypothetical CD components attributed to the configuration around the metal, the conformation of the chelate rings, and asymmetric nitrogen atoms; the actual situation in the present case is not so simple, however, because no additivity rule holds for the CD spectra of the III and IV isomers, or for those of the V, VI, and VII isomers, each pair of which has the same configuration around the metal. Concerning the CD spectrum in the charge transfer region, the peak intensity seems to be proportional to the net sum of the absolute configurations of the skew chelate pairs, as is shown in Table 3.

The Infrared Spectra. The infrared spectra of the I—VII isomers in the region 2000—4000 cm^{-1} are shown in Fig. 4. It may be noted that the III—VII isomers show a strong band at about 2880 cm^{-1} which

Table 3. The relationship between the net sum of the absolute configurations of the skew chelate pairs and the peak intensity of the CD spectrum in the charge transfer region

Isomer	The net sum	The order of the peak intensity
(+)-II	"Λ"=3Λ=ΛΛΛΛΔ	1
(−)-V (−)-VI (−)-VII	"Δ"=2Δ=ΔΔΔΔΛΛ	2
(+)-I	"Λ"=2Λ=ΛΛΛΔ	2
(+)-III (+)-IV	"Λ"=Λ=ΛΛΛΔΔ	3

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[5] "Λ" and "Δ" denote the net sum of Λ and Δ of the skew chelate pairs, IUPAC Information Bulletin, No. 33, 68 (1968); *Inorg. Chem.*, **9**, 1 (1970).

[6] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

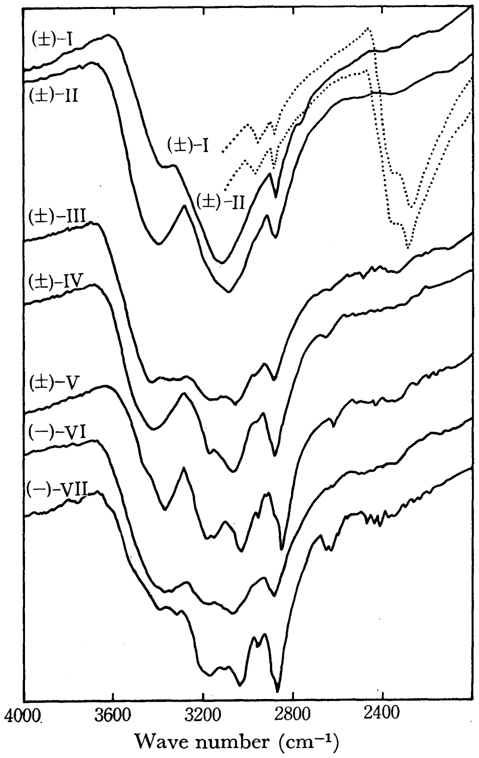

Fig. 4. Infrared spectra of the isomers of [Co(linpen)]Cl_3. …… deuterated complexes.

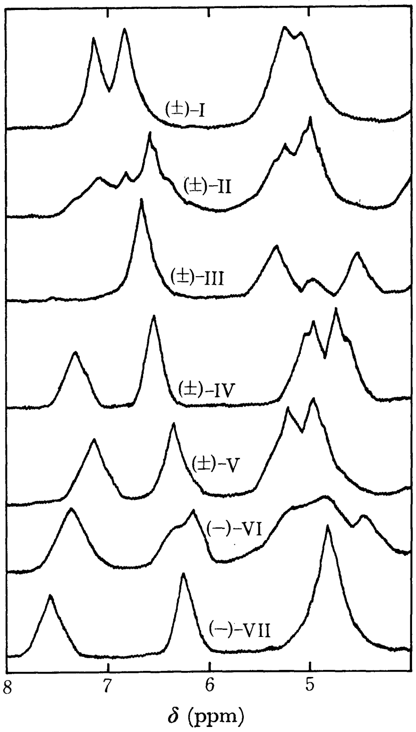

Fig. 5. PMR spectra of the isomers of [Co(linpen)]$^{3+}$ in 0.1 N DCl(D_2O) at 25 °C.

is similar to the band at 2879[7] cm^{-1} of *mer*-[Co(dien)$_2$]-$Br_3 \cdot 2H_2O$,[8] dien being diethylenetriamine. The band of the dien complex has been identified as the >NH stretching vibration, which is characteristic of the *mer* structure. Therefore, the band at about 2880 cm^{-1} of the III—VII isomers can be assigned to the same vibration. The I and II isomers also have a weak-medium band at about 2880 cm^{-1}, but this band does not seem to be assignable to the same >NH stretching vibration, for it does not shift on deuteration. As the I isomer has no >NH group of the *mer* structure, the absence of the above >NH vibration is understandable. The II isomer is identified as having the B structure with a *mer* structure (*vide infra*). Nevertheless, it does not show a band similar to those of the III—VII isomers shown above. The reason for this is not yet clear, though it may be due to some structural differences between them.

The PMR Spectra and the Assignment of the Structures. The PMR spectra of the I—VII isomers were studied in 0.1N DCl(D_2O) in order to obtain information on their configurations. The spectra are shown in Fig. 5. The signals due to HOD are omitted in Fig. 5 for the sake of simplicity. Since the signals due to the methylene protons are very complicated, they were not taken into consideration, either; only the protons attached to nitrogen were considered. The most complicated spectrum, which the II isomer shows, may be assigned to the isomer with the least symmetric structure, that is, to the B structure with the C_1 symmetry. The I isomer exists as a single isomer, and neither is separated further nor isomerizes into other isomers in a neutral solution. Therefore, the I isomer is identified as having the A structure. The PMR spectrum of I is symmetrical in shape, in accordance with the C_2 symmetry.

Since the V, VI, and VII isomers isomerize to their mixtures in a neutral solution, these isomers may be identified as having the D structure, which has three isomers. On the basis of the PMR spectral pattern, the VI isomer may presumably be assigned to the unsymmetrical *RS* configuration connected with the N2 and N5 atoms. Further, based on a very simple conformational analysis and the fact that the V isomer is formed more abundantly than VII, the V isomer is identified as having the *SS* configuration, and the VII isomer, the *RR* configuration connected with the N2 and N5 atoms. Finally, the remaining III and IV isomers are identified as having the C structure. As the amount of III and IV formed are not appreciably different, it is not possible to decide which isomer of the C structure is to be assigned to III or IV.

The structures assigned on the basis of the facts presented above are summarized in Table 1.

The X-ray determination of the structures of several isomers is now under way in the laboratory of Professor Y. Saito, The University of Tokyo.

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[7] The frequency of this band was erroneously printed in the previous report (Ref. 4) as 2848 cm^{-1}.

[8] Y. Yoshikawa and K. Yamasaki, This Bulletin, **45**, 179 (1972).