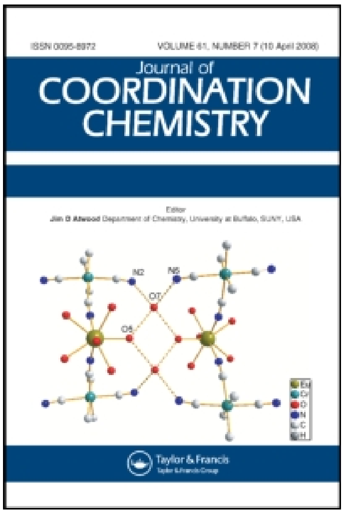


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

OPTICAL ISOMERS OF 2,2'-DIAMINOBIPHENYLBIS(ETHYLENEDIAMINE) COBALT(III) CHLORIDE AND ITS RELATED COMPLEXES[1]

Taisei Tanimura[a]; Haruko Ito[a]; Junnosuke Fujita[a]; Kazuo Saito[a]; Shigeo Hirai[b]; Kazuo Yamasaki[b]
[a] Department of Chemistry, Faculty of Science Tohoku University, Sendai, Japan [b] Department of Chemistry, Faculty of Science Nagoya University, Nagoya, Japan

To cite this Article Tanimura, Taisei , Ito, Haruko , Fujita, Junnosuke , Saito, Kazuo , Hirai, Shigeo and Yamasaki, Kazuo(1973) 'OPTICAL ISOMERS OF 2,2'-DIAMINOBIPHENYLBIS(ETHYLENEDIAMINE) COBALT(III) CHLORIDE AND ITS RELATED COMPLEXES1', Journal of Coordination Chemistry, 3: 2, 161 — 167

To link to this Article: DOI: 10.1080/00958977308073803

URL: http://dx.doi.org/10.1080/00958977308073803

J. Coord. Chem.
1973, Vol. 3, pp. 161–167

OPTICAL ISOMERS OF 2,2′-DIAMINOBIPHENYLBIS(ETHYLENEDIAMINE) COBALT(III) CHLORIDE AND ITS RELATED COMPLEXES[1]

TAISEI TANIMURA, HARUKO ITO, JUNNOSUKE FUJITA, KAZUO SAITO

Department of Chemistry, Faculty of Science, Tohoku University, Sendai, 980 Japan

and

SHIGEO HIRAI, and KAZUO YAMASAKI†

Department of Chemistry, Faculty of Science, Nagoya University, Nagoya, 464 Japan

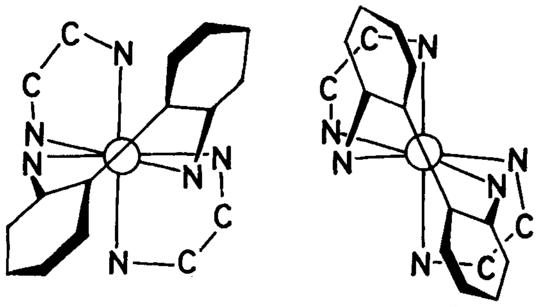
(*Received April 18, 1973 in final form*)

Several cobalt(III) complexes incorporating 2,2′-diaminobiphenyl(dabp) and other 2(2N)- or 4N-type ligands were prepared and resolved by chemical and chromatographic methods: (1) $[Co(en)_2(dabp)]Cl_2 2H_2O$, (2) $[Co(l\text{-}pn)_2(dabp)](ClO_4)_3 4H_2O$, (3) $[Co(l\text{-}chxn)_2(dabp)](ClO_4)_3 3H_2O$, (4) α-$[Co(trien)(dabp)](ClO_4)_3$, (5) α-$[Co(2S,9S\text{-}dimetrien)(dabp)](ClO_4)_3 2H_2O$, (6) α-$[Co(3S,8S\text{-}dimetrien)(dabp)](ClO_4)_3 3H_2O$, (7 $[Co(tren)(dabp)]Cl_3 5H_2O$, (8) $[Co(bpy)_2(dabp)]Cl_3 3H_2O$. The complexes (1), (4) and (8) gave one pair of enantiomers, Δ(λ) and Λ(δ), and the complexes (2) and (3) gave only one Δ-isomer. The absolute configuration of the complexes (5) and (6) was found to be Λ, and that of (7) was not determined because of unsuccessful resolution. The three geometric isomers of the complex (2) were separated and their structures assigned.

INTRODUCTION

Biphenyl can rotate freely around the common axis connecting the two benzene rings. If the rotation is hindered or prohibited, for example, by introducing bulky groups in the 2, 2′, 6 and 6′ positions, or by linking the 2 and 2′ positions by a ring, a pair of optical isomers is produced, unless the two benzene rings are coplanar, or perpendicular to each other. Some optically active organic compounds of this type have been prepared,[2] and their optical activity studied.[3] If the substituents in the 2,2′-position are coordinated to a metal ion, a chelate ring results and by analogy to the above cases the metal chelate formed should be optically active. McCollough and Bailar[4] found first such an optical activity for $[Co(en)_2(dabp)]^{3+}$ ion, dabp representing 2,2′-diaminobiphenyl. The dabp ligand in this complex will take a dissymmetric conformation, δ or λ[5], as shown in Figure 1, and the complex ion can have four possible stereoisomers, Δ(λ), Δ(δ), Λ(λ) and Λ(δ). Their existence was reported by McCollough and Bailar[4] together with their optical rotatory dispersion (ORD) curves.

In the present investigation, however, we have found that the $[Co(en)_2(dabp)]_3^+$ ion gives only one pair of enantiomers, Δ(λ) and Λ(δ) or Δ(δ) and Λ(λ). This result may suggest that the confomation of dabp depends on the absolute configuration of the complex. In other words, the conformation of dabp is stereospecific in this complex. In order to confirm such a stereospecificity, we have prepared and resolved several dabp complexes analogous to the $[Co(en)_2(dabp)]_3^+$ ion. The present paper deals with the structures of these optically active complexes as well as the conformation of the coordinated dabp.



Δ(λ) Δ(δ)

FIGURE 1 Δ(λ)- and Δ(δ)-$[Co(en)_2(dabp)]^{3+}$ ions.

---

†Author to whom correspondence is addressed.

EXPERIMENTAL

Ligands

2,2′-Diaminobiphenyl(dabp) was prepared by reduction of 2,2′-dinitrobiphenyl with metallic tin and hydrochloric acid.[6] 2,2′,2″-Triaminotriethylamine(tren) was prepared from bromoethylphthalimid and ammonia.[7] (−)$_{589}$-Propylenediamine(l-pn) and (−)$_{589}$-cyclohexanediamine(l-chxn) were obtained from their commercially available racemates by the methods of Dwyer and Garvan,[8] and of Asperger and Liu,[9] respectively. Other ligands like ethylendiamine(en), triethylenetetraamine(trien), and 2,2′-bipyridine(bpy) were commercial products.

Preparation of Complexes

(1) *Δ, Λ-[Co(en)$_2$(dabp)]Cl$_3$2H$_2$O [Δ,Λ-2,2′-diaminobiphenylbis(ethylenediamine) cobalt(III) chloride dihydrate]*† The complex was prepared by the method of McCollough and Bailar,[4] and resolved by the commonly used fractional crystallization of the diastereoisomers, and by the column chromatography on ion-exchange cellulose or Sephadex developed by us.[10]

Resolution Method A

The complex was resolved by a similar method to that of McCollough and Bailar[4] using silver (+)$_{589}$-tartrate. Two optical isomers were obtained, of which the CD curves were enantiomeric to each other.

Resolution Method B

About 20 mg of the complex dissolved in water was poured on a column (ϕ1.3 x 20 cm) of P-cellulose. After washing the column with water, the yellow band adsorbed was eluted with a 0.15 M aqueous solution of sodium (+)$_{589}$-tartrate at a rate of 0.2 ml per minute. The eluate was fractionated into 5 ml portions and each fraction was checked for its electronic absorption, ORD and circular dichroism (CD) spectra. As Figure 2 shows, the elution curve indicates clearly that only two isomers are obtained, and that the (−)$_{589}$-isomer is eluted faster than the (+)$_{589}$-isomer. The CD curves of these isomers were enantiomeric to each other, and both resolution methods, A and B, gave the same CD data.

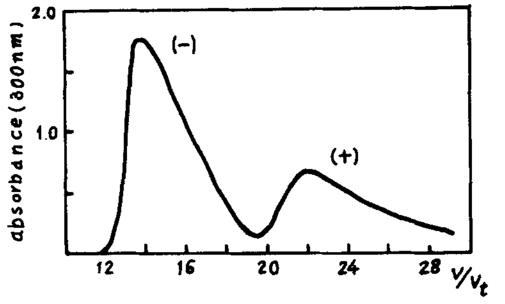


FIGURE 2 Elution curve of [Co(en)$_2$(dabp)]$^{3+}$ ion. Plots of absorbance *vs.* the ratio of the eluate volume (V) to the total bed volume (V$_t$ = 22 ml) of the column.

(2) *Δ-[Co(l-pn)$_2$(dabp)]Cl$_3$4H$_2$O and Δ-[Co(l-pn)$_2$(dabp)](ClO$_4$)$_3$4H$_2$O* The chloride was prepared from trans-[CoCl$_2$(l-pn)$_2$]Cl[11] and dabp by a similar method to that for [Co(en)$_2$(dabp)]$^{3+}$. *Anal.* Calcd. for $C_{18}H_{40}N_6O_4CoCl_3$: Co, 10.34; N, 14.75; H$_2$O, 12.65. Found: Co, 10.15; N, 13.97; H$_2$O, 12.83.

The perchlorate was prepared by adding sodium perchlorate to an aqueous solution of the chloride and by recrystallizing from water. *Anal.* Calcd. for $C_{18}H_{40}N_6O_{16}CoCl_3$: C, 28.36; H, 5.29; N, 11.03. Found: C, 28.74; H, 5.57; N, 10.53.

Separation of geometric isomers Method A An aqueous solution of the perchlorate was crystallized fractionally into five parts by evaporating gradually at room temperature. The last fraction gave large crystals (S$_1$) and powder (U) by evaporating the solution to complete dryness. First four fractions were combined and dissolved again in water. The solution was evaporated to dryness at room temperature to give large crystals (S$_2$) and powder (U). The large crystals (S$_1$ and S$_2$) and powder (U) were separated by hand picking.

Method B An aqueous solution of the above chloride (about 80 mg) was poured on a SE-Sephadex column (ϕ2.7 x 120 cm) and adsorbed yellow band was eluted with a 0.3 M sodium (+)$_{589}$-tartaratoantimonate(III) solution at a rate of 0.3 ml per minute. As Figure 3 shows, three separate bands were obtained, and the ratio of these band areas was 1:2:1. The fastest moving isomer, the middle one and the slowest one were found to correspond to the S$_1$, U and S$_2$, respectively, described in the Method A, by PMR spectroscopy.

(3) *Δ-[Co(l-chxn)$_2$(dabp)](ClO$_4$)$_3$3H$_2$O* The complex was prepared from trans-[CoCl$_2$(l-chxn)$_2$]Cl[12] and dabp by a method similar to that

---

†Other complexes prepared may be named in a similar way.

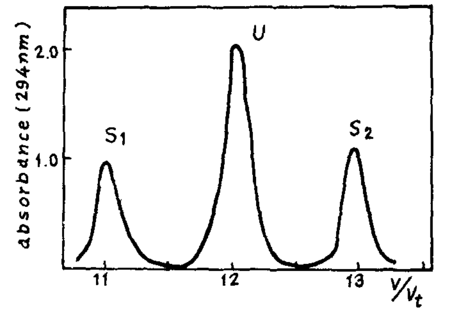


FIGURE 3 Elution curve of $[Co(l\text{-}pn)_2(dabp)]^{3+}$ ion showing separation of three geometric isomers. Plots of absorbance *vs.* the ratio of the eluate volume (V) to the total bed volume (V_t = 685 ml) of the column.

for $[Co(en)_2(dabp]^{3+}$, *Anal.* Calcd. for $C_{24}H_{46}N_6O_{15}CoCl_3$: C, 34.99; H, 5.63; N, 10.20. Found: C, 34.51; H, 5.62; N, 10.13.

(4) Δ,Λ-α-*[Co(trien)(dabp)](ClO$_4$)$_3$* The complex chloride was first prepared from *cis*-α-$[CoCl_2(trien)]Cl^{13}$ and dabp by a method similar to that for $[Co(en)_2(dabp)]^{3+}$, and then the perchlorate was obtained by adding sodium perchlorate to a solution of the chloride. *Anal.* Calcd. for $C_{18}H_{30}N_6O_{12}CoCl_3$: C, 31.43; H, 4.40; N, 12.20. Found: C, 31.12; H, 4.97; N, 12.44.

Resolution The resolution was achieved by column chromatography similar to that for $[Co(en)_2(dabp)]^{3+}$ using a column of SP-Sephadex (ϕ2.7 x 120 cm) and 0.15 M sodium $(+)_{589}$-tartrate solution as an eluent. The yellow band adsorbed was completely separated into the fast moving $(-)_{589}$-isomer and the slow moving $(+)_{589}$-isomer. The CD curves of these isomers were enantiomeric to each other.

(5) Λ-α-*[Co(2S,9S-dimetrien)(dabp)](ClO$_4$)$_3$2H$_2$O* The complex was prepared by a method similar to that for α-$[Co(trien)dabp)]^{3+}$ using trans-$[CoCl_2(2S,9S\text{-}dimetrien)]Cl^{14}$. 2S,9S Dimetrien denotes 2S,9S-dimethyltriethylenetetraamine. *Anal.* Calcd. for $C_{20}H_{38}N_6O_{14}CoCl_3$: C, 31.95; H, 5.09; N, 11.18. Found: C, 32.06; H, 5.45; N, 11.28.

(6) Λ-α-*[Co(3S,8S-dimetrien)(dabp)](ClO$_4$)$_3$3H$_2$O* The complex was prepared in the same way as the preceding one using 3S,8S-dimethyltriethylenetetraamine. *Anal.* Calcd. for $C_{20}H_{40}N_6O_{15}CoCl_3$: C, 31.20; H, 5.24; N, 10.92. Found: C, 31.37; H, 5.56; N, 10.93.

(7) *[Co(tren)(dabp)]Cl$_3$5H$_2$O* The complex was prepared from $[CoCl_2(tren)]Cl^{15}$ and dabp by a method similar to that for $[Co(en)_2(dabp)]^{3+}$. Bailar and Dempsey[16] obtained $[Co(tren)(dabp)]Cl_3 4H_2O$. *Anal.* Calcd. for $C_{18}H_{40}N_6O_5CoCl_3$: C, 36.90; H, 6.88; N, 14.35. Found: C, 37.03; H, 6.85; N, 14.63. Attempts to resolve this complex by fractional crystallization of the iodide tartrate,[16] and by column chromatography on P-cellulose were unsuccessful. This complex decomposed gradually in water.

(8) Δ,Λ-*[Co(bpy)$_2$(dabp)]Cl$_3$3H$_2$O* The complex was prepared from cis-$[CoCl_2(bpy)_2]Cl^{17}$ and dabp by a method similar to that for $[Co(en)_2(dabp)]^{3+}$. *Anal.* Calcd. for $C_{32}H_{34}N_6O_3CoCl_3$: Co, 8.23; N, 11.74; H_2O, 7.55. Found: Co, 7.78; N, 11.68; H_2O, 7.78.

Resolution An attempt to resolve this complex into optical isomers by the SE-Sephadex column chromatography with 0.25 M sodium $(+)_{589}$-tartratoantimonate(III) solution as an eluent was successful only partially because the complex decomposed gradually in water. The first and last fractions of the eluate gave CD peaks at 22.5, 31.1 and 33.2 kK with the signs, –,+,– and +,–,+, respectively, showing the existence of the complex in a pair of enantiomers.

Measurements

Electronic absorption, ORD and CD spectra were recorded with a HITACHI 124 recording spectrophotometer and a JASCO ORD/UV-5 spectrophotometer with the CD attachment, respectively. PMR spectra in D_2O were obtained with a VARIAN T-60 and JEOL C-60H spectrometers using DSS as an internal reference. Most of the measurements were made at 25°C.

RESULTS AND DISCUSSION

Structure of the Complexes

As stated previously the complex $[Co(en)_2(dabp)]^{3+}$ seems to give only one pair of enantiomers, Δ(λ) and Λ(δ), or Δ(δ) and Λ(λ) from the reaction of trans-$[CoCl_2(en)_2]^+$ and dabp. No indication for the presence of more than two isomers was found in both chemical and chromatographic resolutions employed here. The elution curve shown in Figure 2 clearly demonstrates the presence of only two isomers. These two isomers give completely mirror image CD curves to each other, and can be assigned to a pair of enantiomers (Figure 4). In the chemical resolution

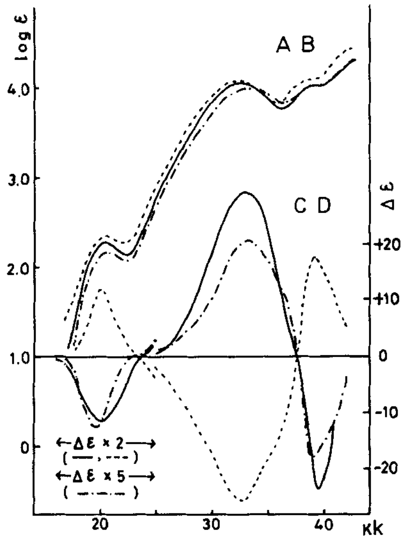


FIGURE 4 The absorption and CD spectra of Δ-$[Co(en)_2(dabp)]^{3+}$ (—— · —— · ——), Δ-α-$[Co(trien)(dabp)]^{3+}$ (————) and Λ-α-[Co(2S,9S-dimetrien)(dabp)]$^{3+}$ (· · · · · ·).

with $(+)_{589}$-tartrate ion, all the fractions of $[Co(en)_2(dabp)]Cl \cdot tart$ showed CD peaks at 19.5, 33.8 and 39.8 kK with the signs –,+,–, or +,–,+, respectively. The magnitudes of these CD peaks varied considerably depending on the optical purity of the fraction, but the ratios of magnitudes, $\Delta\epsilon_{33.8\,kK}/\Delta\epsilon_{19.5\,kK}$ for each fraction were almost constant and the sign was always minus, –8.4. The CD peak at 19.5 kK corresponds to the first absorption band, and its sign is known to depend generally on the absolute configuration of ligands around the cobalt(III) ion: Λ-isomer shows plus sign, and Δ-isomer minus sign. The origin of the CD peaks at 33.8 and 39.8 kK is not clear yet, but these CD peaks should correlate closely with the electronic transitions of the coordinated dabp, and their signs will depend on the conformation of dabp in the complex. Therefore, a constant and minus value of $\Delta\epsilon_{33.8\,kK}/\Delta\epsilon_{19.5\,kK}$ indicates that the $[Co(en)_2(dabp)]^{3+}$ is present in a pair of enantiomers. If other stereoisomers had been formed, the ratios of some fractions would have given different values from the above or shown a positive sign. Thus the results obtained by both the chemical and chromatographic resolutions indicate that the dabp takes a preferred conformation stereospecifically in a given configuration of two ethylenediamine chelate rings in the complex. The same result has been obtained by Douglas and his co-workers.[18]

The absolute configuration of the $[Co(en)_2(dabp)]^{3+}$ can be assigned on the basis of the CD sign in the first absorption band region as described before, while the conformation, δ or λ of the dabp may not be assigned without ambiguity at present from the CD pattern in the region 30–45 kK. However, molecular models indicate that Δ(λ)-isomer seems to have less steric interactions among the chelate rings than Δ(δ) has, as is seen in Figure 1. The same relation holds for Λ(δ) and Λ(λ). Therefore, it may be concluded that the only pair of enantiomers of $[Co(en)_2(dabp)]^{3+}$ is the Δ(λ) and Λ(δ) forms. The crystal structure of $\Delta(S_1)$-$[Co(l\text{-}pn)_2(dabp)]Cl_3$ which shows almost identical CD spectrum with that of Δ-$[Co(en)_2(dabp)]^{3+}$ has been determined by the X-ray method[19] and found to be $\Delta(S_1)(\lambda)$ (*vide infra*). This fact also supports the above assignment. Douglas and his co-workers[18] reached the same conclusion and confirmed it by the stereospecific formation of Δ(λ)-$[Co(en)_2(R\text{-}dmdabp)]^{3+}$, R-dmdabp being R-6,6′-dimethyl-2,2′-diaminobiphenyl.

Alpha-$[Co(trien)(dabp)]^{3+}$ gives also only one pair of enantiomers, Δ(λ) and Λ(δ), no additional stereoisomer being detected by column chromatography. The geometrical structure of this complex was assigned to α-form from comparison of its absorption and CD spectra with those of stereospecifically formed α-[Co(2S,9S-dimetrien)(dabp)]$^{3+}$ and α-[Co(3S,8S-dimetrien)(dabp)]$^{3+}$, as shown in Figure 4 and Table I. The magnitudes of the CD peak at about 20 kK of the trien-dabp-type complexes are about twice as large as those of the bis(diamine)-dabp complexes, although those of the CD peaks at about 33 and 40 kK do not change remarkably among the complexes. The reason is not clear at present, but the presence of asymmetric nitrogen atoms in the trien-type complexes will be related to the magnitude of the CD peak corresponding to the d-d transitions of the cobalt(III) ion.

$[Co(bpy)_2(dabp)]^{3+}$ seems to show the same stereospecificity to give only two isomers, Δ(λ) and Λ(δ). However, we could not obtain optically pure isomers, because the complex was rather unstable in water. The magnitudes of the CD peaks for this complex given in Table I are only qualitative.

Such a stereospecific conformation of dabp in the bis(diamine)dabp complexes will be supported further by the fact that the complexes, $[Co(l\text{-}pn)_2(dabp)]^{3+}$, $[Co(l\text{-}chxn)_2(dabp)]^{3+}$, α-[Co(2S,9S-dimetrien)(dabp)]$^{3+}$ and α-[Co(3S,8S-dimetrien)(dabp)]$^{3+}$ give only one isomer each. Since l-propylenediamine and l-cyclohexanediamine will take a λ conformation upon coordination,[20,21] the tris-complexes with these diamines have two possible

TABLE I
Electronic absorption and CD spectra of the dabp complexes with their absolute configurations

Absolute Configuration	Ligand other than dabp	Absorption band (log ϵ^a) (10^3 cm^{-1})	CD peak ($\Delta\epsilon$) (10^3 cm^{-1})
Δ	en	20.7(2.13)	19.5(−2.48)
		33.1(3.99)	33.8(+20.8)
		39.1 sh(4.0)[b]	39.8(−20.2)
Δ	l-pn	20.7(2.20)	19.5(−2.80)
		33.6(4.06)	33.1(+25.0)
		39.5sh(4.1)	39.1(−21.3)
Δ	l-chxn	20.41(2.16)	19.42(−2.31)
		32.79(4.00)	32.79(+24.8)
		39.3sh(4.1)	39.27(−21.3)
Δ	trien	20.6(2.31)	20.2(−5.67)
		32.9(4.05)	33.1(+29.6)
		39.1sh(4.0)	39.4(−20.6)
Λ	2S,9S-dimetrien	20.52(2.36)	20.20(+5.44)
		32.26(4.06)	32.79(−25.5)
		38.7sh(4.1)	39.27(+17.6)
Λ	3S,8S-dimetrien	20.41(2.25)	20.00(+5.18)
		32.79(4.05)	32.79(−25.9)
		39.0sh(4.0)	39.27(+20.7)
Δ	bpy	21.7sh(1.9)	22.5(−)
		31.3(3.47)	31.1(+)
		32.5(4.50)	33.2(−)
		39.8sh(4.6)	

[a] ϵ = molar extinction coefficient.
[b] sh = shoulder.

diastereoisomers, $\Delta(\lambda\lambda\lambda)$(lel) and $\Lambda(\lambda\lambda\lambda)$(ob).[20] However, the lel isomer is known to be more stable than the ob isomer,[20] and the products obtained in the reaction between a cobalt salt and these l-diamines consist mostly of the Δ(lel) isomer.[22] Although the bis(diamine)-dabp complexes studied here have somewhat different structures from those of the tris(diamine)-type complexes, the reactions between dabp and trans-$[CoCl_2(l\text{-}pn)_2]^+$ or trans-$[CoCl_2(l\text{-}chxn)_2]^+$ produced only the Δ-isomer, as was described in the Experimental part, and the CD spectra of the products are very similar to that of $\Delta(\lambda)$-$[Co(en)_2(dabp)]^{3+}$, as shown in Figure 4 and Table I.

The dabp complexes of both 2S,9s- and 3S,8s-dimethyltriethylenetetraamines would form only the Λ-α or Δ-β isomer owing to the presence of the methyl groups favoring an equatorial orientation on the tetraamine chelate ring.[14,23] All the fractions of these S,S-tetraamine complexes exhibit an almost enantiomeric CD spectrum with those of Δ-α-$[Co(trien)(dabp)]^{3+}$ and Δ-$[Co(en)_2(dabp)]^{3+}$ as shown in Figure 4. Therefore, the complexes can be assigned to Λ-α form, and the dabp will take a δ conformation as well as the dabp in Λ-$[Co(en)_2(dabp)]^{3+}$. The Δ-β isomer seems to be less stable than the Λ-α isomer because of the steric interactions between the dabp and the tetraamine ligands.[18] These results will support the previous conclusion that dabp takes a preferred conformation stereospecifically in a given configuration of other chelate ligands in a complex.

Whenever a dabp complex has no chiral configuration around a metal ion as in the case of $[Co(NH_3)_4(dabp)]^{3+}$ or $[Co(tren)(dabp)]^{3+}$, a pair of enantiomers, δ- and λ-(dabp), will be produced. Bailar and Dempsey[16] reported the resolution of $[Co(tren)(dabp)]^{3+}$ with $(+)_{589}$-tartrate ion. We have also attempted to resolve the same complex by their method and by column chromatography, but the

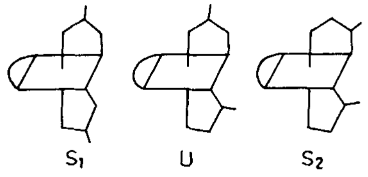


FIGURE 5 Schematic representation of the geometric isomers of Λ-[Co(l-pn)$_2$(dabp)]$^{3+}$. When two ?-pn ligands are linked by an ethylene linkage in S_1 and S_2, the complexes of 2S,9S- and 3S,8S-dimetrien result respectively.

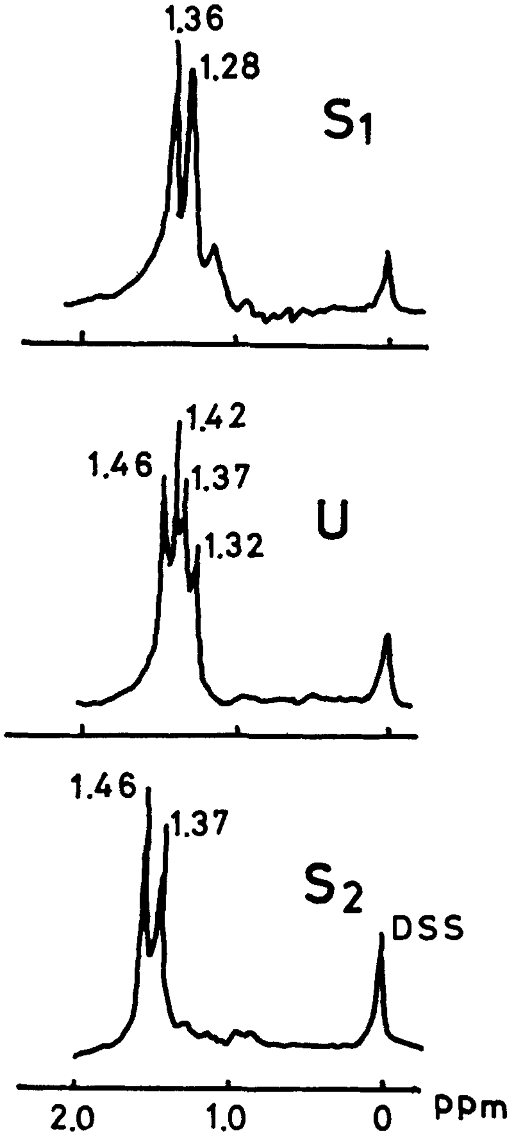


FIGURE 6 PMR spectra of the geometric isomers of Δ-[Co(l-pn)$_2$(dabp)]$^{3+}$ in D_2O at 60 MHz.

resolution was unsuccessful as was described in the Experimental part. Attempts to prepare [Co(NH$_3$)$_4$-(dabp)]$^{3+}$ were not successful, and the complex seemed to be unstable as described in the literature.[24]

Geometric Isomers of Δ-[Co(l-pn)$_2$(dabp)]$^{3+}$

Delta-[Co(l-pn)$_2$(dabp)]$^{3+}$ has three geometric isomers with respect to the location of the methyl groups on the l-propylenediamine ligands. The isomers are designated as S_1, S_2 and U as shown in Figure 5, and they were isolated successfully by fractional crystallization or by column chromatography. Of these isomers, the U isomer is identified easily by the PMR spectrum, since it is has no symmetry element, and the two methyl groups should be magnetically unequivalent to each other. Figure 6 shows that this isomer gives clearly two kinds of methyl signal at τ1.37 and 1.42 ppm. On the other hand, both S_1 and S_2 isomers have C_2 symmetry and the two methyl groups of each isomer are in equivalent environment. Each isomer exhibits only one kind of the methyl doublet signal, although the chemical shifts of the peaks are different from each other. In order to assign the structures of these two isomers, we have compared their PMR spectra with those of the dabp complexes of 2S,9S- and 3S,8S-dimethyltriethylenetetraamines. With respect to the location of the methyl groups in the complexes, the S_1 isomer should correspond to the Λ-α-[Co(2S,9S-dimetrien)-(dabp)]$^{3+}$ and the S_2 to Λ-α-[Co(3S,8S-dimetrien)-(dabp)]$^{3+}$ (Fig. 5). The former complex gives a methyl doublet signal in a higher field (1.33 ppm) than does the latter (1.38 ppm). Therefore, the isomer which exhibits a doublet signal of 1.32 ppm can be assigned the structure of the S_1 isomer, and the other (1.42 ppm), that of the S_2 isomer. This assignment has been confirmed by the X-ray analysis on the S_1 isomer.[19]

Finally it is noted that the electronic absorption and CD spectra of the three geometric isomers are almost identical with one another. The isomers are produced in a statistical ratio 1:2:1, as is seen in Figure 3, indicating that no energy difference exists among these isomers.

REFERENCES

1. A part of the present investigation was presented at the annual meeting of the Chemical Society of Japan held in April, 1970.
2. For example, G. H. Christie and J. Kenner, *J. Chem. Soc.*, 121, 614 (1922); S. Sako, *Mem. Coll. Eng. Kyushu*

Imp. Univ., **6**, 263 (1932); D. C. Iffland and H. Siegel, *J. Amer. Chem. Soc.*, **80**, 1947 (1958).

3. K. Mislow, E. Bunnenberg, R. Record, K. Wellman and C. D. Djerassi, *J. Amer. Chem. Soc.*, **85**, 1342 (1963).
4. F. McCollough, Jr. and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **78**, 714 (1956).
5. The designations, Δ,Λ and δ, λ are in accordance with the I.U.P.A.C. rules. *Inorg. Chem.*, 9, 1 (1970).
6. D. Balcom and A. Furst, *J. Amer. Chem. Soc.*, **75**, 4334 (1953).
7. P. Paoletti, M. Ciampolini and L. Sacconi, *J. Chem. Soc.*, **1963**, 3589.
8. F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **81**, 2955 (1959).
9. R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1492 (1965).
10. Y. Yoshikawa and K. Yamasaki, *Inorg. Nucl. Chem. Lett.*, **4**, 697 (1968); **6**, 523 (1970).
11. A. Werner and A. Frohlich, *Ber.*, **40**, 2225 (1907).
12. R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966).
13. A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).
14. These complexes were kindly provided by Professor S. Yoshikawa, University of Tokyo. M. Saburi and S. Yoshikawa, *Bull. Chem. Soc. Japan*, **45**, 806 (1972).
15. E. Kimura, S. Young and J. P. Collman, *Inorg. Chem.*, 9, 1183 (1970).
16. J. C. Bailar, Jr. and L. F. Dempsey, *Rev. Chim. Minérale*, 3, 1029 (1966).
17. F. M. Jaeger and J. A. van Dijk, *Z. anorg. allg. Chem.*, **227**, 317 (1936).
18. B. E. Douglas, University of Pittsburgh, private communication.
19. Y. Saito, University of Tokyo, private communication.
20. E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, 81, 2620 (1959).
21. S. Yano, H. Ito, Y. Koike, J. Fujita and K. Saito, *Bull. Chem. Soc. Japan*, **42**, 3184 (1969).
22. F. P. Dwyer, T. E. MacDermott and A. M. Sargeson, *J. Amer. Chem. Soc.*, **85**, 2913 (1963).
23. M. Saburi, T. Sawai and S. Yoshikawa, *Bull. Chem. Soc. Japan*, **45**, 1086 (1972).
24. F. McCollough, Thesis, University of Illinois, 1955. Cited in the Reference 4.