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Isolation and Assignment of Two Isomers of *trans*(NO_2)-Dinitrobis[(S)-2-aminomethylpyrrolidine]cobalt(III) Perchlorate

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Two possible isomers (trans,cis and trans,trans) of *trans*-(NO_2)-[(Co(NO_2)$_2$(ampr)$_2$]ClO_4 (ampr=(S)-2-aminomethylpyrrolidine) were isolated separately by fractional recrystallization. The dinitro complexes were converted to the corresponding *trans*(Cl,NO_2)-[CoCl(NO_2)(ampr)$_2$]$^+$ complexes. Based on the circular dichroism and ^{13}C-NMR spectral data, it was shown that the less soluble dinitro complex gave the single isomer of the chloronitro complex, while the more soluble one yielded two diastereomeric chloronitro complexes. Thus, the former is assigned to the trans,cis configuration, and the latter to the trans,trans, taking the geometries of the complexes into consideration.

Two stereoisomers, designated as trans,trans and trans,cis,[1] are possible for the *trans*(X)-[CoX_2(N-N')$_2$]$^{n+}$ complexes, where N-N' refers to an unsymmetrical diamine ligand (see Fig. 1). Each pair of two equivalent amino groups, N and N', disposes in trans fashion for the trans,trans and in cis for the trans,cis isomer, respectively. 1,2-Propanediamine, one of the representative unsymmetrical diamine, has been shown to give the trans,trans isomer for its dichlorocobalt(III) complex with the optically active form.[2]

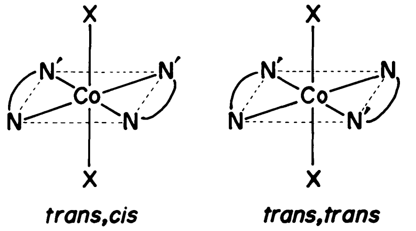


Fig. 1. Two possible isomers of *trans*(X)-[CoX_2-(N-N')$_2$]$^{n+}$ ion.

Although the formation of *trans,cis*-[CoCl_2((R)-pn)$_2$]$^+$ ion ((R)-pn=(R)-1,2-propanediamine) was claimed,[3] no detailed spectral evidence has been reported.

Most of mono-N-alkyl-substituted 1,2-diamines gave rise to the trans,trans configuration, as exemplified by N-methyl-1,2-ethanediamine,[1,4] (S)-1-methylamino-2-propanamine,[5] and (S)-1-ethylamino-2-propanamine.[6] It was found that (R)-N,N'-dimethyl-1,2-propanediamine afforded both of the trans,trans and trans,cis isomers of dinitrocobalt(III) complex.[7] This is the sole example reported so far, where the two possible isomers were isolated separatly.

In a previous paper,[8] we reported on the cobalt(III) complexes of (S)-2-(methylaminomethyl)pyrrolidine (=N-Meampr), which is a chiral unsymmetrical 1,2-diamine derived from (S)-proline. The [CoX_2(N-Meampr)$_2$]$^+$ (X=NO_2^- or Cl^-) complexes take specifically the trans,cis configuration.[8] We supposed that the unique predominance of the trans,cis isomer over the trans,trans for N-Meampr complexes was due, at least in part, to the presence of pyrrolidine ring in the ligand. With a view to elucidate the effect of pyrrolidinyl moiety build in a diamine molecule, the stereochemical features of cobalt(III) complexes with (S)-2-amino-methylpyrrolidine (=ampr) were investigated in this study. If the steric effect of pyrrolidine ring supresses any other factors controlling the geometry of complexes, the trans,cis isomer would be exclusively formed even for the ampr complexes.

Experimental

trans,cis-*Dinitrobis[(S)-2-aminomethylpyrrolidine]cobalt(III) Perchlorate,* trans,cis-*[Co(NO*$_2$*)*$_2$*(ampr)*$_2$*]ClO*$_4$. Sodium hexanitrocobaltate(III) (4.04 g; 0.01 mol) was added to a solution of ampr (2.00 g; 0.02 mol) in water (30 cm^3), and the resultant solution was heated at 60—65 °C for 15 min. Sodium perchlorate (4.0 g) dissolved in water (4 cm^3) was added, and the solution was cooled in a refrigerator overnight. Yellow crystals were filtered off, washed with ethanol and diethyl ether, and air-dried. Yield; 1.5—2.0 g. The filtrate (designated as F-1) was kept for obtaining the trans,trans isomer.

The crystals obtained above were recrystallized fractionally from warm water (80 °C). Less soluble yellow fine needle crystals were collected, washed with ethanol and diethyl ether, and air-dried. Yield; 0.5—0.8 g. Found: C, 26.24; H, 5.64; N, 18.82%. Calcd for $C_{10}H_{24}N_6O_8ClCo$: C, 26.65; H, 5.37; N, 18.65%.

trans,trans-*Dinitrobis[(S)-2-aminomethylpyrrolidine]cobalt(III) Perchlorate,* trans,trans-*[Co(NO*$_2$*)*$_2$*(ampr)*$_2$*]ClO*$_4$. The filtrate from the trans,cis isomer was gradually evaporated at room temperature to separate out brown crystals (0.5—1.0 g) after several days. The same product was also obtained from the filtrate F-1. Brown crystals were recrystallized from warm water (80 °C). Found: C, 26.92; H, 5.75; N, 18.39%. Calcd for $C_{10}H_{24}N_6O_8ClCo$: C, 26.65; H, 5.37; N, 18.65%.

trans,cis-*Chloronitrobis[(S)-2-aminomethylpyrrolidine]cobalt(III) Perchlorate,* trans,cis-*[CoCl(NO*$_2$*)(ampr)*$_2$*]ClO*$_4$ *(Chloronitro-1).* *trans,cis*-[Co(NO_2)$_2$(ampr)$_2$]ClO_4 (0.65 g) was added to 1 M HCl (10 cm^3; 1 M=1 mol dm^{-3}), and heated for 5 min at 65 °C with occasional stirring. To the mixture was added $LiClO_4$ (1.0 g), and cooled in an ice bath. The crystals were filtered off, washed with ethanol and diethyl ether, and air-dried. Yield; 0.55 g. The crude product was recrystallized from hot water. Found: C, 27.07; H, 5.38; N, 16.01%. Calcd for $C_{10}H_{24}N_5O_6Cl_2Co$: C, 27.28; H, 5.50; N, 15.91%.

trans,trans-*Chloronitrobis[(S)-2-aminomethylpyrrolidine]cobalt(III) Perchlorate,* trans,trans-*[CoCl(NO*$_2$*)(ampr)*$_2$*]ClO*$_4$ *(Chloronitro-2).* *trans,trans*-[Co(NO_2)$_2$(ampr)$_2$]ClO_4 (7.8 g) was added to 8 M HCl (27 cm^3), and the mixture was heated at 70—75 °C for 5 min with occasional stirring. To the mixture was added $LiClO_4$ (4 g), and the whole was cooled in an ice bath for 3 h. Orange-red precipitate thus formed was filtered off, and washed with ethanol and diethyl ether. Yield; *ca.* 5 g. The precipitate was dissolved in warm water (80 cm^3 at 70 °C), and filtered while hot. To the filtrate was added concd. HCl (5 cm^3), and cooled in a refrigerator overnight. Orange-red crystals were collected, washed with ethanol and diethyl ether, and air-dried. Found: C, 27.22; H, 5.11; N, 15.48%. Calcd for $C_{10}H_{24}N_5O_6Cl_2Co$: C, 27.28; H, 5.50; N, 15.91%.

trans,trans-*Chloronitrobis[(S)-2-aminomethylpyrrolidine]cobalt(III) Chloride,* trans,trans-*[CoCl(NO_2)(ampr)$_2$]Cl (Chloronitro-3).* The filtrate after the removal of crude *trans,trans*-[CoCl(NO_2)(ampr)$_2$]ClO_4 mentioned above was poured into a mixture of ethanol (100 cm^3) and diethyl ether (500 cm^3), and the mixture was cooled in a refrigerator. Reddish pink precipitate deposited was collected and washed with diethyl ether. The crude product was recrystallized from methanol and diethyl ether. Found: C, 31.52; H, 6.16; N, 18.47%. Calcd for $C_{10}H_{24}N_5O_2Cl_2Co$: C, 31.93; H, 6.44; N, 18.62%.

trans,cis-*Dichlorobis[(S)-2-aminomethylpyrrolidine]cobalt(III) Perchlorate,* trans,cis-*[CoCl$_2$(ampr)$_2$]ClO$_4$.* *trans,cis*-[Co(NO_2)$_2$(ampr)$_2$]ClO_4 (1.5 g) was added to concd HCl (15 cm^3) and heated on a steam bath, until deep green crystals began to appear. The mixture was cooled in a refrigerator overnight, and the crystals were collected and washed with ethanol and diethyl ether. Yield; 0.75 g. The crude product was recrystallized from concd HCl. Found: C, 27.91; H, 5.78; N, 13.39%. Calcd for $C_{10}H_{24}N_4O_4Cl_3Co$: C, 27.94; H, 5.63; N, 13.05%.

trans,trans-*Dichlorobis[(S)-2-aminomethylpyrrolidine]cobalt(III) Perchlorate,* trans,trans-*[CoCl$_2$(ampr)$_2$]ClO$_4$.* *trans,trans*-[Co(NO_2)$_2$(ampr)$_2$]ClO_4 (3.3 g) was added to concd HCl (35 cm^3), and heated on a steam bath, until the solution became deep green. To the solution was added 70% $HClO_4$ (5 cm^3), and the whole was cooled in a refrigerator overnight. Green crystals were collected and washed in a usual way. Yield; 0.9 g. Found: C, 27.69; H, 5.59; N, 12.98%. Calcd for $C_{10}H_{24}N_4O_4Cl_3Co$: C, 27.94; H, 5.63; N, 13.05%.

Measurements. Visible and ultraviolet absorption spectra were obtained with a Hitachi 340 spectrophotometer. Circular dichroism spectra were recorded with a JASCO J-500 spectropolarimeter. ^{13}C-NMR spectra were obtained on a JEOL PFT-100 spectrometer (24.75 MHz), using TMS as an external reference.

Results and Discussion

It was demonstrated that [Co(NO_2)$_2$(ampr)$_2$]ClO_4, the dinitrocobalt(III) complex of ampr prepared by a reaction of ampr with Na_3[Co(NO_2)$_6$] and succesive addition of $NaClO_4$, could be fractionated into two distinct crystalline products from aqueous solution; *i.e.* less soluble brownish yellow needles and more soluble brown blocks. Both forms equally showed the elemental analytical data corresponding to the formula [Co(NO_2)$_2$($C_5H_{12}N_2$)$_2$]ClO_4, and, further, exhibited almost identical electronic absorption spectra. The spectra showed the absorption band characteristic of cobalt(III) complexes with the nitro group at 29000 cm^{-1}, so that the nitro ligands were considered to locate at the trans position to each other in the two forms.[1,5] The circular dichroism (CD) spectra of these dinitro complexes were, however, apparently different to each other as shown in Fig. 2. The numerical spectral data are summarized in Table 1. These findings unambiguously indicated that the two possible isomers of *trans*(NO_2)-[Co(NO_2)$_2$(ampr)$_2$]-ClO_4 (illustrated as structures **a** and **b** in Fig. 3) were isolated.

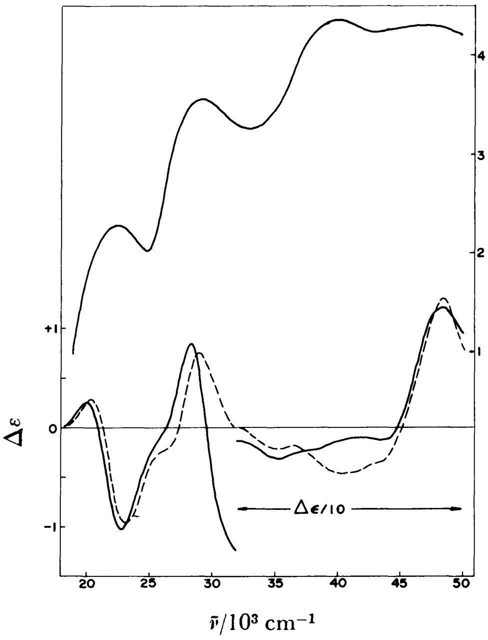


Fig. 2. Electronic absorption and CD spectra for the less soluble (trans,cis isomer; ——) and the more soluble form (trans,trans isomer; — — —) of *trans*-(NO_2)[Co(NO_2)$_2$(ampr)$_2$]ClO_4.

With a view to assign both the fractions of *trans*-(NO_2)-[Co(NO_2)$_2$(ampr)$_2$]ClO_4 to either of structure **a** (trans,cis) and **b** (trans,trans), the dinitro complexes were converted into the chloronitro complexes. Figure 3 suggests that *trans,cis*-[Co(NO_2)$_2$(ampr)$_2$]$^+$ ion gives the single species of *trans,cis*-[CoCl(NO_2)-(ampr)$_2$]$^+$ ions (structure **c**), while *trans,trans*-[Co-(NO_2)$_2$(ampr)$_2$]$^+$ ion yield, in principle, two diastereomeric *trans,trans*-[CoCl(NO_2)(ampr)$_2$]$^+$ ions (structure **d** and **e**). In practice, the less soluble dinitro complex gave a chloronitro complex as perchlorate (chloronitro-1) in an almost quantitative yield, and the more soluble dinitro complex also afforded another chloronitro complex as perchlorate (chloronitro-2). It was interestingly found that the third chloronitro complex could be isolated from the filtrate of chloronitro-2 as chloride salt (chloronitro-3).

It was reported that *trans*- and *cis*-[CoCl(NO_2)(en)$_2$]$^+$ ion (en=1,2-ethanediamine) showed the absorption bands assignable to the d-d transition at 21600 and 20100 cm^{-1}, respectively.[9] The absorption spectra of chloronitro complexes of ampr resembled to one another, and exhibited the first absorption bands at *ca.* 20900 cm^{-1} (Fig. 4 and Table 1). It is certain that the ligand field provided by ampr, an *N*-substituted 1,2-diamine, is somewhat weaker than that of en,[10] so that three chloronitro complexes could be reasonably assigned to the *trans*(Cl,NO_2) configuration.

TABLE 1. ABSORPTION AND CD DATA OF [CoXY(ampr)$_2$]$^+$ COMPLEXES

Complex	Absorption		CD	
	$\tilde{\nu}_{\mathrm{max}}$/cm^{-1}	(log ε)	$\tilde{\nu}_{\mathrm{ext}}$/cm^{-1}	($\Delta\varepsilon$)
trans,cis-[Co(NO$_2$)$_2$(ampr)$_2$]ClO$_4$[a)]	22,700	(2.29)	20,040	(+0.26)
			22,620	(−1.03)
	29,000	(3.54)	28,250	(+0.84)
	39,600	(4.38)	35,210	(−2.97)
			38,600	(−2.0)[d)]
	47,500	(4.26)	43,860	(−1.4)
			48,250	(+12.1)
trans,trans-[Co(NO$_2$)$_2$(ampr)$_2$]ClO$_4$[a)]	22,400	(2.28)	20,400	(+0.29)
			23,090	(−0.96)
	29,000	(3.54)	26,000	(−0.25)[d)]
			28,980	(+0.75)
	39,800	(4.36)	35,210	(−2.1)
			40,500	(−4.6)
	47,300	(4.30)	43,860	(−3.0)[d)]
			48,250	(+12.7)
trans,cis-[CoCl(NO$_2$)(ampr)$_2$]ClO$_4$[b)] (Chloronitro-1)	20,400	(1.97)	17,330	(+0.12)
			19,650	(−0.81)
			22,320	(+0.30)
	28,900	(3.10)	27,030	(+0.34)
			32,790	(−0.88)
trans,trans-[CoCl(NO$_2$)(ampr)$_2$]ClO$_4$[b)] (Chloronitro-2)	20,350	(1.96)	16,260	(−0.03)
			17,240	(+0.03)
			19,570	(−0.83)
	28,740	(3.19)	26,880	(+0.51)
			30,030	(−0.12)[d)]
			33,600	(−1.1)[d)]
trans,trans-[CoCl(NO$_2$)(ampr)$_2$]Cl[b)] (Chloronitro-3)	20,420	(1.97)	19,340	(−1.03)
			22,220	(+0.42)
	28,800	(3.17)	26,880	(+0.79)
			29,500	(−0.53)[d)]
trans,cis-[CoCl$_2$(ampr)$_2$]ClO$_4$[c)]	16,000	(1.72)	14,750	(+0.37)
			16,470	(−0.77)
	21,410	(1.46)	20,880	(+0.63)
	25,450	(1.77)	26,740	(+0.42)
trans,trans-[CoCl$_2$(ampr)$_2$]ClO$_4$[c)]	16,000	(1.71)	14,750	(+0.33)
			16,450	(−0.74)
	21,410	(1.50)	20,870	(+0.59)
	25,640	(1.81)	26,740	(+0.39)

a) In H$_2$O. b) In 1 M NaCl. c) In methanol. d) Shoulder.

Further, the CD spectra of chloronitro complexes were obviously different from one another, and did not change after recrystallization. This means that the three possible diastereomer of *trans*(Cl,NO$_2$)-[CoCl(NO$_2$)(ampr)$_2$]$^+$ ion could be isolated separately. Thus, the more soluble dinitro complex, which gave rise to two isomers of chloronitro complex, should have the trans,trans structure, and, therefore, the less soluble dinitro complex should take the trans,cis configuration.

If the above mentioned assignments are valid, chloronitro-1 must have the trans,cis configuration (structure **c**), in which the two ampr ligands are in unequal circumstances due to the C$_1$ symmetry of **c**. On the other hand, chloronitro-2 and -3 are considered to adopt either of the trans,trans configurations (structure **d** or **e**) with C$_2$ symmetry. In those structures, the two ampr molecules should be situated in the identical environment, though the environment of ampr in **d** is intrinsically different from that in **e**. In order to make sure the assignment, ^{13}C-NMR spectra of chloronitro complexes were examined.

The ^{13}C-NMR spectrum of chloronitro-3 was obtained in 1 M DCl solution, the data being given in Table 2. The spectrum showed five resonances, with the incidental overlap of two signals at 49.8 ppm. This support that chloronitro-3 certainly adopts the trans,trans configuration and consists of the single species, though the exact structure, **d** or **e**, of this isomer has not been established. The chloro-

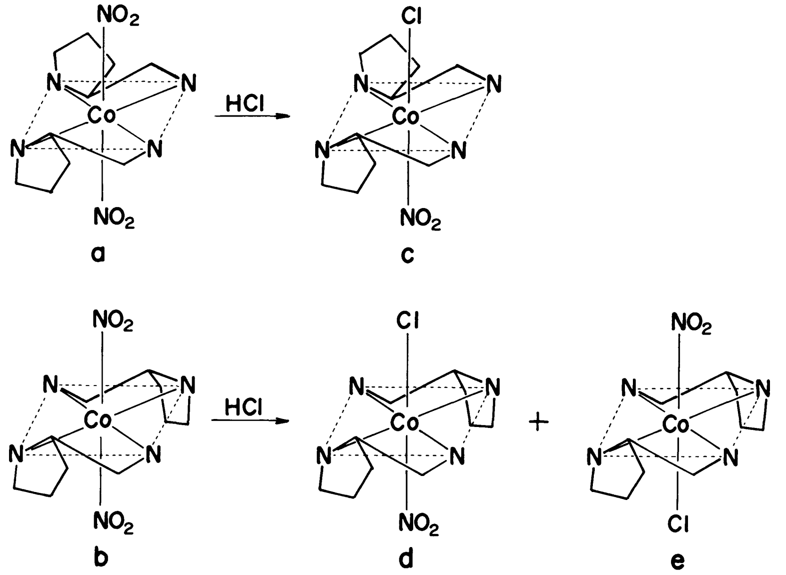


Fig. 3. Structures of *trans,cis*-$[Co(NO_2)_2(ampr)_2]^+$ ion (**a**), *trans,trans*-$[Co(NO_2)_2(ampr)_2]^+$ ion (**b**), *trans,cis*-$[CoCl(NO_2)(ampr)_2]^+$ ion (**c**), and *trans,trans*-$[CoCl(NO_2)(ampr)_2]^+$ ion (**d** and **e**).

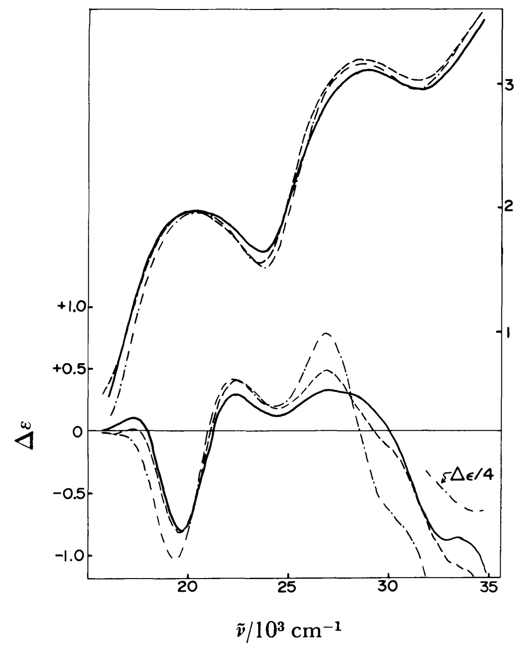


Fig. 4. Absorption and CD spectra of chloronitro-1 (——), chloronitro-2 (— — —), and chloronitro-3 (-·-·-·-).

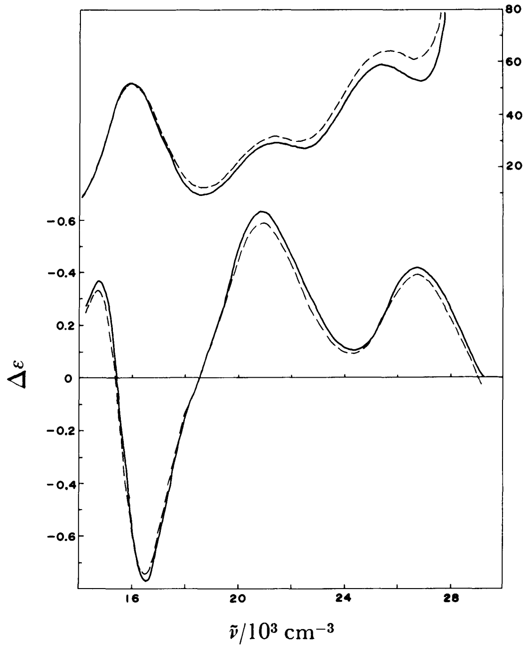


Fig. 5. Visible absorption and CD spectra of *trans,cis*-$[CoCl_2(ampr)_2]ClO_4$ (——), and *trans,trans*-$[CoCl_2(ampr)_2]ClO_4$ (— — —).

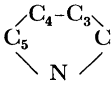
nitro-1 and -2 provided no satisfactory spectra in DCl solution because of the low solubility of the complexes and structural changes (the aquation of the chloride ligand and/or trans-cis isomerization) occured during the measurements.

The ¹³C-NMR spectrum of chloronitro-1 could, however, be taken in a mixture of 1 M DCl and acetone. Although a few signals were occasionally overlapped, the spectrum could be analyzed to be composed of ten resonances as given in Table 2. This means that two ampr ligands are in the different circumstances, being consistent with the expected stereochemical requirements from the structure **c**. Thus, the ¹³C-NMR features of chloronitro complexes, as well as the absorption and CD spectral data, confirmed without conflict that the less soluble dinitro complex adopted the trans,cis configuration, while the more soluble one took the trans,trans configuration.

It is clarified, therefore, that both trans,cis and trans,trans isomers exist with respect to ampr complexes. The steric effects brought about by pyrrolidine ring appeared not to be so significant in ampr complexes, compared with those found in *N*-Meampr complexes, where only the trans,cis isomer is existent. This is possibly due to the difference in the steric repulsions

Table 2. ^{13}C-NMR spectral data[a)] of chloronitro complexes

trans,trans- $[CoCl(NO_2)(ampr)_2]Cl$[b)] (chloronitro-3)	*trans,cis*- $[CoCl(NO_2)(ampr)_2]ClO_4$[c)] (chloronitro-1)	Assignments[d)]
27.01 (1)[e)]	27.00 (2)	C_3, C_4
27.68 (1)	27.35 (1)	
	27.78 (1)	
49.81 (2)	49.24 (1)	C_1, C_5
	50.10 (3)	
65.41 (1)	65.04 (1)	
	65.47 (1)	C_2

a) Ppm from TMS (external). b) Measureed in 1 M DCl. c) Measured in a mixture of 1 M DCl and acetone. d) The order of carbon atoms in ampr is as follows;  e) The values in parentheses are approximate relative intensities of the signals.

between pyrrolidinyl moiety and *N*-methylamino ($-NH(CH_3)$) group in *N*-Meampr complexes, and between pyrrolidinyl and primary amino ($-NH_2$) group in ampr complexes, particularly in the trans,trans configuration. The steric repulsion must be considerably severer in *N*-Meampr complexes than in ampr complexes. Hence, it is shown that the steric effect of pyrrolidine ring is not so pronounced as to give solely the trans,cis isomer for complexes with any diamines having this ring.

Finally, both of the dinitro complexes were converted into the corresponding *trans*(Cl)-dichloro complexes. No configurational change was expected during this conversion, as the cases of other *N*-substituted 1,2-diamine complexes.[1,5,6)] The absorption and CD spectra of two isomers resembled closely to each other, though slight differences were still acknowledged (Fig. 5). This displays a novel example of isolation of two diastereomers possible for *trans*(Cl)-$[CoCl_2(N\text{-}N')_2]^+$ ion.

References

1) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **7**, 915 (1968).

2) Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Jpn.*, **35**, 1131 (1962).

3) C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

4) W. T. Robinson, D. A. Buckingham, G. Chandler, L. G. Marzilli, and A. M. Sargeson, *J. Chem. Soc., D*, **1970**, 539.

5) M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Chem.*, **9**, 1476 (1970).

6) T. Kitamura, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, **16**, 585 (1977).

7) J. A. Tiethof and D. W. Cooke, *Inorg. Nucl. Chem. Lett.*, **8**, 1013 (1972).

8) T. Kitamura, Y. Sato, M. Saburi, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **50**, 1780 (1977).

9) K. Yamasaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **50**, 2624 (1977).

10) For example: J. A. Tiethof and D. W. Cooke, *Inorg. Chem.*, **11**, 315 (1972).