Inorganic Chemistry, Vol. 14, No. 10, 1975 **2347**

Contribution from the Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Sendai 980, Japan

New Nickel(II) Complexes of Some Optically Active Tetraamines with Pyrrolidinyl Groups

SADAO KITAGAWA, TASUKU MURAKAMI, and MASAHIRO HATANO*[1]

Received October 29, 1974 AIC40751O

The following five optically active tetraamines including two pyrrolidinyl groups in each molecule were prepared from L-proline, 1,2-bis[2(*S*)-2-aminomethyl-1-pyrrolidinyl]ethane, 1,2-bis[2(*S*)-2-*N*-methylaminomethyl-1-pyrrolidinyl]ethane, *N*,*N*'-bis[2(*S*)-2-pyrrolidinylmethyl]ethylenediamine, *N*,*N*'-bis[2(*S*)-2-pyrrolidinylmethyl]-1(*R*),2(*R*)-cyclohexanediamine, and *N*,*N*'-bis[2(*S*)-2-pyrrolidinylmethyl]-1(*S*),2(*S*)-cyclohexanediamine. A type of stereospecificity was found in the coordination of these tetraamines to nickel(II) ion; the two former tetraamines form blue octahedral complexes, whereas the latter three tetraamines form yellow square-planar ones in aqueous solutions. Futhermore, the planar complexes are converted into octahedral mixed complexes with α-amino acids or ethylenediamine. The conformations of the planar and mixed complexes are discussed on the basis of their circular dichroism spectra.

Linear tetraamines such as triethylenetetramine (trien) are flexible and able to coordinate to a metal ion in either a planar or a nonplanar arrangement. Coordination of the linear tetraamine about a six-covalent metal ion can give many geometrical and optical isomers.[2,3] In the complexes of the tetraamine with cobalt(III) ion, some of these isomers have been isolated on the basis of the inert character of the cobalt(III) ion and identified X-ray crystallographically.[4,5]

On the other hand, nickel(II) complexes have labile character for the ligand-exchange reactions, and therefore it is much more difficult to isolate each of the optical and/or geometrical isomers of the nickel(II) complexes with the linear tetraamine by procedures similar to that in the cobalt(III) complexes. A tetraamine having a type of steric restriction within itself may coordinate stereospecifically to the labile nickel(II) ion, and only one of the isomers may be isolated. In other words, one of the purposes of this paper is to find the tetraamine which can ligate to nickel(II) ion stereospecifically.

A great stereoselectivity is possible with L-proline since the nitrogen within the pyrrolidine ring can coordinate only with the *S* configuration.[6-9] This requirement also puts a restriction on the overall geometry of the complex of the ligand with nickel(II) ion. In fact, from an aqueous solution containing nickel(II) carbonate and L-proline, predominantly *fac*(*N*)-Λ-[Ni(L-prolinate)$_3$]$^-$ was isolated.[10]

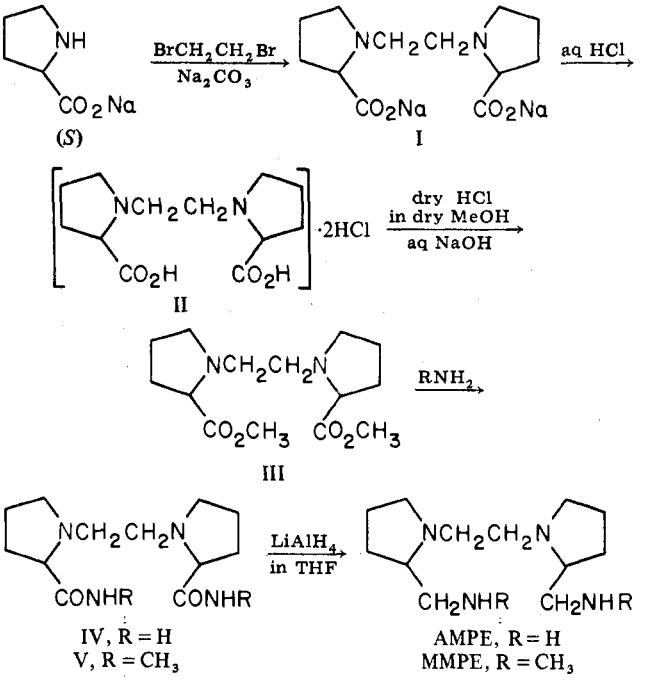
On the basis of the above consideration of the steric restriction for the ligation of L-prolinate ion, optically active tetraamines including the pyrrolidinyl groups are also expected to form stereospecific nickel(II) complexes. We prepared the five tetraamines including two pyrrolidinyl groups in each molecule from L-proline (Figure 1).

A type of stereospecificity was found in the coordination of these tetraamines to nickel(II) ion; 1,2-bis[2(*S*)-2-aminomethyl-1-pyrrolidinyl]ethane (abbreviated to AMPE) and 1,2-bis[2(*S*)-2-*N*-methylaminomethyl-1-pyrrolidinyl]-ethane (MMPE) formed octahedral complexes, whereas *N*,*N*'-bis[2(*S*)-2-pyrrolidinylmethyl]ethylenediamine (PMEN), *N*,*N*'-bis[2(*S*)-2-pyrrolidinylmethyl]-1(*R*),2(*R*)-cyclohexanediamine (*RR*-PMCN), and *N*,*N*'-bis[2(*S*)-2-pyrrolidinylmethyl]-1(*S*),2(*S*)-cyclohexanediamine (*SS*-PMCN) formed square-planar ones.[11] Furthermore, the planar PMEN, *RR*-PMCN, and *SS*-PMCN complexes were converted into the octahedral mixed complexes with α-amino acids or ethylenediamine.

Experimental Section

Materials. 1(*R*),2(*R*)- and 1(*S*),2(*S*)-cyclohexanediamines were obtained by resolution of their commercial racemate according to the literature;[12] bp 78–80° (15 mm) (crystallized soon after distillation). The values of the specific rotation, $[\alpha]_D$, were −35.8° for the (*R*),(*R*)-diamine and +35.4° for the (*S*),(*S*)-diamine at 25° (3% in H_2O). The absolute configurations of the two enantiomers were adopted according to Gillard.[13] Nickel(II) perchlorate was obtained from nickel(II) sulfate and barium perchlorate. Other materials were commercial grades which were purified, if necessary, by the usual procedures.

Scheme I



Preparation of Tetraamines. 1,2-Bis[2(*S*)-2-aminomethyl-1-pyrrolidinyl]ethane (AMPE) and 1,2-bis[2(*S*)-2-*N*-methylaminomethyl-1-pyrrolidinyl]ethane (MMPE) were prepared according to Scheme I.

N,*N*'-Bis[2(*S*)-2-pyrrolidinylmethyl]-1(*R*),2(*R*)-cyclohexanediamine (*RR*-PMCN), *N*,*N*'-bis[2(*S*)-2-pyrrolidinylmethyl]-1(*S*),2(*S*)-cyclohexanediamine (*SS*-PMCN), and *N*,*N*'-bis[2(*S*)-2-pyrrolidinylmethyl]-1,2-ethylenediamine (PMEN) were prepared according to Scheme II.

1,2-Bis[2(*S*)-2-carbomethoxy-1-pyrrolidinyl]ethane(III). To a solution of L-proline (115 g, 1.0 mol) in 200 ml of water was added a solution of sodium hydroxide (40 g, 1.0 mol) in 250 ml of water under stirring and water cooling. After stirring for 30 min at 40°, 53 g (0.5 mol) of sodium carbonate and 86.7 g (0.46 mol) of 1,2-dibromoethane were added. The mixture was then heated at 70° for 4 hr under vigorous stirring. After washing with petroleum ether, the reaction mixture was acidified (to pH 2) with 17% hydrochloric acid and evaporated, and the residue was dried in vacuo at 45°. The solid obtained was dissolved into 1000 ml of absolute methanol and filtered. The filtrate, which contains mainly 1,2-bis[2(*S*)-2-carboxyl-1-pyrrolidinyl]ethane dihydrochloride (II), was used for the following esterification.

The methanol solution of II was poured into a 2000-ml four-necked

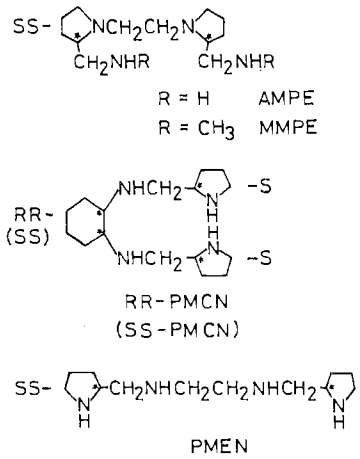


Figure 1. Tetraamines including pyrrolidinyl groups; *R* and *S* represent the absolute configurations of asymmetric carbon atoms.

flask, saturated with dry hydrogen chloride gas with stirring, and then heated to reflux for 4 hr. The reaction mixture was filtered, and the filtrate was concentrated under vacuum to give a yellow syrup. The syrup was made alkaline (above pH 10) with 5 *N* sodium hydroxide and extracted with ether. The extract was dried with anhydrous sodium sulfate, evaporated, and then fractionated under reduced pressure to give III, bp 136–137° (1 mm); yield 50 g (38% based on 1,2-dibromoethane); $[\alpha]^{28}D$ −131° (4% in H_2O); $n^{21.5}D$ 1.4812; d^{24} 1.080. Anal. Calcd for $C_{14}H_{24}N_2O_4$: C, 59.1; H, 8.50; N, 9.84. Found: C, 59.3; H, 8.51; N, 10.4.

1,2-Bis[2(*S*)-2-carbamoyl-1-pyrrolidinyl]ethane (IV). Compound III, 21.6 g (0.076 mol), was dissolved in 250 ml of absolute methanol and saturated with dry ammonia, and the solution was allowed to stand for 10 days at room temperature. The precipitated white needles were filtered and the filtrate was evaporated to give a further amount of needles. The combined needles were washed with ether and dried in vacuo. The yield was almost quantitative (19.2 g); mp 203–204° dec. Anal. Calcd for $C_{12}H_{22}N_4O_2$: C, 56.7; H, 8.72; N, 22.0. Found: C, 56.7; H, 8.80; N, 24.2.

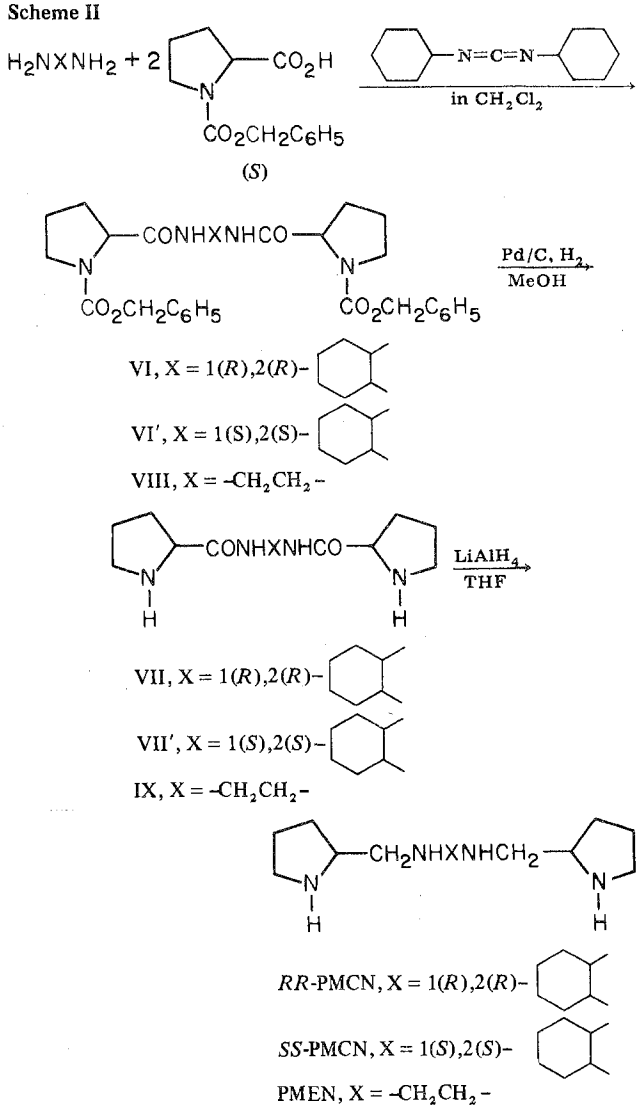
1,2-Bis[2(*S*)-2-aminomethyl-1-pyrrolidinyl]ethane (AMPE). A suspension of IV (8.0 g, 0.032 mol) in 100 ml of anhydrous tetrahydrofuran (THF) was added dropwise to a suspension of 4.8 g (0.126 mol) of lithium aluminum hydride in 100 ml of anhydrous THF in an ice bath; the mixture was stirred and heated to reflux for 50 hr. The reaction mixture was chilled and 20 g (1.11 mol) of water was added dropwise with vigorous stirring in an ice bath. The precipitated mass was filtered off and washed with THF. The combined filtrate and washings were dried with anhydrous sodium sulfate, followed by evaporation of the solvent under vacuum to give AMPE as a light yellow oil which crystallized in a refrigerator; yield 6.1 g (85%); $[\alpha]^{23}D$ −137.6° (3% in H_2O). Anal. Calcd for $C_{12}H_{26}N_4$: C, 63.6; H, 11.6; N, 24.7. Found: C, 62.9; H, 11.3; N, 23.7.

1,2-Bis[2(*S*)-2-*N*-methylcarbamoyl-1-pyrrolidinyl]ethane (V). Compound V was prepared with the same procedure as in the case of IV, by using 21.6 g (0.076 mol) of III and methylamine instead of ammonia. Quantitative yield (21.2 g) of V was obtained as white crystals after evaporation of the solvent. The crystals were washed with petroleum ether and dried in vacuo; mp 133–134°; $[\alpha]^{24.5}D$ −146.4° (2.5% in H_2O). Anal. Calcd for $C_{14}H_{26}N_4O_2$: C, 59.6; H, 9.23; N, 19.8. Found: C, 59.5; H, 9.53; N, 21.6.

1,2-Bis[2(*S*)-2-*N*-methylaminomethyl-1-pyrrolidinyl]ethane (MMPE). MMPE was prepared with the same procedure as AMPE, by using 15.0 g (0.053 mol) of V and 6.5 g (0.171 mol) of lithium aluminum hydride in 250 ml of anhydrous THF. MMPE was obtained as a yellowish oil; yield 12.1 g (90%); $[\alpha]^{24}D$ −128.9° (3% in H_2O). Anal. Calcd for $C_{14}H_{30}N_4$: C, 66.1; H, 11.8; N, 22.0. Found: C, 66.0; H, 11.5; N, 21.0.

***N,N'*-Bis[*N*-carbobenzoxy-(*S*)-prolyl]-1(*R*),2(*R*)-cyclohexanediamine (VI).** A solution of 11.4 g (0.10 mol) of 1(*R*),2(*R*)-cyclohexanediamine, 49.8 g (0.20 mol) of *N*-carbobenzoxy-(*S*)-proline, and 41.3 g (0.20 mol) of dicyclohexylcarbodiimide (DCC) in 200 ml of dichloromethane was allowed to stand for 3 days at room temperature. Precipitated white crystals were filtered off and the filtrate was washed with 1 *N* hydrochloric acid, water, a saturated sodium bicarbonate solution, and then water. Thus treated, the solution was dried with anhydrous sodium sulfate and evaporated to give a white solid. This crude product was recrystallized from dichloromethane and petroleum ether. White needles were obtained; yield 13.0 g (23%); mp 184–185°. Anal. Calcd for $C_{32}H_{40}N_4O_6$: C, 66.8; H, 6.99; N, 9.71. Found: C, 66.5; H, 7.40; N, 9.88.

Scheme II



***N,N'*-Bis[(*S*)-prolyl]-1(*R*),2(*R*)-cyclohexanediamine (VII).** Compound VII was prepared by hydrogenolysis of VI (13.0 g, 0.023 mol) in 450 ml of methanol, by using 1.0 g of palladium black as catalyst. The reaction was carried out at room temperature for 12 hr under stirring and introducing hydrogen gas. The reaction mixture was then filtered and the filtrate was evaporated and dried in vacuo to give VII as a white solid in quantitative yield (6.9 g).

***N,N'*-Bis[2(*S*)-2-pyrrolidinylmethyl]-1(*R*),2(*R*)-cyclohexanediamine (*RR*-PMCN).** *RR*-PMCN was prepared by reducing 6.9 g (0.023 mol) of II with 3.4 g (0.09 mol) of lithium aluminum hydride in 170 ml of anhydrous THF according to the procedure mentioned in the preparation of AMPE. A viscous yellowish oil was obtained. The crude product was purified as follows; the product was dissolved in 50 ml of water, and a small amount of charcoal was added and shaken. After filtration, the filtrate was evaporated and dried in vacuo to give pure *RR*-PMCN; yield 4.9 g (78%); $[\alpha]^{22}D$ −5.66° (4.3% in H_2O). Anal. Calcd for $C_{16}H_{32}N_4$: C, 68.6; H, 11.5; N, 19.9. Found: C, 68.1; H, 11.5; N, 19.4.

***N,N'*-Bis[2(*S*)-2-pyrrolidinylmethyl]-1(*S*),2(*S*)-cyclohexanediamine (*SS*-PMCN).** *SS*-PMCN was prepared with the same procedure as *RR*-PMCN by using 1(*S*),2(*S*)-cyclohexanediamine instead of 1-(*R*),2(*R*)-cyclohexanediamine.

***N,N'*-Bis[*N*-carbobenzoxy-(*S*)-prolyl]ethylenediamine (VIII).** Compound VIII was prepared with the same procedure as used for

Table I. Analytical Data of Isolated Complexes

Complex	%C		%H		%N	
	Calcd	Found	Calcd	Found	Calcd	Found
[Ni(AMPE)(en)]-$(ClO_4)_2$	30.90	31.03	6.30	6.35	15.44	15.35
[Ni(PMEN)(en)]-$(ClO_4)_2$	30.90	30.04	6.30	6.27	15.44	15.29
[Ni(*RR*-PMCN)-(en)]$(ClO_4)_2$	36.15	36.03	6.74	6.79	14.04	13.36
[Ni(*SS*-PMCN)-(en)]$(ClO_4)_2$	36.15	36.10	6.74	6.72	14.04	13.76
[Ni(*RR*-PMCN)]-$(ClO_4)_2$	35.72	35.45	5.99	5.95	10.41	10.35
[Ni(*SS*-PMCN)]-$(ClO_4)_2$	35.72	35.84	5.99	6.01	10.41	10.41

VI, by using 30 g (0.121 mol) of *N*-carbobenzoxy-(*S*)-proline, 24.2 g (0.121 mol) of DCC, and 3.59 g (0.598 mol) of ethylenediamine in 300 ml of dichloromethane; yield 10.5 g (34%); mp 158–159°. Anal. Calcd for $C_{28}H_{34}N_4O_6$: C, 64.4; H, 6.56; N, 10.7. Found: C, 64.4; H, 6.90; N, 10.0.

***N,N'*-Bis[(*S*)-prolyl]ethylenediamine (IX).** Compound IX was prepared by decarbobenzoxylation of VIII (10.0 g, 0.019 mol) with the procedure mentioned in the preparation of VII. The yield was quantitative (4.90 g; white solid).

***N,N'*-Bis[2(*S*)-2-pyrrolidinylmethyl]ethylenediamine (PMEN).** PMEN was prepared by reducing IX (4.90 g, 0.019 mol) with 2.90 g (0.076 mol) of lithium aluminum hydride in 100 ml of anhydrous THF. The viscous oily product crystallized in a refrigerator after several weeks; yield 3.69 g (91%); $[\alpha]^{25}D$ −3.62°. Anal. Calcd for $C_{12}H_{26}N_4$: C, 63.7; H, 11.6; N, 24.7. Found: C, 63.4; H, 11.8; N, 23.9.

Preparation of Nickel(II) Complexes. Equimolar amounts of nickel(II) perchlorate and each of the five tetraamines were mixed in aqueous solutions. The complex solutions containing AMPE and MMPE were blue, whereas those containing PMEN, *RR*-PMCN, and *SS*-PMCN were yellow.

[Ni(*RR*-PMCN)]$(ClO_4)_2$. To an aqueous solution of nickel(II) perchlorate (0.242 *M*; 2.1 ml) was added the aqueous solution of *RR*-PMCN (0.155 *M*; 3.2 ml). The mixture was allowed to stand for 5 days at room temperature in an evaporating dish. The separated yellow crystals were collected, washed with cold water, ethanol, and ether, and then dried in vacuo; yield 0.24 g (89%). [Ni(*SS*-PMCN)]$(ClO_4)_2$ was isolated with the same method as [Ni(*RR*-PMCN)]$(ClO_4)_2$. The analytical data are summarized in Table I.

[Ni(AMPE)(en)]$(ClO_4)_2$ (en = Ethylenediamine). Equimolar amounts (1.25 mmol) of nickel(II) perchlorate, AMPE, and ethylenediamine were mixed in an aqueous solution. After the mixture was concentrated on a steam bath and allowed to stand overnight at room temperature, purple prisms separated out. The prisms were washed with ethanol and then dried in vacuo; yield 0.59 g (86%).

[Ni(PMEN)(en)]$(ClO_4)_2$, [Ni(*RR*-PMCN)(en)]$(ClO_4)_2$, and [Ni(*SS*-PMCN)(en)]$(ClO_4)_2$ were also isolated with similar procedures, except for the use of 2 or 3 times excess ethylenediamine. See Table I for analysis.

Measurements. Visible and ultraviolet absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. Circular dichroism (CD) spectra in the region of 185–1000 nm were measured with a JASCO J-20A recording spectropolarimeter, and those above 1000 nm were obtained by a JASCO J-100 recording spectropolarimeter, which was specially designed in our laboratory for the measurement between 400 and 2400 nm.[14] Optical rotations were measured with an ATAGO Polax polarimeter. The pH measurements were carried out using a TOA Model HM-20B pH meter.

Each of the complex solutions for spectral observation was prepared by dissolving isolated complexes in water or acetonitrile or by mixing equimolar aliquots of nickel(II) perchlorate or chloride with aqueous tetraamines. In the case of ternary mixed complexes, an equimolar amount of α-amino acids or ethylenediamine was added to the tetraamine complexes. The nickel(II) solution was standardized by an EDTA titration, murexide being used as an indicator.[15]

Results and Discussion

Formation of Nickel(II) Complexes with AMPE, MMPE, PMEN, *RR*-PMCN, and *SS*-PMCN. The five nickel(II) complexes with the tetraamines including the pyrrolidine rings were classified into the two groups as follows. Aqueous solutions of the AMPE and MMPE complexes were blue, whereas those of the *RR*-PMCN, *SS*-PMCN, and PMEN complexes were yellow. The blue and yellow complexes of nickel(II) ion, as is well-known, correspond to the octahedral-type and the square-planar-type complexes, respectively. As seen in Figure 2, the absorption spectra obtained for the blue complexes have three d–d bands being typical of an octahedrally coordinated nickel(II) ion, and the absorption band at about 22,500 cm^{-1} which was observed for the yellow complexes is characteristic of a planar form.[16]

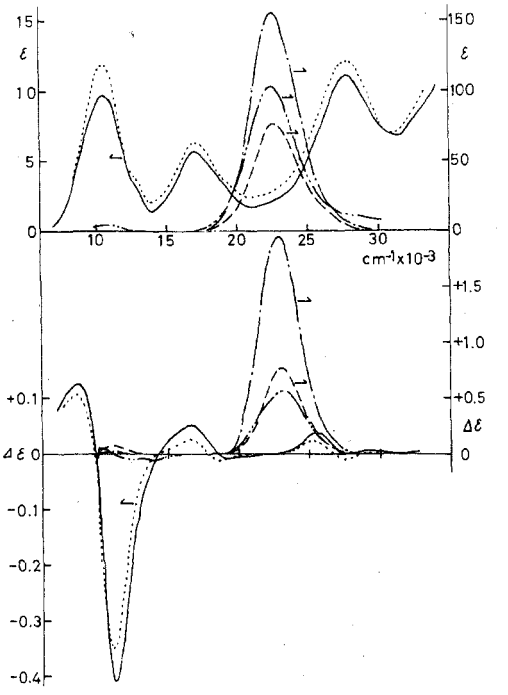


Figure 2. Absorption and CD spectra of the tetraamine–nickel(II) complexes in aqueous solutions: ——, AMPE; · · · · ·, MMPE; — · —, *RR*-PMCN; – – –, PMEN; – · · –, *SS*-PMCN.

Thus, a type of stereospecificity was found in the coordination of these tetraamines to nickel(II) ion. This specificity may be related to the position of the two pyrrolidinyl groups within the tetraamines; AMPE and MMPE have the two pyrrolidinyl groups in their inner parts, whereas the other three tetraamines have them as the terminal groups (see Figure 1). It has been reported that aqueous solutions of nickel(II) complexes of other linear tetraamines, such as trien and 2,-3,2-tet ($NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$), contain small amounts of the planar form at room temperature and that the planar form increases with the addition of an excess of neutral salts or with the rise of temperature.[16–19] In the complexes of PMEN, *RR*-PMCN, and *SS*-PMCN, however, the planar species was predominantly formed in an aqueous solution at room temperature and under the absence of neutral salt.

The preference of square-planar to octahedral coordination in *RR*-PMCN, *SS*-PMCN, and PMEN is very interesting. But the cause of this preference is not obvious, since octahedral coordination of these tetraamines is expected to be not difficult sterically. In fact, the yellow complexes can be readily converted into the blue complexes by the addition of amino acids or ethylenediamine, as described below.

In Figure 2, three strong absorption bands observed for the blue complexes of AMPE and MMPE are assigned to the spin-allowed d–d transitions. The CD spectra reveal optical activity in all three absorption bands but not to the same degree. This behavior can be explained on the basis of

Table II. Electronic Absorption Frequencies of Nickel(II) Complexes with Tetraamines in Aqueous Solutions

Complex system[a]	pH	Absorption max, $cm^{-1} \times 10^{-3}$ ν_1 (ϵ_1)	ν_2 (ϵ_2)	ν_3 (ϵ_3)	Ligating atoms expected from absorption max
Ni-AMPE		10.5 (10.0)	17.2 (5.7)	27.8 (11.2)	N_4O_2
Ni-AMPE-gly	9	10.8 (9.3)	17.6 (7.8)	28.6 (13.2)	N_5O
Ni-AMPE-L-ala	9	10.8 (9.6)	17.6 (7.8)	28.6 (13.5)	N_5O
Ni-AMPE-L-val	10	10.7 (9.8)	17.3 (8.0)	28.3 (15.2)	N_5O
Ni-AMPE-en	8	11.1 (8.2)	18.0 (7.3)	28.6 (13.1)	N_6
Ni-MMPE		10.4 (12.1)	17.0 (6.6)	27.7 (12.2)	N_4O_2
Ni-MMPE-gly	7	10.7 (11.3)	17.4 (8.5)	28.3 (14.1)	N_5O
Ni-MMPE-L-ala	8	10.7 (11.8)	17.3 (9.0)	28.3 (15.3)	N_5O
Ni-MMPE-L-val	10	10.3 (11.7)	16.9 (7.8)	27.8 (17.3)	
Ni-MMPE-L-pro	10	10.2 (10.8)	16.7 (7.3)	27.5 (16.6)	
Ni-MMPE-en	10	10.5 (10.1)	17.5 (6.5)	28.2 (11.9)	
Ni-PMEN-gly	10	11.1 (11.2)	17.9 (9.6)	28.2 (19.0)	N_5O
Ni-PMEN-L-ala	10	11.0 (12.8)	17.8 (11.8)	28.2 (21.9)	N_5O
Ni-PMEN-en		11.2 (11.8)	18.1 (7.3)	28.5 (12.8)	N_6
Ni-*SS*-PMCN-gly[b]	8	11.1 (11.2)	17.9 (10.2)	28.2 (21.2)	N_5O
Ni-*SS*-PMCN-en[b]		11.2 (12.0)	17.9 (8.2)	28.5 (18.4)	N_6
Ni-*RR*-PMCN-en[b]		11.2 (12.9)	18.2 (7.5)	28.5 (12.9)	N_6
$Ni(en)(gly)_2$[e]		10.5 (8,7)	17.8 (8.0)	27.8 (12.7)	N_4O_2
$Ni(en)_2(gly)^+$[e]		10.8 (9.2)	17.9 (8.7)	28.6 (12.0)	N_5O
$Ni(en)_3^{2+}$[e]		11.2 (4.7)	18.4 (4.5)	29.0 (4.6)	N_6
$Ni(l\text{-pn})_3^{2+}$[c,f]		11.1 (6.9)	18.2 (6.3)	28.8 (8.7)	N_6
$Ni(l\text{-chxn})_3^{2+}$[g]		11.3 (7.4)	18.2 (6.8)	28.9 (9.2)	N_6
$Ni(trien)(H_2O)_2^{2+}$[h]		10.2	17.3	28.2	N_4O_2
$Ni(trien)(en)^{2+}$[d,h]		11.0 (10.7)	18.4 (7.9)	28.8 (10.2)	N_6

[a] Abbreviations: gly, glycinate; ala, alaninate; val, valinate; pro, prolinate; pn, propylenediamine; chxn, cyclohexanediamine. [b] Three times excess amount of en or gly was added to the solutions of the tetramine complexes. [c] In acetonitrile. [d] In methanol. [e] C. K. Jorgensen, *Acta Chem. Scand.*, **10**, 887 (1956). [f] H. Ito and J. Fujita, *Bull. Chem. Soc. Jpn.*, **44**, 741 (1971). [g] R. S. Treptow, *Inorg. Chem.*, 7, 1229 (1968). [h] N. F. Curtis and D. A. House, *J. Chem. Soc.*, 6194 (1965).

magnetic dipole selection rules.[20] Thus, only the band ($^3A_{2g} \rightarrow {}^3T_{2g}$) at the lowest wave number is magnetically allowed in the octahedral approximation. Correspondingly, this transition has the most intense circular dichroism. The other two bands ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3T_{1g}(P)$) exhibit only weak optical activity. Furthermore, the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition has a small, positive CD component at about 8500 cm^{-1} and a large, negative one at about 11,000 cm^{-1}, as shown in Figure 2. The splitting of this transition indicates that these blue complexes possess a lower effective symmetry around the nickel(II) ion than an octahedral one. The CD spectra of the AMPE and MMPE complexes are almost identical with each other. This indicates that the two tetraamines coordinate with the same conformation around the central nickel ion, showing that the terminal *N*-methyl groups in MMPE do not affect the conformation of the complex.

For the yellow complexes with *RR*-PMCN, *SS*-PMCN, and PMEN, only one strong absorption band was observed at about 22,500 cm^{-1}, where an intense circular dichroism band was also detected, as shown in Figure 2. In addition, a tiny CD band was detected at the wave number corresponding to the first absorption band ($^3A_{2g} \rightarrow {}^3T_{2g}$) of the blue complexes. This observation shows that in the aqueous solutions of the *RR*-PMCN, *SS*-PMCN, and PMEN complexes small quantities of some sort of octahedrally coordinated species are present besides the square-planar ones. In the previous paper,[21] we found that the blue species increased with lowering of the temperature for bis(*meso*-stilbenediamine)nickel(II) complex in an alcoholic solution. However, the yellow complex of *RR*-PMCN or PMEN in the mixed solvent (ethanol–water, 3:1 by volume) exhibited no spectral change with a variation of temperature to −78°. This finding supports the preference of square-planar to octahedral coordination in these tetraamines as described above.

Formation of Mixed Nickel(II) Complexes of Tetraamines with α-Amino Acids or Ethylenediamine. When an equimolar amount of α-amino acids (amH) or ethylenediamine (en) was added to the solution of the AMPE complex, the solution exhibited a color change from blue to violet, and the absorption maxima shifted slightly to higher wave numbers. Table II shows the absorption maxima observed in the various systems including the tetraamines and ethylenediamine or some α-amino acids, together with those of the related nickel(II) complexes. As expected from the absorption maxima in Table II, it is clear that the AMPE complex is completely converted into the mixed complexes $[Ni(AMPE)(am)]^+$ and $[Ni(AMPE)(en)]^{2+}$ by the addition of an equimolar amount of each amino acid and ethylenediamine, respectively.

However, under the same condition as the AMPE complex, prolinate and valinate ions and ethylenediamine hardly coordinated to the MMPE complex, whereas glycinate and alaninate ions coordinated. This is obvious from the color change of the solution and the shifts of the absorption bands (Table II). These findings are very interesting because ethylenediamine has higher value of stability constant than α-amino acids have for nickel(II) ion. The results lead to the assumption that the terminal *N*-methyl groups in MMPE would interfere with the coordination of ethylenediamine which is bulky because of its gauche structure compared with the planar character of α-amino acidate ions. The assumption is also supported by the fact that prolinate and valinate ions coordinated with more difficulty than glycinate and alaninate ions did.

To the complex of PMEN, glycinate and alaninate ions and ethylenediamine coordinated accompanied by a color change from yellow to violet. The absorption spectra also exhibited three peaks typical of octahedral species, together with a small peak at about 22,500 cm^{-1} which comes from the remaining planar species (Figure 3). These results indicate that the equilibrium

$$[Ni(PMEN)]^{2+} + am^- \text{ (or en)} \rightleftharpoons [Ni(PMEN)(am(\text{or en}))]^{+ \text{ (or } 2+)}$$

exists in each aqueous solution. In acetonitrile, however, the equilibrium above lies completely to the formation of the mixed complexes; no absorption or CD peak was detected at about 22,500 cm^{-1} (Figure 3). It is well-known that planar $[NiN_4]$-type complexes can be converted into octahedral ones by the coordination of additional ligands.[22,23] The ease of the

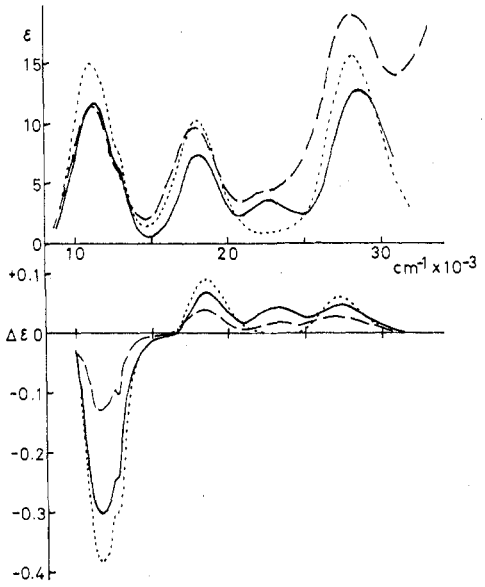


Figure 3. Absorption and CD spectra of the mixed complexes of PMEN with glycine or ethylenediamine: ——, [Ni(PMEN)(en)]$^{2+}$ in water; – – –, [Ni(PMEN)(gly)]$^{+}$ in water; · · · · ·, [Ni(PMEN)(en)]$^{2+}$ in acetonitrile.

conversion depends on the stabilities of the planar and octahedral species and the coordination ability of the second ligand. Furthermore, these factors are affected by the variation in solvents. Similar behavior to the PMEN complex was also observed for the *SS*-PMCN complex in the formation of the mixed complexes. The absorption band at about 22,500 cm^{-1} disappeared by the addition of 3 times excess amount of ethylenediamine or glycine, which indicates that the similar equilibrium described above lies completely to the mixed complexes.

In the case of the *RR*-PMCN complex, on the other hand, the yellow solution did not turn in color by the addition of large excess of glycine up to pH 10, which indicates that the similar equilibrium lies almost to the left. However, it was found that ethylenediamine shifts the equilibrium to the right. When 3 times excess amount of ethylenediamine was added, the solution changed its color from yellow to violet. The spectrum was almost identical with that obtained for the mixed complex of PMEN and ethylenediamine. Thus, *RR*-PMCN prefers remarkably the planar coordination to the octahedral one compared with PMEN and *SS*-PMCN.

The terminal pyrrolidinyl groups in *RR*-PMCN, *SS*-PMCN, and PMEN are more bulky than the terminal *N*-methyl groups in MMPE, and then it was expected that ethylenediamine does not coordinate to the *RR*-PMCN, *SS*-PMCN, and PMEN complexes as well as to the MMPE complex. Contrary to the expectation, however, ethylenediamine coordinated more easily to the former complexes than the MMPE complex. The phenomena are not well explained in terms of only the steric hindrance.

Conformations. As seen in Figure 1, *RR*-PMCN has one *RR*-cyclohexane ring in its central diamine part and two (*S*)-pyrrolidinyl groups at the terminal diamine parts. Since (*R*),(*R*)-cyclohexanediamine can coordinate only with a λ-gauche form,[13,24] the central chelate ring of the complex with *RR*-PMCN should be fixed to the λ form. For the chelate of an (*S*)-diamine moiety a δ-gauche form is expected to be stable.[25] Thus, the conformation of the two terminal chelates with the (*S*)-pyrrolidinyl group may be the δ form. Therefore, when *RR*-PMCN coordinates in a plane, conformation I depicted in Figure 4 is suitable for its planar complex. In conformation I, the central chelate is λ gauche and the terminal chelates are δ gauche.

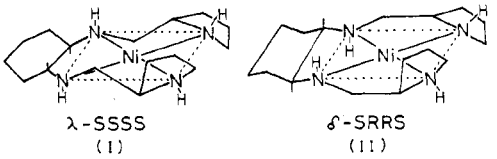


Figure 4. Schematic drawing of the structures for the planar *RR*-PMCN and *SS*-PMCN complexes; δ and λ represent the forms of the central chelate rings, and *R* and *S*, the configurations of the secondary nitrogen atoms.

On the other hand, the central chelate ring of the complex with *SS*-PMCN is fixed to a δ form by its central (*S*),(*S*)-cyclohexane ring. Then, in the planar complex of *SS*-PMCN, the two terminal chelate rings containing the (*S*)-pyrrolidinyl group cannot adopt a δ-gauche form and are forced to take an envelope structure. Therefore, the planar *SS*-PMCN complex may adopt the conformation II shown in Figure 4, in which the central chelate is δ gauche and the terminal chelates are envelope.

It is generally accepted that the envelope form is more thermodynamically unstable than the gauche forms with respect to the five-membered chelate ring.[26] Then, it is very interesting that *SS*-PMCN formed selectively a square-planar nickel(II) complex in spite of the inclusion of the unstable chelate rings. Yoshikawa et al. have isolated trans-type cobalt(III) complexes of *ms*-3*R*,8*S*-dimetrien and *ms*-5*R*,-6*S*-dimetrien, in which the conformation of the central chelate ring is an envelope form.[5,27] This envelope form is stabilized due to the unique specificities arising from the meso-substituted methyl groups. In our case, the fixation of the central chelate ring by the (*S*),(*S*)-cyclohexane ring plays a signficant role for the formation of the envelope chelate ring in the terminal (*S*)-diamine moiety.

It is noteworthy that the planar *RR*-PMCN complex exhibited a much more intense CD band at about 23,000 cm^{-1} than the planar complexes of *SS*-PMCN and PMEN did, as shown in Figure 2. Conformation I for the *RR*-PMCN complex has one λ-gauche chelate ring and two δ chelate rings. The λ- and δ-gauche chelate rings impose one positive and one negative CD band, respectively, with respect to the square-planar complex of nickel(II) ion.[21,28] The four secondary nitrogen atoms in the *RR*-PMCN complex are asymmetric and all of them have *S* configurations (see Figure 4). In the *SS*-PMCN complex with conformation II, on the other hand, the two secondary nitrogen atoms at the inner parts of its tetraamine have an *R* configuration opposite to that of the terminal nitrogen atoms in the pyrrolidine ring. Therefore, it is expected that the contributions of the inner and terminal asymmetric nitrogen atoms to the optical activity partially compensate each other in the *SS*-PMCN complex. This may be a main reason for the small CD band observed for the *SS*-PMCN complex, though the contribution of the envelope-type chelate ring is unknown. In other words, the additive contribution of the asymmetric nitrogen atoms probably accounts for the fact that the *RR*-PMCN complex exhibited the most intense positive CD band.

Figure 5 shows the absorption and CD spectra of the mixed complexes of *RR*-PMCN, *SS*-PMCN, and PMEN with ethylenediamine in acetonitrile. The mixed complexes of *RR*-PMCN and PMEN exhibited a small, positive CD component at a lower wave number in the region of the first (lowest energy) band and a large, negative one at a higher wave number. For the *SS*-PMCN complex, however, the positive component was not observed, probably because this component is concealed by the large negative component. This CD pattern in the first absorption band suggests that the absolute configuration about the central nickel ion of these mixed complexes is Λ.[10,29-31]

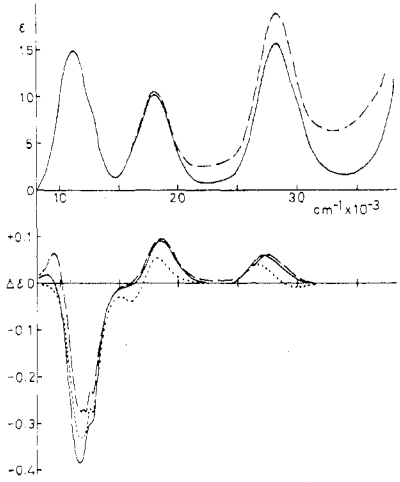


Figure 5. Absorption and CD spectra of the mixed complexes of PMEN, *RR*-PMCN, and *SS*-PMCN with ethylenediamine in acetonitrile: ———, [Ni(PMEN)(en)]$^{2+}$; – – –, [Ni(*RR*-PMCN)(en)]$^{2+}$; · · · · ·, [Ni(*SS*-PMCN)(en)]$^{2+}$.

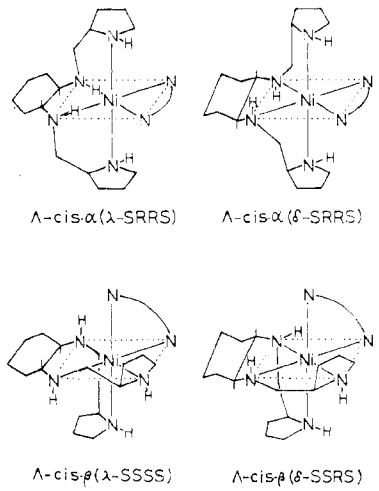


Figure 6. Schematic drawing of the probable structures with the Λ configuration for the mixed complexes of *RR*-PMCN and *SS*-PMCN; δ and λ represent the forms of the central chelate ring, and *R* and *S*, the configurations of the secondary nitrogen atoms.

Generally, a tris((*S*)-diamine) complex prefers the Λ configuration with an lel form to the Δ configuration with an ob form.[25] This supports the idea that *RR*-PMCN, *SS*-PMCN, and PMEN having the two (*S*)-diamine parts in themselves coordinate predominantly with the Λ configuration to nickel(II) ion in the mixed complexes.

The Λ configuration has two different geometrical arrangements, cis α and cis β. The possible structures for the mixed complexes of *RR*-PMCN and *SS*-PMCN with the Λ configuration are depicted in Figure 6. The left two isomers in the figure correspond to the *RR*-PMCN complex, in which the central chelate ring is fixed to a λ-gauche form by the cyclohexane ring. Similarly, the right two isomers correspond to the *SS*-PMCN complex. In the two cis-β forms shown in Figure 6, one of the pyrrolidinyl groups points toward (endo) the central chelate ring, and one of the two terminal chelate rings is envelope. In the cis-α forms, on the other hand, both of the two pyrrolidinyl groups point away (exo) from the central chelate ring. So, the interaction between nonbonding atoms is expected to be smaller in the exo-cis-α forms than in the endo-cis-β forms.[32,33] However, no spectral evidence that these mixed complexes adopt predominantly the cis-α forms is yet obtained. The detailed structure of the mixed complex of AMPE with ethylenediamine is also not clear at present.

Acknowledgment. The authors thank Professors Kazuo Saito and Junnosuke Fujita for their helpful advice. The authors are indebted to Mr. Ichiro Hirako in this laboratory for some parts of the preparation of tetraamines. The authors also wish to thank the referees for their useful comments.

Registry No. II, 56030-25-2; III, 56030-26-3; IV, 56030-27-4; V, 56030-29-6; VI, 56030-31-0; VII, 56030-32-1; VIII, 54985-57-8; IX, 54985-58-9; AMPE, 56030-28-5; MMPE, 56030-30-9; *RR*-PMCN, 56030-33-2; PMEN, 56030-34-3; [Ni(AMPE)(en)]$(ClO_4)_2$, 56030-15-0; [Ni(PMEN)(en)]$(ClO_4)_2$, 56029-98-2; [Ni(PMCN)(en)]$(ClO_4)_2$, 56030-00-3; [Ni(*RR*-PMCN)]$(ClO_4)_2$, 53553-37-0; [Ni(*SS*-PMCN)]$(ClO_4)_2$, 56086-19-2; [Ni(AMPE)$(H_2O)_2]^{2+}$, 53553-29-0; [Ni(AMPE)(gly)]$^+$, 56030-01-4; [Ni(AMPE)(L-ala)]$^+$, 55331-58-3; [Ni(AMPE)(L-val)]$^+$, 55186-39-5; [Ni(MMPE)$(H_2O)_2]^+$, 53596-09-1; [Ni(MMPE)(gly)]$^+$, 56030-02-5; [Ni(MMPE)(L-ala)]$^+$, 55331-59-4; [Ni(PMEN)(gly)]$^+$, 56030-03-6; [Ni(PMEN)(L-ala)]$^+$, 56030-04-7; [Ni(PMCN)(gly)]$^+$, 56030-05-8; [Ni(PMEN)]$^{2+}$, 53553-38-1; sodium L-prolinate, 15383-56-9; 1,2-dibromoethane, 106-93-4; 1(*R*),2(*R*)-cyclohexanediamine, 20439-47-8; *N*-carbobenzoxy-(*S*)-proline, 1148-11-4; ethylenediamine, 107-15-3.

References and Notes

(1) To whom correspondence should be addressed.
(2) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).
(3) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967); A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 787 (1967).
(4) G. R. Brubaker and D. P. Schaefer, *Coord. Chem. Rev.*, **7**, 161 (1971).
(5) M. Goto, H. Matsushita, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, **12**, 1498 (1973), and references therein.
(6) T. Yasui, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **38**, 2025 (1965).
(7) H. C. Freeman, *Adv. Protein Chem.*, **22**, 257 (1967).
(8) T. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **27**, 1062 (1971).
(9) *R* and *S* refer to the configurations about the asymmetric carbon or nitrogen atoms of ligands, according to the sequence rules of R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).
(10) J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **43**, 2999 (1970).
(11) S. Kitagawa, T. Murakami, and M. Hatano, *Chem. Lett.*, 925 (1974).
(12) F. M. Jager and L. Bijkerk, *Z. Anorg. Allg. Chem.*, **233**, 97 (1937).
(13) R. D. Gillard, *Tetrahedron*, **21**, 503 (1965).
(14) M. Hatano, T. Nozawa, and T. Sasaki, to be submitted for publication in *Rev. Sci. Instrum.*
(15) G. Schwarzenbach, "Complexometric Titrations", Methuen, London, 1957, p 82.
(16) C. K. Jorgensen, *Acta Chem. Scand.*, **11**, 399 (1957).
(17) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, 1331 (1966).
(18) R. G. Willkinson, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *J. Am. Chem. Soc.*, **91**, 4326 (1969).
(19) R. D. Gillard and H. M. Sutton, *J. Chem. Soc. A*, 1309 (1970).
(20) W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).
(21) S. Arakawa, T. Nozawa, and M. Hatano, *Bull. Chem. Soc. Jpn.*, **47**, 2643 (1974).
(22) M. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).
(23) A. Kirchess, *Z. Chem.*, **9**, 33, 34, 67 (1969).
(24) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley-Interscience, New York, N.Y., 1971, p 75.
(25) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).
(26) A. T. Advani, D. S. Barnes, and L. D. Pettit, *J. Chem. Soc. A*, 2691 (1970).
(27) M. Saburi and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **45**, 1443 (1972).
(28) B. Bosnich, J. H. Dunlop, and R. D. Gillard, *Chem. Commun.*, 274 (1965).
(29) See Table II, footnote *c*.
(30) F. Woldbye, "Studies over Optisk Aktivitet", Polyteknisk Forlag, Copenhagen, 1969.
(31) Δ and Λ refer to the absolute configurations about the central metal atom as defined in *Inorg. Chem.*, **9**, 1 (1970).
(32) B. Bosnich and A. T. Phillip, *J. Am. Chem. Soc.*, **90**, 6352 (1968); *J. Chem. Soc. A*, 264 (1970).
(33) See Table II, footnote *b*.