Optical Resolution of *rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane (L), Circular Dichroism Spectra of Ni(II) Complexes with the Active Ligand, and the Absolute Configuration of $(-)_{589}$-[{Ni(*SS*-L)}$_2$(*d*-tart)(H$_2$O)](ClO$_4$)$_2$·2H$_2$O as Determined by the X-Ray Analysis

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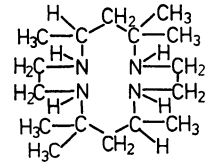
The title ligand (L) has been resolved through its *d*-tartrato-nickel(II) complex. The X-ray analysis shows that the less-soluble $(-)_{589}$-diastereomer has a dimer structure with the folded macrocycles, [{NiL}$_2$(*d*-tart)(H$_2$O)]-(ClO$_4$)$_2$·2H$_2$O, and that the chiral carbon atoms have the absolute configuration of *S*. Axial methyl groups of geminal dimethyl pairs of each nickel(II) complex in the dimer provide stereoselective environment for the coordination site of the *d*-tartrate ion. Stereospecific hydrogen-bonds between a secondary amine group of the macrocyclic ligand or coordinated water and hydroxyl or carboxyl oxygens of the *d*-tartrate ion play also an important role in the optical resolution. Pairs of enantiomers of the free ligand and three isomers of the four-coordinate nickel(II) complex have been isolated. Circular dichroism spectra of various four- and six-coordinate complexes with the optically active ligand have been described.

Transition metal complexes of the tetraaza-fourteen membered macrocyclic ligand (L) **1** have been studied in depth.[1] However, the optically active form of the ligand has not been reported so far, although unsuccessful attempts of the optical resolution of its nickel(II) complex, [Ni(*rac*-L)]$^{2+}$, by column chromatography have been documented.[2] In this study, we aimed to resolve *rac*-L into the optically active form. The nickel(II) complex, [Ni(*rac*-L)]$^{2+}$, has been known to exist as three isomeric α-, β-, and γ-forms and their structures have been determined by X-ray analyses and ^{1}H NMR study as shown in structural formulae **2**—**4**.[3,4] The isomerism arises from a difference in conformations of six- and five-membered chelate rings associated with combination of chiralities of the four coordinated secondary amine nitrogens. Of these three isomers, only the α-isomer reacts readily with a bidentate ligand such as oxalate, acetylacetonate, acetate, or nitrate ion to form *cis*-type six-coordinate complexes with the macrocycle folded.[4-6] It was anticipated that optically active bidentate ligands such as (*R*)-1,2-propanediamine, (*S*)-amino acidate, and (*R*,*R*)-*d*-tartrate ions might react stereospecifically with the α-isomer to give sterically favored six-coordinate diastereomers and thereby the racemic ligand could be resolved into the enantiomers. The optical resolution of *rac*-L has been achieved successfully with *d*-tartrate ions. The absolute configurations of chiral centers have been determined by the X-ray crystallographic analysis of the less-soluble diastereomer. Preparations and circular dichroism spectra of various nickel(II) complexes with the optically active ligand are also described. Throughout this paper, abbreviations, *SS*-L and *RR*-L, are used for the ligand with the C(7)*S*,C(14)*S*- and C(7)*R*,C(14)*R*-configurations, respectively. The racemic mixture is designated as *rac*-L.



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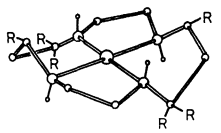
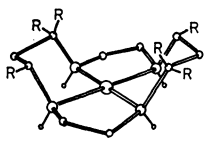
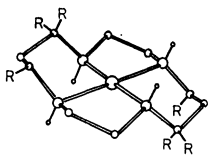


2(α)



3(β)



4(γ)

Experimental

Materials. The racemic complex, α-[Ni(*rac*-L)](ClO$_4$)$_2$, was prepared as reported previously.[4]

$(-)_{589}$-[{Ni(SS-L)}$_2$(d-tart)(H$_2$O)](ClO$_4$)$_2$·2H$_2$O. Addition of 7.2 g of tetrabutylammonium bromide to an acetonitrile solution of α-[Ni(*rac*-L)](ClO$_4$)$_2$ (4.0 g in 160 cm^3) gives green precipitate of the bromide salt (yield, 3.6 g). Found: C, 38.61; H, 7.43; N, 11.00%. Calcd for NiC$_{16}$H$_{36}$N$_4$Br$_2$: C, 38.20; H, 7.21; N, 11.14%. Four grams of the bromide (8.0 mmol) are dissolved in 160 cm^3 of water at room temperature and 0.50 g of sodium *d*-tartrate dihydrate (2.2 mmol) dissolved in a minimum amount of water are added portionwise. Color of the solution turns gradually greenish brown. After 30 min, 0.60 g of sodium perchlorate (4.0 mmol) dissolved in a minimum amount of water is added to this solution. Then the solution is chilled in an ice-bath for 1 h. The blue-violet precipitate is filtered and washed with chilled water, ethanol, and ether. Yield, 1.70 g. The filtrate (solution A) contains the other enantiomer and is used in the subsequent treatment (see below). The optical purity is checked by the *g*-value of the product in 1 mol dm^{-3} perchloric acid, where $g=|\Delta\varepsilon_{440}|/\varepsilon_{450}$ is 0.018 for the optically pure form. Judging from the *g*-value, the optical purity of the product at this stage is more than 90%. Recrystallization from acetonitrile gives blue-violet crystals. Found: C, 40.33; H, 7.71; N, 10.78%. Calcd for Ni$_2$C$_{36}$H$_{82}$N$_8$Cl$_2$O$_{17}$: C, 39.76; H, 7.60; N, 10.30%.

α-, β-, and γ-[Ni(SS-L)](ClO$_4$)$_2$. The optically active α-isomer is prepared by stirring 2.0 g of (−)$_{589}$-[{Ni(*SS*-L)}$_2$-(*d*-tart)(H$_2$O)](ClO$_4$)$_2$·2H$_2$O in 30 cm^3 of 70% perchloric acid at room temperature. Within a few min, the starting blue-violet complex decomposes to give a bright orange solution. A yellow product is obtained upon addition of cold water to the solution, and is recrystallized from 0.1 mol dm^{-3} perchloric acid. Found: C, 34.73; H, 6.73; N, 10.03%. Calcd for $NiC_{16}H_{36}N_4Cl_2O_8$: C, 35.45; H, 6.69; N, 10.34%. The β-derivative is prepared from the α-isomer following the reported procedure for the racemate[3] and recrystallized from 0.1 mol dm^{-3} perchloric acid. Found: C, 34.60; H, 6.53; N, 10.05%. Large red-orange crystals are obtained from a dilute solution of either α- or β-[Ni(*SS*-L)](ClO$_4$)$_2$ upon standing the solution for several days. These are identified with the ^{1}H NMR spectrum in CH_3CN-d_3 to be the γ-isomer. In contrast to the α- and β-isomers, the ^{1}H NMR spectrum of the γ-isomer shows that the six methyl groups are not pairwise equivalent.[3] Found: C, 34.88; H, 6.59; N, 10.32%.

(+)$_{589}$-[{Ni(RR-L)}$_2$ox](ClO$_4$)$_2$·H$_2$O. To the solution A (see above) is added 1.0 g of sodium oxalate and 1.0 g of sodium perchlorate. The solution is basified to pH ≈10 with aqueous sodium hydroxide to give a pale blue product. This is a well characterized racemic oxalate dimer, [{Ni(*rac*-L)}$_2$ox]-(ClO$_4$)$_2$,[1a,4] and is filtered off (*ca.* 1.3 g).[7] The pH of the blue filtrate is adjusted to ≈1 with dropwise addition of 60% perchloric acid in an ice-bath to yield a blue-violet product. This is almost optically pure (+)$_{589}$-[{Ni(*RR*-L)}$_2$ox](ClO$_4$)$_2$·H$_2$O (yield, 1.12 g) and is recrystallized from methanol. Found: C, 40.93; H, 7.54; N, 11.30%. Calcd for Ni_2C_{34}-$H_{74}N_8Cl_2O_{13}$: C, 41.12; H, 7.52; N, 11.30%. The structural formula is tentative. The addition of excess perchloric acid results in decomposition of the blue-violet product and formation of the yellow α-isomer.

α-, β-, and γ-[Ni(RR-L)](ClO$_4$)$_2$. α-, β-, and γ-Complexes of *RR*-L are obtained from (+)$_{589}$-[{Ni(*RR*-L)}$_2$ox]-(ClO$_4$)$_2$·H$_2$O in a manner similar to synthetic procedures for the *SS*-L complexes from (−)$_{589}$-[{Ni(*SS*-L)}$_2$(*d*-tart)(H$_2$O)]-(ClO$_4$)$_2$·2H$_2$O. Crude products are recrystallized from 0.1 mol dm^{-3} perchloric acid. Found for α: C, 34.65; H, 6.59; N, 10.09%. Found for β: C, 34.85; H, 6.60; N, 10.16%. Found for γ: C, 34.78; H, 6.63; N, 10.28%.

Optically Active Free Ligands. Following the reported procedures for the racemate,[8,9] the optically active free ligand is obtained from α-[Ni(*SS*- or *RR*-L)](ClO$_4$)$_2$ by sodium cyanide decomposition in strongly alkaline aqueous media (yield>90%). Found for *SS*-L: C, 66.03; H, 13.16; N, 19.18% (C/N=4.02). Found for *RR*-L: C, 66.14; H, 13.14; N, 19.43% (C/N=4.03). Calcd for $C_{16}H_{36}N_4$·0.5H$_2$O: C, 65.48; H, 12.70; N, 19.08% (C/N=4.00).

Measurements. The electronic absorption and circular dichroism spectra were recorded on a Hitachi 340 spectrophotometer and a JASCO J-40 spectropolarimeter, respectively. Optical rotations were measured with a JASCO DIP-4 polarimeter.

X-Ray Analysis. Blue-violet prismatic single crystals of the less-soluble diastereoisomer, (−)$_{589}$-[{Ni(*SS*-L)}$_2$(*d*-tart)-(H$_2$O)](ClO$_4$)$_2$·2H$_2$O, were obtained from an acetonitrile solution. A specimen with dimensions 0.28 mm × 0.32 mm × 0.36 mm was used for the X-ray study. Diffraction data were measured on a Rigaku AFC-5 diffractometer with graphite monochromatized Mo *Kα* radiation. Within the range $2\theta < 60°$, 5310 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were obtained. Intensities were corrected for Lorentz and polarization factors but not for absorption.

Crystal data are: Monoclinic, $P2_1$, $a=17.568$ (3), $b=11.482$ (2), $c=13.272$ (2) Å, $\beta=102.59$ (1)°, $U=2612.8$ (6) Å^3, $Z=2$, $D_m=1.39$, $D_x=1.39$ g cm^{-3}, μ(Mo*Kα*)=8.95 cm^{-1}.

The structure was solved by the heavy atom method and refined by a block-diagonal least-squares method. The weighting scheme, $w=[\sigma_{count}^2+(0.015|F_o|)^2]^{-1}$, was employed. All hydrogen atoms except for those of water of crystallization and one of the methyl protons were located by the difference Fourier syntheses, and included in the final refinement with the isotropic temperature factors. The final R indicies were $R=0.047$ and $R_w=0.057$. Table 1 lists the final atomic coordinates.[10]

Table 1. Atomic coordinates (×10^5) and their standard deviations

Atom	*x*	*y*	*z*
NI(1)	22929(4)	46899(7)	5120(5)
N(1)	14435(30)	43099(45)	-8101(36)
N(4)	29849(29)	51602(45)	-5668(35)
N(8)	28850(32)	31323(47)	8746(39)
N(11)	15677(32)	40754(52)	15049(39)
C(2)	16762(38)	50050(80)	-16189(44)
C(3)	25082(39)	48219(74)	-15995(43)
C(5)	38319(37)	48193(65)	-3853(51)
C(6)	39191(39)	35212(65)	-824(57)
C(7)	37464(42)	31525(67)	9482(56)
C(9)	26961(49)	27670(71)	18625(56)
C(10)	18263(52)	28462(78)	17431(58)
C(12)	6908(42)	41677(73)	11990(56)
C(13)	4069(42)	37556(84)	884(59)
C(14)	6104(42)	44776(80)	-7743(54)
C(15)	41499(42)	49965(84)	-13688(59)
C(16)	42861(42)	56027(72)	4791(58)
C(17)	41212(65)	19516(93)	12419(87)
C(18)	2830(58)	34581(110)	19093(72)
C(19)	4787(46)	54388(90)	13195(75)
C(20)	598(59)	40334(195)	-17453(74)
NI(2)	27155(4)	100000(7)	53275(5)
N(1')	34506(27)	109031(40)	65493(33)
N(4')	18117(29)	111006(44)	56710(34)
N(8')	23286(28)	86615(45)	61711(34)
N(11')	36804(29)	88392(46)	52921(38)
C(2')	30096(41)	119391(55)	67336(48)
C(3')	21761(39)	116236(59)	66933(46)
C(5')	10034(39)	106290(65)	56060(48)
C(6')	10379(38)	95175(73)	62363(49)
C(7')	14599(39)	84574(62)	59521(46)
C(9')	27783(42)	76158(54)	59779(52)
C(10')	36093(39)	79254(58)	60450(54)
C(12')	44960(40)	92928(61)	53958(54)
C(13')	47127(35)	101024(67)	63421(51)
C(14')	42431(36)	112005(56)	63740(46)
C(15')	6505(41)	104245(77)	44512(53)
C(16')	4948(46)	115238(83)	60368(66)
C(17')	12525(46)	73939(76)	65269(63)
C(18')	45267(44)	99196(79)	43861(57)
C(19')	50927(47)	82937(80)	55467(70)
C(20')	46834(41)	120402(66)	71959(57)
C(21)	25793(36)	65048(56)	15315(46)
C(22)	27374(36)	75867(57)	22096(45)
C(23)	19873(35)	80733(52)	24096(41)
C(24)	21599(36)	91633(53)	30668(44)
O(1)	29411(25)	55796(40)	18505(31)
O(2)	20740(26)	65479(40)	6980(30)
O(3)	21508(25)	90698(35)	40120(29)
O(4)	23421(32)	100666(41)	26461(30)
O(5)	32666(28)	73141(47)	31679(37)
O(6)	15827(28)	72269(45)	28421(34)
OW(C)	29283(28)	113268(39)	42681(31)
CL(1)	65260(14)	37981(23)	9793(15)
OP(1)	63506(50)	38103(84)	-894(44)
OP(2)	58153(49)	35896(127)	13599(64)
OP(3)	70102(65)	28658(97)	13386(61)
OP(4)	68169(67)	47629(86)	13791(54)
CL(2)	20760(21)	-55488(21)	-52284(18)
OP(5)	16115(68)	-47162(68)	-57536(76)
OP(6)	19849(65)	-66050(76)	-56694(60)
OP(7)	21814(86)	-54949(82)	-42196(58)
OP(8A)	28025(156)	-54100(229)	-47074(206)
OP(8B)	27290(194)	-48853(256)	-57804(214)
OP(8C)	29587(215)	-59882(375)	-53608(210)
OW(1)	17872(47)	15638(79)	-8388(51)
OW(2A)	17027(81)	618(147)	4123(100)
OW(2B)	15627(131)	-15958(225)	-4642(155)

The calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with Universal Crystallographic Computation Program System UNICS III.[11]

Results and Discussion

Optical Resolution and Syntheses of the Nickel(II) Complexes with the Optically Active Ligand. The optical resolution of *rac*-L was performed by taking advantage of the characteristic nature of α-[Ni(*rac*-L)]$^{2+}$; this isomer readily forms *cis*-type six-coordinate complex with a bidentate chelate ligand. The use of *d*-tartrate has proved successful. But attempts by use of (*R*)-1,2-propanediamine and (*S*)-proline were ineffective, although they reacted with the α-complex to give six-coordinate complexes.

As has been well characterized, the α-isomer isomerizes in neutral or at much faster rate in basic media to the thermodynamically more stable β-isomer to give an equilibrium mixture.[4] Therefore, the perchlorate salt of the α-isomer was converted to the bromide salt so as to enhance the solubility and to dissolve quickly the racemic compound in the α-form in water. Reaction of α-[$NiBr_2$(*rac*-L)] with *d*-tartrate salt and subsequent addition of sodium perchlorate yielded the crystalline less-soluble diastereomer. Addition of excess sodium perchlorate gave less optically pure product. On account of the two facts mentioned above, the conversion of the perchlorate to the bromide is essential for the present synthetic procedures.

The less-soluble diastereomer was shown to be $(-)_{589}$-[{Ni(*SS*-L)}$_2$(*d*-tart)(H_2O)](ClO_4)$_2$·$2H_2O$ by the X-ray analysis (*vide infra*). The other enantiomer was isolated as the oxalate dimer, $(+)_{589}$-[{Ni(*RR*-L)}$_2$ox]-(ClO_4)$_2$·H_2O. When sodium oxalate is added to the filtrate obtained after the isolation of the less-soluble diastereomer, two kinds of oxalate dimers, optically active and racemic ones, are obtained. Since the perchlorate of the racemic compound is practically insoluble while the optically active one is fairly soluble in methanol, the separation of these two oxalate dimers are accomplished easily.

The optical purities of the diastereomer and the oxalate dimers were examined at each step of procedures by monitoring *g*-values ($\Delta\varepsilon_{440}/\varepsilon_{450}$) of the complexes dissolved in 1 mol dm^{-3} perchloric acid, where all the compounds are converted to four-coordinate complexes in the α-form.

The optically active four-coordinate complexes of α-, β-, and γ-[Ni(*SS*- or *RR*-L)](ClO_4)$_2$ were obtained from [{Ni(*SS*-L)}$_2$(*d*-tart)(H_2O)](ClO_4)$_2$·$2H_2O$ or [{Ni(*RR*-L)}$_2$ox](ClO_4)$_2$·H_2O in a way similar to the procedure for the isolation of the respective racemic complexes.

A pair of enantiomers of free ligand has been isolated successfully from the optically active nickel(II) complexes in a synthetic scale. Using these ligands, optically active complexes of other metal ions can be prepared.[12]

X-Ray Structure Analysis of $(-)_{589}$-[{*Ni*(SS-*L*)}$_2$(*d*-*tart*)(*H_2O*)](*ClO_4*)$_2$·*$2H_2O$*. The structure analysis revealed that the compound is a dimer of [Ni(*SS*-L)]$^{2+}$ with a bridged *d*-tartrate ion. A stereoscopic view of the dimer is shown in Fig. 1, in which only hydrogen atoms of NH groups and those bonded to chiral carbon atoms are depicted. Bond lengths and angles within the dimer are listed in Tables 2 and 3, respectively. Each Ni(II) in the dimer has a six-coordinate structure with

Table 2. Bond lengths (*l*/Å) within the complex cation and their estimated standard deviations

NI(1) -N(1)	2,087(4)	NI(2) -N(1')	2,112(4)
NI(1) -N(4)	2,140(5)	NI(2) -N(4')	2,154(5)
NI(1) -N(8)	2,072(5)	NI(2) -N(8')	2,100(5)
NI(1) -N(11)	2,142(6)	NI(2) -N(11')	2,165(5)
NI(1) -O(1)	2,148(4)	NI(2) -O(3)	2,102(4)
NI(1) -O(2)	2,191(5)	NI(2) -OW(C)	2,160(5)
N(1) -C(2)	1,465(9)	N(1') -C(2')	1,469(8)
N(1) -C(14)	1,487(9)	N(1') -C(14')	1,500(8)
N(4) -C(3)	1,493(7)	N(4') -C(3')	1,494(7)
N(4) -C(5)	1,506(8)	N(4') -C(5')	1,504(9)
N(8) -C(7)	1,495(9)	N(8') -C(7')	1,508(8)
N(8) -C(9)	1,482(10)	N(8') -C(9')	1,490(9)
N(11) -C(10)	1,495(11)	N(11')-C(10')	1,473(9)
N(11) -C(12)	1,509(9)	N(11')-C(12')	1,503(9)
C(2) -C(3)	1,471(10)	C(2') -C(3')	1,498(10)
C(5) -C(6)	1,543(11)	C(5') -C(6')	1,520(11)
C(6) -C(7)	1,524(11)	C(6') -C(7')	1,515(11)
C(5) -C(15)	1,541(11)	C(5') -C(15')	1,541(9)
C(5) -C(16)	1,537(10)	C(5') -C(16')	1,550(12)
C(7) -C(17)	1,541(13)	C(7') -C(17')	1,525(11)
C(9) -C(10)	1,504(13)	C(9') -C(10')	1,486(10)
C(12) -C(13)	1,525(10)	C(12')-C(13')	1,544(10)
C(13) -C(14)	1,518(12)	C(13')-C(14')	1,512(10)
C(12) -C(18)	1,536(14)	C(12')-C(18')	1,530(11)
C(12) -C(19)	1,523(13)	C(12')-C(19')	1,537(11)
C(14) -C(20)	1,521(13)	C(14')-C(20')	1,533(9)
C(21) -O(1)	1,263(8)	C(24) -O(3)	1,263(7)
C(21) -O(2)	1,259(7)	C(24) -O(4)	1,252(8)
C(22) -O(5)	1,437(7)	C(23) -O(6)	1,399(8)
C(21) -C(22)	1,524(9)	C(23) -C(24)	1,518(8)
C(22) -C(23)	1,507(9)		

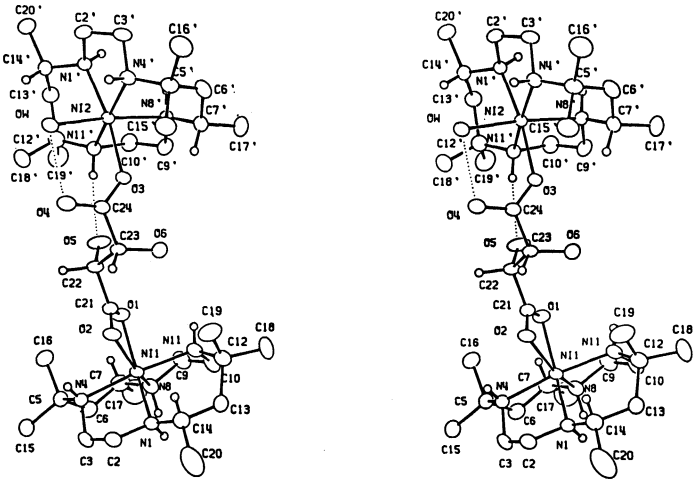


Fig. 1. Stereoview of the structure of $(-)_{589}$-[{Ni(*SS*-L)}$_2$-(*d*-tart)(H_2O)]$^{2+}$. Dotted lines indicate hydrogen-bonds.

Table 3. Bond angles (ϕ/°) within the complex cation and their estimated standard deviations

N(1)	-Ni(1)	-N(4)	84,1(2)	N(1')	-Ni(2)	-N(4')	84,6(2)
N(1)	-Ni(1)	-N(8)	104,2(2)	N(1')	-Ni(2)	-N(8')	99,5(2)
N(1)	-Ni(1)	-N(11)	92,1(2)	N(1')	-Ni(2)	-N(11')	88,2(2)
N(1)	-Ni(1)	-O(1)	161,4(2)	N(1')	-Ni(2)	-O(3)	170,5(2)
N(1)	-Ni(1)	-O(2)	100,8(2)	N(1')	-Ni(2)	-OW(C)	89,4(2)
N(4)	-Ni(1)	-N(8)	92,5(2)	N(4')	-Ni(2)	-N(8')	88,7(2)
N(4)	-Ni(1)	-N(11)	174,6(2)	N(4')	-Ni(2)	-N(11')	169,2(2)
N(4)	-Ni(1)	-O(1)	99,0(2)	N(4')	-Ni(2)	-O(3)	103,7(2)
N(4)	-Ni(1)	-O(2)	88,2(2)	N(4')	-Ni(2)	-OW(C)	87,9(2)
N(8)	-Ni(1)	-N(11)	84,8(2)	N(8')	-Ni(2)	-N(11')	84,7(2)
N(8)	-Ni(1)	-O(1)	94,0(2)	N(8')	-Ni(2)	-O(3)	85,5(2)
N(8)	-Ni(1)	-O(2)	154,9(2)	N(8')	-Ni(2)	-OW(C)	170,1(2)
N(11)	-Ni(1)	-O(1)	85,8(2)	N(11')	-Ni(2)	-O(3)	84,2(2)
N(11)	-Ni(1)	-O(2)	96,3(2)	N(11')	-Ni(2)	-OW(C)	99,9(2)
O(1)	-Ni(1)	-O(2)	61,2(2)	O(3)	-Ni(2)	-OW(C)	86,3(2)
Ni(1)	-N(1)	-C(2)	103,9(4)	Ni(2)	-N(1')	-C(2')	105,6(3)
Ni(1)	-N(1)	-C(14)	118,3(4)	Ni(2)	-N(1')	-C(14')	115,2(3)
Ni(1)	-N(4)	-C(3)	105,2(4)	Ni(2)	-N(4')	-C(3')	103,8(4)
Ni(1)	-N(4)	-C(5)	120,9(4)	Ni(2)	-N(4')	-C(5')	120,4(4)
Ni(1)	-N(8)	-C(7)	116,8(4)	Ni(2)	-N(8')	-C(7')	116,3(4)
Ni(1)	-N(8)	-C(9)	104,6(4)	Ni(2)	-N(8')	-C(9')	104,6(4)
Ni(1)	-N(11)	-C(10)	104,3(5)	Ni(2)	-N(11')	-C(10')	104,0(4)
Ni(1)	-N(11)	-C(12)	121,4(4)	Ni(2)	-N(11')	-C(12')	121,4(4)
C(2)	-N(1)	-C(14)	112,7(5)	C(2')	-N(1')	-C(14')	112,5(5)
C(3)	-N(4)	-C(5)	114,6(5)	C(3')	-N(4')	-C(5')	114,1(5)
C(7)	-N(8)	-C(9)	111,4(5)	C(7')	-N(8')	-C(9')	113,2(5)
C(10)	-N(11)	-C(12)	111,6(6)	C(10')	-N(11')	-C(12')	114,0(5)
N(1)	-C(2)	-C(3)	110,1(6)	N(1')	-C(2')	-C(3')	110,2(5)
N(1)	-C(14)	-C(13)	110,4(6)	N(1')	-C(14')	-C(13')	110,2(5)
N(4)	-C(3)	-C(2)	109,6(5)	N(4')	-C(3')	-C(2')	110,6(5)
N(4)	-C(5)	-C(6)	109,3(5)	N(4')	-C(5')	-C(6')	110,3(5)
N(8)	-C(7)	-C(6)	110,0(5)	N(8')	-C(7')	-C(6')	110,9(5)
N(8)	-C(9)	-C(10)	107,9(6)	N(8')	-C(9')	-C(10')	110,4(5)
N(11)	-C(10)	-C(9)	109,5(7)	N(11')	-C(10')	-C(9')	110,9(5)
N(11)	-C(12)	-C(13)	109,8(6)	N(11')	-C(12')	-C(13')	110,0(6)
N(1)	-C(14)	-C(20)	112,2(7)	N(1')	-C(14')	-C(20')	112,0(5)
N(4)	-C(5)	-C(15)	111,0(5)	N(4')	-C(5')	-C(15')	106,4(5)
N(4)	-C(5)	-C(16)	107,5(6)	N(4')	-C(5')	-C(16')	110,7(6)
N(8)	-C(7)	-C(17)	111,9(7)	N(8')	-C(7')	-C(17')	111,7(5)
N(11)	-C(12)	-C(18)	112,5(6)	N(11')	-C(12')	-C(18')	107,4(5)
N(11)	-C(12)	-C(19)	107,3(6)	N(11')	-C(12')	-C(19')	111,3(6)
C(5)	-C(6)	-C(7)	118,3(6)	C(5')	-C(6')	-C(7')	120,0(6)
C(12)	-C(13)	-C(14)	118,6(7)	C(12')	-C(13')	-C(14')	119,1(5)
C(6)	-C(5)	-C(15)	108,3(6)	C(6')	-C(5')	-C(15')	112,2(6)
C(6)	-C(5)	-C(16)	111,4(5)	C(6')	-C(5')	-C(16')	108,1(6)
C(15)	-C(5)	-C(16)	109,3(6)	C(15')	-C(5')	-C(16')	109,2(6)
C(6)	-C(7)	-C(17)	108,5(7)	C(6')	-C(7')	-C(17')	109,6(6)
C(13)	-C(12)	-C(18)	109,3(7)	C(13')	-C(12')	-C(18')	112,3(6)
C(13)	-C(12)	-C(19)	111,3(7)	C(13')	-C(12')	-C(19')	107,6(5)
C(18)	-C(12)	-C(19)	106,6(8)	C(18')	-C(12')	-C(19')	108,3(7)
C(13)	-C(14)	-C(20)	104,2(9)	C(13')	-C(14')	-C(20')	110,5(5)
Ni(1)	-O(1)	-C(21)	89,2(3)	Ni(2)	-O(3)	-C(24)	132,5(4)
Ni(1)	-O(2)	-C(21)	87,3(4)				
O(1)	-C(21)	-O(2)	122,3(6)	O(3)	-C(24)	-O(4)	125,0(5)
C(22)	-C(21)	-O(1)	118,3(5)	C(23)	-C(24)	-O(3)	117,2(5)
C(22)	-C(21)	-O(2)	119,3(5)	C(23)	-C(24)	-O(4)	117,7(5)
C(21)	-C(22)	-O(5)	110,2(5)	C(22)	-C(23)	-O(6)	110,9(5)
C(23)	-C(22)	-O(5)	110,3(5)	C(24)	-C(23)	-O(6)	113,1(5)
C(21)	-C(22)	-C(23)	110,6(5)	C(22)	-C(23)	-C(24)	109,5(5)

a folded macrocycle as anticipated. The bridged *d*-tartrate ion is coordinated to Ni(1) and Ni(2) unsymmetrically: one carboxyl group of the *d*-tartrate ion is coordinated to Ni(1) bidentately (O(1) and O(2)), while the other carboxyl group is coordinated to Ni(2) unidentately (O(3)). The sixth coordination site of Ni(2) is occupied by water (Ow(c)).

Each macrocycle (L) in the NiL dimer is folded about N(4)–Ni(1)–N(11) and N(4')–Ni(2)–N(11'). All these nitrogens are adjacent to the geminal dimethyl carbon atoms. A similar structural feature has been found in the crystal structure of [Ni(OAc)(*rac*-L)]$(ClO_4)_2$, where OAc is an acetate ion.[5] This is most likely owing to the following reason. When the macrocycle is folded from its coplanar nitrogen geometry, the nitrogen atom adjacent to the single methyl carbon is more easily lifted than that adjacent to the geminal dimethyl carbon atom is.[13] As a result, the more crowded side of the macrocycle, *i.e.*, that with the two geminal dimethyl groups, is directed toward the *d*-tartrate ion in each Ni(II) complex in the dimer. As a consequence, the axial methyl groups of the geminal dimethyl pairs in the folded macrocycle give stereoselective environments to the sites of *d*-tartrate coordination. Furthermore, stereospecific intramolecular hydrogen-bonds are observed between a secondary amine group of the macrocyclic ligand and hydroxyl oxygen of the *d*-tartrate ion and between a coordinated water molecule and the uncoordinated carboxyl oxygen : N(11')–H···O(5), 3.246(7) Å; Ow(c)···O(4), 2.605(6) Å (see Fig. 1). The preferred coordination of the *d*-tartrate ion to the *SS*-L complex over the *RR*-L complex is effected by the steric interactions with the axial methyl groups of the macrocyclic ligands and the stereospecific intramolecular hydrogen-bonds. In view of the fact that the use of (*S*)-prolinate ion or (*R*)-1,2-propanediamine as a resolving agent was not effective, the stereospecific hydrogen-bonds play more important roles in the optical resolution.

Each chelate ring adopts the most strain free conformation: all the six-membered rings take the chair form with the single methyl groups in equatorial positions; all the five-membered rings are in the gauche conformation. It should be noted that the macrocycle cannot adopt such a most strain free chelate ring conformation in the planar coordination.

The observed Ni–N and Ni–O distances are within the normal range for octahedral nickel(II) complexes. Chelation of the carboxyl group of the *d*-tartrate ion to Ni(1) results in a small angle of O(1)–Ni(1)–O(2) (61.0(2)°), giving a distorted octahedral geometry around the Ni(1) atom. The value is comparable to the corresponding angle of 62.4(3)° reported for [Ni(OAc)(*rac*-L)](ClO_4).[5]

Absolute configurations of the chiral centers were determined on the basis of that of the *d*-tartrate ion. All the chiral carbon atoms have the absolute configuration of *S* and all the chiral nitrogen atoms have *R*

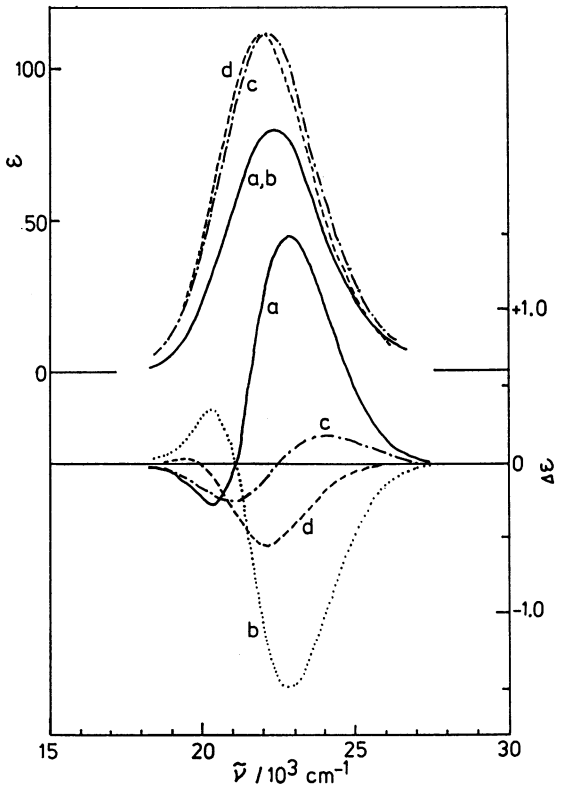


Fig. 2. AB (top) and CD (bottom) spectra of α-[Ni(*SS*-L)]$(ClO_4)_2$ (a) and α-[Ni(*RR*-L)]$(ClO_4)_2$ (b) in 60% $HClO_4$, and β-[Ni(*SS*-L)]$(ClO_4)_2$ (c) and γ-[Ni(*SS*-L)]$(ClO_4)_2$ (d) in 0.1 mol dm^{-3} $HClO_4$.

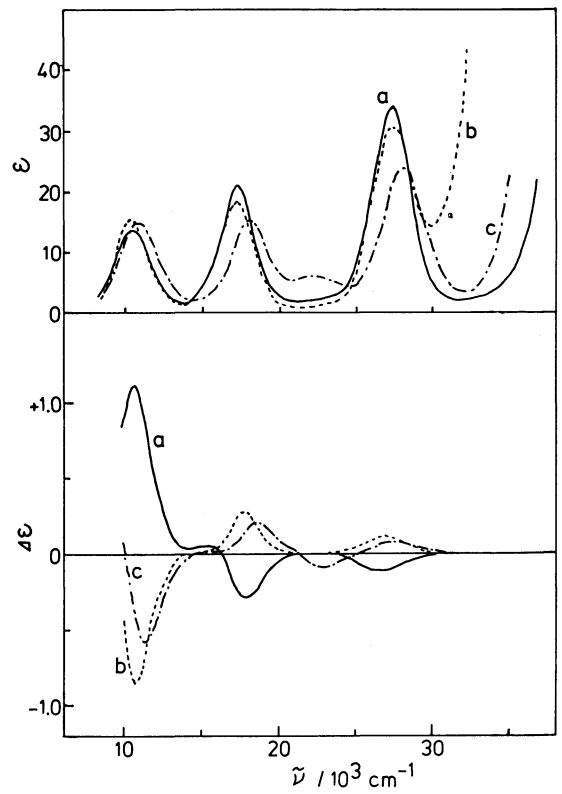


Fig. 3. AB (top) and CD (bottom) spectra of [{Ni(*SS*-L)}$_2$(*d*-tart) (H_2O)] (ClO_4)$_2$·2H_2O (a), [{Ni(*RR*-L)}$_2$-ox](ClO_4)$_2$}·H_2O (b), and α-[Ni(*SS*-L)](ClO_4)$_2$ (c) in CH_3CN at 20 °C.
Halves of the ε and Δε values are plotted for the dimers ((a) and (b)).

configuration.

Intermolecular hydrogen-bonds are observed among water of crystallization (Ow), secondary amine groups of the macrocyclic ligands, hydroxyl oxygen atom of the *d*-tartrate ion (O(6)), a coordinated water molecule, and perchlorate oxygen atoms (Op).[14] Other intermolecular contacts appear to be normal.

Absorption and Circular Dichroism Spectra. Absorption (AB) and circular dichroism (CD) spectra of some four- and six-coordinate complexes are presented in Figs. 2 and 3, respectively. The spectral data are summarized in Table 4. As reported for other tetraazamacrocyclic nickel(II) complexes,[1] AB spectra of the present complexes in the d-d region consists of single bands for four-coordinate complexes and three main bands for six-coordinate complexes.

As for the spectra of four-coodinate complexes, perchlorates of the three isomers in acidic aqueous solutions show similar AB spectra but their CD spectra are significantly different from each other (Fig. 2). The difference in the CD spectra provides some informations on subtle solution behaviors of the compounds, which had not been detected from absorption spectral studies.

It has been reported that α-[Ni(*rac*-L)](ClO_4)$_2$ gives blue, green, and violet solutions when dissolved in *N*,*N*-dimethylformamide, dimethylsulphoxide, and acetonitrile, respectively, in spite of the yellow-orange color in the solid state.[4] This has been interpreted as equilibria between four-coordinate species having singlet ground states and six-coordinate triplet species with two solvent molecules in the first coordination sphere:

α-[Ni(*rac*-L)]$^{2+}$+2 solvent⇌α-[Ni(*rac*-L)(solvent)$_2$]$^{2+}$.

Absorption spectra of these solutions show the charac-

Table 4. AB and CD spectral data in the d-d transition region[a]

Compound	Medium	AB $\tilde{\nu}/10^3$ cm^{-1} (ε)	CD $\tilde{\nu}/10^3$ cm^{-1} (Δε)	Assignment[b]
α-[Ni(*SS*-L)](ClO_4)$_2$	60% $HClO_4$	22.4(80)	20.3(−0.35), 22.8(+1.45)	s
	10^{-2} mol dm^{-3} $HClO_4$[c]	10.3(3.8)	10.4(+0.12)	t
		17.1(3.5)	17.4(−0.03)	t
		22.4(67)	20.4(−0.27), 23.0(+1.20)	s
	CH_3CN[c]	10.8(15)	11.2(+0.59)	t
		18.0(15)	18.5(−0.40)	t
		22.2(6)	22.7(+0.15)	s
		28.2(23)	27.8(−0.15)	t
α-[N(*RR*-L)](ClO_4)$_2$	60% $HClO_4$	22.4(80)	20.3(+0.35), 22.8(−1.47)	s
β-[Ni(*SS*-L)](ClO_4)$_2$	10^{-2} mol dm^{-3} $HClO_4$	22.1(111)	21.1(−0.27), 23.9(+0.15)	s
	CH_3CN	21.8(101)	20.7(−0.20), 23.6(+0.11)	s
γ-[Ni(*SS*-L)](ClO_4)$_2$	10^{-2} mol dm^{-3} $HClO_4$	21.8(111)	≈19.6(+0.01), 22.1(−0.55)	s
	CH_3CN	21.5(104)	≈19.0(+0.02), 21.9(−0.52)	s
α-, β-, or γ-[Ni(*SS*-L)](ClO_4)$_2$	10^{-3} mol dm^{-3} NaOH	22.2(104)	21.1(−0.24), 23.8(+0.15)	s
$(-)_{589}$-[{Ni(*SS*-L)}$_2$(*d*-tart)-(H_2O)](ClO_4)$_2$·2H_2O	CH_3CN	10.4(27)	10.6(+2.20)	t
		17.2(41)	17.8(−0.59)	t
		27.4(67)	26.5(−0.21)	t
$(+)_{589}$-[{Ni(*RR*-L)}$_2$ox]-(ClO_4)$_2$·H_2O	CH_3CN	10.3(31)	10.6(−1.68)	t
		17.2(36)	17.7(+0.55)	t
		27.4(61)	26.7(+0.22)	t

a) Data for the β- and γ-isomers of *RR*-L are not listed. They are enantiomeric to the data for the *SS*-L complexes. b) s: four-coordinate singlet species; t: six-coordinate triplet species. c) In this solvent, the compound exists as an equilibrium mixture. The apparent values for ε and Δε at 20 °C are given.

teristic absorptions both for four-coordinate singlet species and six-coordinate triplet species of nickel(II).[4] The AB and CD spectra in acetonitrile are shown in Fig. 3, the equilibrium being shifted toward the triplet form. In water, however, which should have strong coodinating ability, only an absorption band corresponding to the four-coordinate species has been reported.[4] This has been in contrast to the case with unsubstituted fully-saturated tetraaza-macrocyclic nickel(II) complexes, where such equilibria in water are clearly observed and the equilibrium constants and the thermodynamic parameters are studied in detail.[15-20] The CD spectrum of α-[Ni(*SS*-L)]$(ClO_4)_2$ in 0.01 mol dm^{-3} perchloric acid shows clearly a positive band ($\Delta\varepsilon=+0.12$) at 10400 cm^{-1} and a weak negative band ($\Delta\varepsilon=-0.03$) at 17400 cm^{-1} as well as strong bands due to the four-coordinate species. The exactly enantiomeric CD spectrum was observed with α-[Ni(*RR*-L)]$(ClO_4)_2$. These facts indicate an equilibrium between the four-coordinated and the diaquated six-coordinate species attains in water. It is difficult to detect the corresponding AB bands under usual experimental conditions because of the low solubility of the compound. But careful measurements revealed very weak AB bands at 10000 and 17100 cm^{-1} (see Table 4).

It is well known for analogous systems that the equilibria can be shifted toward the four-coordinate species by increasing the temperature and/or by increasing the concentration of perchlorate ions.[15-20] In 60% perchloric acid solution of the present α-complex, no AB and CD bands corresponding to the diaquated species were detected at 30 °C. From this spectrum, the molar extinction coefficient (ε) at the absorption maximum of the pure four-coordinate species was evaluated to be $\varepsilon_{447}=80$ dm^3 mol^{-1} cm^{-1}. Using this value, the equilibrium constant ($K=$[[α-Ni(*rac*-L)$(H_2O)_2]^{2+}$]/[α-[Ni(*rac*-L)]$^{2+}$]) in 0.01 mol dm^{-3} perchloric acid solution was determined to be 0.19 at 20 °C: the complexes in the solution consist of 16% six-coordinate and 84% four-coordinate species. The positions of the AB and CD bands due to the diaquated six-coordinate species are close to those observed for [{Ni(*SS*-L)}$_2$(*d*-tart)$(H_2O)]^{2+}$ and [{Ni(*RR*-L)}$_2$ox]$^{2+}$ (see Table 4). This indicates that the diaquated species of α-[Ni(*rac*-L)]$^{2+}$ has a *cis*-NiO_2N_4 structure. Compounds of the *trans*-NiO_2N_4 type show AB bands around 9000, 15000, and 29000—30000 cm^{-1}.[7,21,22]

The perchlorates of all the α-, β-, and γ-isomers give finally identical AB and CD spectra when dissolved in 10^{-3} mol dm^{-3} sodium hydroxide solution, where the compounds can isomerize to more stable forms. The resulting CD spectra are almost the same as that of the β-isomer in weakly acidic solution (Table 4). In the equilibrated solution, the predominant species is the β-form and the amounts of the α- and γ-forms are very small, if any. Nevertheless, the γ-isomer can easily be isolated as large crystals, because of the very low solubility, upon standing the equilibrated dilute solution for a long time.

As shown in Fig. 3, the AB spectra of $(-)_{589}$-[{Ni(*SS*-L)}$_2$(*d*-tart)$(H_2O)]^{2+}$ and $(+)_{589}$-[{Ni(*RR*-L)}$_2$ox]$^{2+}$ are quite similar and their CD spectra are almost enantiomeric. This fact indicates that the CD patterns are determined by the chiralities associated with the coordinated macrocyclic ligand and that the effects of the *d*-tartrate ion on the CD pattern are small.

Figure 3 shows that the CD intensity of the α-isomer is stronger than those of the β- and γ-isomers. This is most likely because only the α-isomer has a skeletal chirality (see **2**—**4**). In view of the structure found in the crystal of the α-isomer of the racemic perchlorate **2**,[3] the optically active α-isomer containing *RR*-L would have six-membered rings in the λ twist conformation and five-membered rings in the δ gauche conformation.

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3) a) N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, **1973**, 1963; b) The γ-perchlorate crystallizes with six-membered ring moieties randomly adopting the chair or twist conformation.[3a]

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7) The product contains a small amount of $(+)_{589}$-[{Ni(*RR*-L)}$_2$ox]$(ClO_4)_2$ in addition to the main component of [{Ni(*rac*-L}$_2$ox]$(ClO_4)_2$. These can be separated by methanol extraction (see text).

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10) The final atomic parameters and a list of the observed and calculated structure factors are kept in the Office of the Chemical Society of Japan (Document No. 8153). One of the two water molecules of crystallization (Ow(2)) is disordered and located at two positions, Ow(2a) and Ow(2b), with the populations of 0.7 and 0.3, respectively. The difference syntheses suggested large thermal oscillation, or static disorder, for the perchlorate oxygen atoms. One of the perchlorate oxygens, Op(8), was located at three positions Op(8a), O(8b), and Op(8c) with the population of 0.333.

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12) Details will be reported elsewhere.

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1981, Abstr. pp. 65—68. The folding of the macrocyclic ligand in the present study can be explained in the same way.

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