Synthesis and Characterization of *trans*-[$CoCl_2(N_4x)$]$^+$ (N_4x = 1,4,7,10-Tetraazacycloheptadecane, -cyclooctadecane, -cyclononadecane, -cycloicosane, -cyclohenicosane, and -cyclodocosane)

Masanobu TSUCHIMOTO and Junnosuke FUJITA*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-01
(Received September 4, 1991)

New macrocyclic ligands, 1,4,7,10-tetraazacyclooctadecane (N_411), -cyclononadecane (N_412), -cycloicosane (N_413), -cyclohenicosane (N_414), and -cyclodocosane (N_415), and the Co(III) complexes, *trans*-[$CoCl_2(N_4x)$]$^+$ (x = 10—15) were prepared and characterized. While two isomers, one has an *RSSR*(*SRRS*) and the other an *RSSS*(*SRRR*) configuration for the four chiral nitrogen atoms, were obtained for the N_4x (x = 12—15) complexes, only the *RSSR*(*SRRS*) isomer was isolated for the N_410 and N_411 complexes. The ligand field strength of N_4x (Δ(N)) decreases largely from x = 6 to 9 or 10, and then shows an increasing tendency with the increasing ring members. The reduction potential for the Co(III)/Co(II) couple ($E_{1/2}$) becomes less negative with the increasing ring members, and the $\Delta E_p(=E_{pa}-E_{pc})$ values are very large for the N_48—N_411 complexes. The variations of these observed values with the number of ring members indicate that medium-sized chelate rings are unstable compared with other sized ones.

Medium-sized chelate rings (8—11 ring members) in metal complexes are known to be unstable owing to the strain arising from repulsions among atoms of the ring, and their complexes are rather limited to those with diphosphines[1-4] and tetraazamacrocycles.[5-9] In our previous papers,[10-12] we have reported the preparation and properties of 1,4,7,10-tetraazacyclotetradecane, -cyclopentadecane and -cyclohexadecane complexes of cobalt(III) which involve a seven-, eight-, and nine-membered chelate ring, respectively. With an increase in ring memberes in these complexes, the ligand field strength of macrocycles is reduced, and the Co(III)/Co(II) redox potential becomes less negative. Thus it is interesting to investigate how such spectral and electrochemical properties vary with a further increase in ring members. This paper deals with new 1,4,7,10-tetraazamacrocyclic ligands and their *trans*-dichlorocobalt(III) complexes involving a larger-membered chelate ring than nine. The abbreviations, N_410, N_411, N_412, N_413, N_414, and N_415 are used for 1,4,7,10-tetraazacycloheptadecane, -cyclooctadecane, -cyclononadecane, -cycloicosane, -cyclohenicosane, and -cyclodocosane, respectively.

Experimental

Measurements. ^{13}C NMR spectra were recorded on a Hitachi R-90HS NMR spectrometer, and absorption spectra on a Hitachi U-3400 spectrophotometer. Gaussian curve fitting analyses of absorption spectra were performed with the modified LGNS program.[10] Cyclic and RDE voltammetric measurements were carried out on acetonitrile solutions (1 mmol dm^{-3} complex, 0.1 mol dm^{-3} $N(C_4H_9)_4BF_4$) at 24 °C. Other experimental details for electrochemical measurements were described in a previous paper.[10]

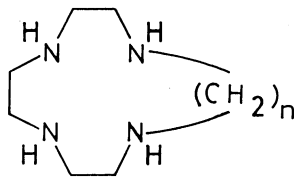

Fig. 1. Ligands N_4x ($x(n)$=10(7)—15(12)).

Materials. *trans*-[$CoCl_2(N_46)$]BF_4,[10,13] *trans*-[$CoCl_2(N_4x)$]-(ClO_4 or BF_4) (x=7, 8, 9),[10] and the ligand $N_410{\cdot}3HBr$[14] were prepared by the literature methods.

1,4,7,10-Tetrakis(*p*-tolylsulfonyl)-1,4,7,10-tetraazacyclooctadecane (1). This compound was prepared by a method similar to those for analogous cyclotetradecane, -cyclopentadecane, and -cyclohexadecane.[5] Yield: 20.4%. ^{13}C NMR ($CDCl_3$, TMS) δ=21.3$_9$, 21.4$_2$ (C–Ts-), 25.1, 27.3, 28.0 (C–C–C), 48.1, 50.1 (N–C–C), 127.2, 127.3, 129.6, 129.7, 135.0, 135.5, 143.2, 143.6 (phenyl).

1,4,7,10-Tetrakis(*p*-tolylsulfonyl)-1,4,7,10-tetraazacyclononadecane (2), -cycloicosane (3), -cyclohenicosane (4), and -cyclodocosane (5). These compounds were prepared by a method of Vriesema et al.[15] from 1,4,7,10-tetrakis(*p*-tolylsulfonyl)-1,4,7,10-tetraazadecane (**6**)[5] and 1,ω-dirbomoalkane (ω=9, 10, 11, or 12) in the presence of Cs_2CO_3. The reaction was carried out under a nitrogen atmosphere. To a solution of (**6**) (76.3 g, 0.1 mol) in dry *N*,*N*-dimethylformamide (DMF) (1.5 dm^3) was added Cs_2CO_3 (68.4 g, 0.21 mol). The solution was warmed at 70 °C, and a DMF solution (500 cm^3) of 0.1 mol of 1,ω-dibromoalkane ($Br(CH_2)_9Br$: 28.6 g, $Br(CH_2)_{10}Br$: 30.0 g, $Br(CH_2)_{11}Br$: 31.4 g, $Br(CH_2)_{12}Br$: 32.8 g) was added dropwise to the solution over 3 h with stirring. The mixture was stirred for a day at 70 °C, and then rotoevaporated to ca. 300 cm^3. The concentrate was poured into 1.5 dm^3 of water, and the mixture was stirred to give a pale yellow precipitate. It was collected by filtration, washed with water and air-dried. This product was dissolved in CH_2Cl_2 and chromatographed on a silica gel column (ϕ 7.5 cm×40 cm, eluent: CH_2Cl_2–AcOEt 40:1 v/v). The fractions of the second main band were collected, and the solvent was removed. The crude (often oily) product was recrystallized from CH_2Cl_2 by adding diethyl ether.

Yield of (**2**): 37.8 g (42.7%). ^{13}C NMR ($CDCl_3$, TMS) δ=21.3$_9$, 21.4$_2$ (C–Ts–), 25.2, 26.8, 27.4, 28.0 (C–C–C), 48.6, 50.6 (N–C–C), 127.2, 127.4, 129.6, 129.7, 134.9, 135.3, 143.1, 143.5 (phenyl). Yield of (**3**): 32.8 g (36.4%). ^{13}C NMR

($CDCl_3$, TMS) δ=21.4 (C–Ts–), 25.3, 27.3, 27.8 (C–C–C), 48.2, 48.3, 50.5 (N–C–C), 127.2, 127.3, 129.5, 129.7, 134.8, 135.4, 143.1, 143.5 (phenyl). Yield of (**4**): 41.1 g (44.9%). ^{13}C NMR ($CDCl_3$, TMS) δ=21.4 (C–Ts–), 25.7, 27.4, 27.5, 27.8, 28.2 (C–C–C), 48.4, 50.4, 50.6 (N–C–C), 127.2, 127.4, 129.6, 129.8, 134.9, 135.6, 143.1, 143.6 (phenyl). Yield of (**5**): 14.3 g (15.5%). ^{13}C NMR ($CDCl_3$, TMS) δ=21.4, 21.5 (C–Ts–), 25.7, 27.6, 27.9, 28.1, 28.3 (C–C–C), 48.3, 50.0, 50.4 (N–C–C), 127.2, 127.4, 129.6, 129.8, 135.0, 135.5, 143.1, 143.6 (phenyl).

1,4,7,10-Tetraazacyclooctadecane (N_411), -cyclononadecane (N_412), -cycloicosane (N_413), -cyclohenicosane (N_414), and -cyclodocosane (N_415) Trihydrobromide (N_4x·3HBr, x=11), and Tetrahydrobromide (N_4x·4HBr, x=12, 13, 14, and 15). Each product of finely powdered (**1**)—(**5**) (12.5 mmol, (**1**): 10.9 g, (**2**): 11.1 g, (**3**): 11.3 g, (**4**): 11.4 g, (**5**): 11.6 g) was detosylated by refluxing in a mixture of 47% hydrobromic acid (600 cm^3) and acetic acid (340 cm^3) for 3 d (**1**), for 5 d (**2** and **3**), and for 10 d (**4** and **5**). The resulting red-black solution was filtered, and the filtrate was concentrated to ca. 100 cm^3 under reduced pressure. On addition of 1 dm^3 of an ethanol–diethyl ether mixture (3:1) the concentrate gave a yellow precipitate, which was collected by filtration. When the color of product was grayish, it was mixed with hot methanol, insoluble grayish impurities were removed by filtration, and the filtrate was evaporated to dryness. The product was recrystallized from water and ethanol.

Yield of N_411·3HBr·2H_2O: 5.9 g (89%). Found: C, 31.57; H, 7.27; N, 10.41%. Calcd for $C_{14}H_{39}N_4O_2Br_3$: C, 31.42; H, 7.35; N, 10.47%. Yield of N_412·4HBr: 7.1 g (96%). Found: C, 30.04; H, 6.43; N, 9.19%. Calcd for $C_{15}H_{38}N_4Br_4$: C, 30.33; H, 6.45; N, 9.43%. Yield of N_413·4HBr·H_2O: 7.1 g (91%). Found: C, 30.84; H, 6.82; N, 8.83%. Calcd for $C_{16}H_{42}N_4OBr_4$: C, 30.69; H, 6.76; N, 8.95%. Yield of N_414·4HBr: 6.2 g (80%). Found: C, 32.76; H, 6.83; N, 8.86%. Calcd for $C_{17}H_{42}N_4Br_4$: C, 32.82; H, 6.80; N, 9.01%. Yield of N_415·4HBr: 6.7 g (84%). Found: C, 33.89; H, 7.07; N, 8.78%. Calcd for $C_{18}H_{44}N_4Br_4$: C, 33.98; H, 6.97; N, 8.81%.

***trans*-[$CoCl_2(N_4x)$]ClO_4 (x=10—15).** These complexes were prepared by two methods similar to those for the corresponding N_4x (x=7, 8, 9) complexes.[10]

Method 1. $CoCl_2$·6H_2O (0.24 g, 1 mmol) was added to a methanol solution (100 cm^3) of 1 mmol of N_4x. The free N_4x ligand was obtained by extracting an aqueous NaOH solution of N_4x·nHBr with $CHCl_3$, and then by evaporating $CHCl_3$.[5] Air was bubbled through the solution for 2 h to oxidize Co^{2+} to Co^{3+}, and then concd hydrochloric acid (0.3 cm^3) was added dropwise. Air was bubbled for another 1 h, and the solution was evaporated to dryness under reduced pressure. The residue was dissolved in methanol (ca. 20 cm^3), and undissolved materials were removed by filtration. The filtrate was applied on a column (ϕ 6.5 cm×35 cm) of Sephadex LH-20. Elution with methanol gave a main green or brown band. The eluate was concentrated to a small volume (ca. 10 cm^3) under reduced pressure. On addition of $LiClO_4$ with stirring, the concentrate yielded a brown (the N_410 complex) or a green (the N_411—N_415) precipitate. It was collected by filtration, washed with ethanol, and recrystallized from CH_3CN or CH_3NO_2 and diethyl ether.

The product of the N_410 complex, a mixture of brown and green fine crystals, was shown by the ^{13}C NMR spectrum to contain a small amount of an unknown complex which was supposed to be another isomer of the complex. Attempts to remove it were unsuccessful. The pure N_410 complex was obtained by Method 2 described below. The complex forms green and brown crystals by recrystallization (vide infra). The N_410 complex slowly decomposed in fairly strong hydrochloric acid (>1 mol dm^{-3}) to give Co(II) species, while other N_4x complexes were stable under similar conditions.

Yield of *trans*-[$CoCl_2(N_411)$]ClO_4: 0.17 g (35%). Found: C, 34.38; H, 6.76; N, 11.40%. Calcd for $C_{14}H_{32}N_4O_4CoCl_3$: C, 34.62; H, 6.64; N, 11.54%. Yield of *trans*-[$CoCl_2(N_412)$]ClO_4: 0.19 g (37%). Found: C, 36.15; H, 6.99; N, 11.42%. Calcd for $C_{15}H_{34}N_4O_4CoCl_3$: C, 36.05; H, 6.86; N, 11.21%. Yield of *trans*-[$CoCl_2(N_413)$]ClO_4: 0.21 g (42%). Found: C, 37.55; H, 7.18; N, 10.69%. Calcd for $C_{16}H_{36}N_4O_4CoCl_3$: C, 37.40; H, 7.06; N, 10.90%. Yield of *trans*-[$CoCl_2(N_414)$]ClO_4: 0.15 g (28%). Found: C, 38.86; H, 7.47; N, 10.51%. Calcd for $C_{17}H_{38}N_4O_4CoCl_3$: C, 38.69; H, 7.26; N, 10.62%. Yield of *trans*-[$CoCl_2(N_415)$]ClO_4: 0.27 g (50%). Found: C, 39.90; H, 7.44; N, 10.46%. Calcd for $C_{18}H_{40}N_4O_4CoCl_3$: C, 39.90; H, 7.44; N, 10.34%.

All of the complexes prepared by this method are shown by ^{13}C NMR spectra to have C_2 symmetry, and are designated as C_2 isomer in this paper.

Method 2. To an aqueous solution of $K_3[Co(CO_3)_3]$ prepared in a 2 mmol scale[16] was added N_4x·nHBr (2 mmol), and the mixture was heated on a water bath until evolution of carbon dioxide ceased. The resulting deep red solution was filtered, the filtrate was evaporated to dryness under reduced pressure, and the residue was mixed with ethanol to extract the complex. The extract was evaporated again to dryness under reduced pressure, giving a red oily product. It was dissolved in water, and the solution was applied on a small column (ϕ 2.5 cm×10 cm) of SP-Sephadex C-25. The Sephadex adsorbed the product was placed on the top of a column (ϕ 2.5 cm×60 cm) of SP-Sephadex C-25, and the product was eluted with an aqueous 0.1 mol dm^{-3} LiCl solution (pH ca. 4, HCl) for the N_410—N_413 complexes, and with an aqueous 0.1 mol dm^{-3} KCl solution (pH ca. 4, HCl) for the N_414 and N_415 complexes. Each column of all the complexes except the N_411 complex which showed only one band, gave two purple-red major bands. Each fraction of the bands was mixed with 0.5 cm^3 of concd hydrochloric acid and evaporated to dryness under reduced pressure. The residue was mixed with a minimum amount of ethanol added a drop of hydrochloric acid to dissolve the complex, and undissolved materials were removed by filtration. To the ethanol solution was added $LiClO_4$ with stirring. For the N_410 complex, the C_2 isomer was precipitated from the eluate of the second band, but a mixture of unknown complexes was obtained from the eluate of the first band. The N_411 complex which gave only one band on column chromatography yielded the C_2 isomer. For each of the N_412, N_414, and N_415 complexes, the C_2 isomer was obtained from the eluate of the first band, while another isomer was precipitated from the eluate of the second band. These new isomers are designated as C_1 isomer, since they are shown to have no symmetry axis or plane by ^{13}C NMR spectra. For the N_413 complex, the complex in the eluate of the first band was decomposed during the course of isolation to give a mixture of unknown complexes, but the C_1 isomer was obtained from the eluate of the second band. All the products were recrystallized from CH_3CN or CH_3NO_2 (acidified with HCl or $HClO_4$) and diethyl ether. The C_1 isomers of the N_413 and N_415 complexes yielded a mixture of green and brown crystals,

while other C_1 isomers were brown crystals.

Yield of *trans*-[$CoCl_2(N_410)$]ClO_4 (C_2): 0.25 g (27%). Found: C, 33.10; H, 6.45; N, 11.93%. Calcd for $C_{13}H_{30}N_4O_4CoCl_3$: C, 33.10; H, 6.41; N, 11.88%. Yield of *trans*-[$CoCl_2(N_411)$]ClO_4 (C_2): 0.76 g (78%). Yield of *trans*-[$CoCl_2(N_412)$]$ClO_4 \cdot CH_3NO_2$ (C_1): 0.21 g (19%). Found: C, 34.27; H, 6.56; N, 12.18%. Calcd for $C_{16}H_{37}N_5O_6CoCl_3$: C, 34.27; H, 6.65; N, 12.49%. The presence of CH_3NO_2 of crystallization was confirmed by the ^{13}C NMR spectrum in d^6-DMSO solution. Yield of *trans*-[$CoCl_2(N_412)$]ClO_4 (C_2): 0.24 g (24%). Yield of *trans*-[$CoCl_2(N_413)$]ClO_4 (C_1): 0.55 g (53%). Found: C, 37.02; H, 7.10; N, 10.69%. Calcd for $C_{16}H_{36}N_4O_4CoCl_3$: C, 37.40; H, 7.06; N, 10.90%. Yield of *trans*-[$CoCl_2(N_414)$]ClO_4 (C_1): 0.10 g (9.9%). Found: C, 38.23; H, 7.38; N, 10.33%. Calcd for $C_{17}H_{38}N_4O_4CoCl_3$: C, 38.69; H, 7.26; N, 10.62%. Yield of *trans*-[$CoCl_2(N_414)$]ClO_4 (C_2): 0.32 g (30%). Yield of *trans*-[$CoCl_2(N_415)$]ClO_4 (C_1): 0.23 g (21%). Found: C, 39.35; H, 7.61; N, 10.52%. Calcd for $C_{18}H_{40}N_4O_4CoCl_3$: C, 39.90; H, 7.44; N, 10.34%. Yield of *trans*-[$CoCl_2(N_415)$]ClO_4 (C_2): 0.19 g (17%).

Results and Discussion

Synthesis and Characterization of Ligands and Complexes. New tetraaza macrocyclic ligands N_4x (x=11—15) were prepared in moderate yields. Cyclization reactions were carried out with disodium salt of (**6**) and octamethylene bis(*p*-toluenesulfonate)[5] for N_411, and with dicaesium salt of (**6**) and 1,ω-dibromoalkane[15] for N_412—N_415. In these reactions the high dilution method was not employed. The cyclization products were detosylated by refluxing in a mixture of hydrobromic acid and acetic acid for a long time, 3—10 days, the reaction taking longer time with the increasing number of ring members. The ligands were isolated as tri- or tetrahydrobromides.

Green or brown complexes, [$CoCl_2(N_4x)$]ClO_4 (x=10—15) were obtained by two methods; one is oxidation of a methanol solution containing $CoCl_2 \cdot 6H_2O$ and N_4x with air (Method 1), and the other is reaction of hydrochloric acid and $[Co(CO_3)(N_4x)]^+$ which was prepared from $K_3[Co(CO_3)_3]$ and $N_4x \cdot n$HBr (Method 2). The former method gave only one isomer for all the N_4x complexes, while two isomers were isolated for the N_4x (x=12, 14, 15) complexes by the latter method, although only one isomer was obtained for the N_410, N_411, and N_413 complexes. All of these dichloro complexes show electronic spectra similar to those of *trans*-$[CoCl_2(N_4x)]^+$ (x=7, 8, 9),[10] and can be assigned to a *trans*-dichloro isomer (Table 1). For *trans*-$[CoCl_2(N_4x)]^+$, there are six geometrical isomers arising from the combination of four chiral secondary nitrogen atoms (*R* or *S*); four pairs of enantiomers, *RRRR*(*SSSS*) (C_2 symmetry), *RRRS*(*SSSR*) (=*RSSS*(*SRRR*)) (C_1 symmetry), *RSRR*(*SRSS*) (=*RRSR*(*SSRS*)) (C_1 symmetry), and *RSSR*(*SRRS*) (C_2 symmetry), and two meso isomers (C_s symmetry), *RRSS*(*SSRR*) and *RSRS*(*SRSR*), where symbols *R* and *S* are given in the order of N(1)N(4)N(7)N(10). All of the isomers obtained by Method 1 are indicated by ^{13}C NMR spectra to have either C_2 or C_s symmetry (Table 2). For each pair of two isomers of *trans*-$[CoCl_2(N_4x)]^+$ (x=12, 14, 15) prepared by Method 2, one is the same as the isomer (C_2 or C_s symmetry) obtained by Method 1, and the other is shown to have C_1 symmetry by ^{13}C NMR spectra. The N_413 complex obtained by Method 2 has C_1 symmetry. Molecular models indicate that possible isomers of $[Co(CO_3)(N_4x)]^+$ are only two, *RSSR*(*SRRS*) and *RSSS*(*SRRR*) as shown

Table 1. Electronic Spectral Data[a]

Complex	$\tilde{\nu}/10^3$ cm^{-1} (log (ε/mol^{-1} dm^3 cm^{-1}))			
	1st band		2nd band	CT
trans-[$CoCl_2(N_410)$]ClO_4 (C_2)	15.8 (1.65)	20.5 (2.26)	22.9 (2.25)	31.8 (sh) 39.0 (4.40)
Green[b]	15.8	20.7	22.6	
Brown[b]	15.7	20.3	23.2	
trans-[$CoCl_2(N_411)$]ClO_4 (C_2)	15.8 (1.78)	21.4 (2.29)	22.5 (2.30)	32.4 (sh) 39.1 (4.43)
trans-[$CoCl_2(N_412)$]ClO_4 (C_2)	15.9 (1.75)	21.4 (2.28)	22.5 (2.29)	31.8 (sh) 39.2 (4.43)
trans-[$CoCl_2(N_412)$]$ClO_4 \cdot CH_3NO_2$ (C_1)[c]	15.6 (1.79)	20.2 (2.37)	22.8 (2.34)	31.7 (sh) 38.9 (4.45)
trans-[$CoCl_2(N_413)$]ClO_4 (C_2)	15.9 (1.75)	21.3 (2.30)	22.8 (2.29)	31.8 (sh) 39.1 (4.44)
trans-[$CoCl_2(N_413)$]ClO_4 (C_1)[c]	15.6 (1.78)	20.5 (2.33)	22.7 (2.30)	31.7 (3.30) 39.0 (4.42)
trans-[$CoCl_2(N_414)$]ClO_4 (C_2)	15.9 (1.78)	21.4 (2.31)	22.9 (2.31)	32.2 (sh) 39.1 (4.43)
trans-[$CoCl_2(N_414)$]ClO_4 (C_1)[c]	15.6 (1.75)	20.3 (2.31)	22.7 (2.27)	32.0 (sh) 38.9 (4.39)
trans-[$CoCl_2(N_415)$]ClO_4 (C_2)	15.9 (1.76)	21.3 (2.29)	22.7 (2.29)	32.1 (3.30) 39.1 (4.42)
trans-[$CoCl_2(N_415)$]ClO_4 (C_1)[c]	15.6 (1.79)	20.4 (2.34)	22.7 (2.31)	31.7 (sh) 38.9 (4.42)

a) In CH_3CN. b) By a Nujol mull method. c) In CH_3CN weakly acidified with $HClO_4$.

Table 2. $^{13}C\{^1H\}$ NMR Spectral Data

Compound	δ (C–C–C)	δ (C–C–N)
$N_4$11·3HBr·2H_2O[a]	24.8, 25.4, 26.9	44.5, 45.5, 46.1, 48.8
$N_4$12·4HBr[a]	25.5, 26.1, 27.2, 27.4	45.4, 47.2, 47.9, 48.4
$N_4$13·4HBr·H_2O[a]	25.6, 25.8, 27.9, 28.0	43.7, 44.1, 44.2, 48.8
$N_4$14·4HBr[a]	26.0, 26.1, 28.4, 28.7	44.1, 44.4, 49.1
$N_4$15·4HBr[a]	26.0, 26.1, 28.5, 28.8, 29.0	43.8, 44.2, 44.3, 49.0
trans-[$CoCl_2$($N_4$10)]ClO_4 (C_2)[b]	24.2, 28.1, 28.9	50.3, 53.8, 56.8, 58.5
trans-[$CoCl_2$($N_4$11)]ClO_4 (C_2)[b]	21.2, 24.0, 26.7	50.1, 53.4, 53.8, 57.9
trans-[$CoCl_2$($N_4$12)]ClO_4 (C_2)[b]	25.4, 26.1, 26.8, 27.4	50.1, 53.8, 55.7, 57.4
trans-[$CoCl_2$($N_4$12)]ClO_4·CH_3NO_2 (C_1)[c]	23.7, 23.8, 24.3, 24.5, 25.8, 26.3, 26.8	50.2, 50.4, 53.1, 54.0, 54.3, 54.5, 56.4, 57.4
trans-[$CoCl_2$($N_4$13)]ClO_4 (C_2)[b]	24.6, 26.6, 26.7, 26.8	50.1, 53.7, 54.6, 56.4
trans-[$CoCl_2$($N_4$13)]ClO_4 (C_1)[d]	25.1, 25.6, 25.8, 26.1, 26.3, 26.7, 26.8	50.1, 50.6, 53.8, 54.0, 54.1, 54.5, 56.1, 56.4
trans-[$CoCl_2$($N_4$14)]ClO_4 (C_2)[c]	25.2, 26.4, 28.4	50.7, 54.3, 54.8, 56.9
trans-[$CoCl_2$($N_4$14)]ClO_4 (C_1)[c]	25.3, 25.5, 25.8, 26.0, 26.5, 26.6, 26.9	50.3, 50.7, 53.4, 53.6, 54.0, 54.5, 55.4, 56.0
trans-[$CoCl_2$($N_4$15)]ClO_4 (C_2)[b]	25.7, 26.3, 27.2, 27.4	50.1, 53.7, 55.2, 56.4
trans-[$CoCl_2$($N_4$15)]ClO_4 (C_1)[d]	26.5, 27.3, 27.5, 28.1	50.2, 50.7, 54.0, 54.2, 54.5, 54.9, 56.0

a) In D_2O, dioxane (67.4 ppm) reference. b) In CD_3CN, CD_3CN (1.3 ppm) reference. c) In CD_3NO_2. d) In CD_3NO_2 weakly acidified with $HClO_4$.

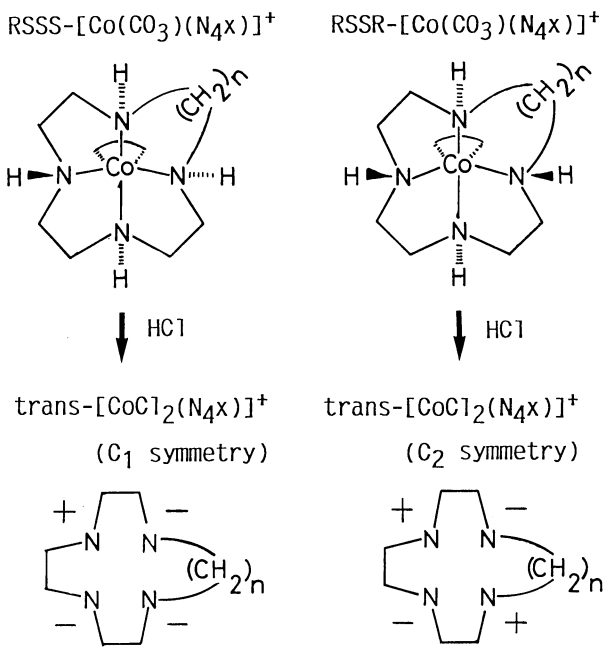

Fig. 2. Possible structures of $[Co(CO_3)(N_4x)]^+$. The signs+and −represent amine protons disposed above and below from the CoN_4 plane, respectively.

in Fig. 2, although there are 16(=2^4) different combinations for the chiral nitrogen atoms. If it is assumed that the chirality of nitrogen in the carbonato complexes is retained in the reaction with hydrochloric acid, the resulting *trans*-dichloro complex is the *RSSR*(*SRRS*) (C_2 symmetry) or *RSSS*(*SRRR*) (C_1 symmetry) isomer. Thus the complexes formed by Method 1 can be assigned to the *RSSR*(*SRRS*) (C_2) isomer, while the other isomers of the N_4x (x=12—15) complexes derived by Method 2 to the *RSSS*(*SRRR*) (C_1) isomer. The *RSSR*(*SRRS*) (C_2) structure in analogous *trans*-$[MX_2(N_4x)]^{n+}$-type complexes has been found by X-ray analysis on *trans*-[$NiCl_2$($N_4$7)],[6] *trans*-[$CoCl_2$($N_4$8)]$^+$,[11] *trans*-[$NiCl_2$-($N_4$9)],[6] and *trans*-[$Co(NO_2)_2$($N_4$10)]BF_4.[14] No structure analysis has been reported for the *RSSS*(*SRRR*) (C_1) isomer.

The *trans*-$[CoCl_2(N_4x)]^+$ complexes seem to be more stable in the C_2 isomer than the C_1 one. The complexes yielded only the C_2 isomer by Method 1. The C_1 isomers of $N_4$13 and $N_4$15 complexes isomerize rapidly in CD_3CN with a color change from brown to green, unless the solutions are acidic. The ^{13}C NMR spectra of the green solutions are identical with those of the C_2 isomers. The C_1 isomers of the $N_4$12 and $N_4$14 complexes are stable in neutral CD_3CN. Attempts to isomerize them by adding a base such as $N(C_2H_5)_3$ resulted in decomposition of the complexes. Relative stability of the C_1 isomer to the C_2 one seems to depend on the number of members of large chelate rings.

As stated in Experimental section, the C_2 isomer of the $N_4$10 complex gives a mixture of green and brown crystals, but all of the other C_2 isomers are green in the solid state. For the C_1 isomers in the solid state, the $N_4$12 and $N_4$14 complexes are brown, while the $N_4$13 and $N_4$15 complexes are a mixture of green and brown fine crystals. Green and brown crystals of the $N_4$10 complex formed by growing slowly in CH_3NO_2 solution can be separated by hand picking. Electronic spectra in Nujol mulls show a little difference between the green and brown products (Table 1). However, these products in CD_3CN solutions give the same spectra in both absorption and ^{13}C NMR. The green and brown crystals afford again a mixture of green and brown crystals by recrystallization. The C_1 isomers of the $N_4$13

and N415 complexes have very similar properties to the C_2 isomer of the N410 complex. Thus the C_2 isomer of N410 and the C_1 isomers of N413 and N415 complexes crystallize in two forms with different colors. The C_2 isomer of *trans*-$[CoCl_2(N48)]BF_4$ also forms green and brown crystals. X-Ray analysis has revealed that the green crystals consist of a mixture of enantiomers formed by spontaneous resolution with the eight-membered chelate ring in a distroted boat-boat conformation, while the brown crystals are a racemate and have the ring conformation disordered in boat-boat (40%) and twist-boat-chair (60%) forms.[11]

Electronic Spectra. All of the dichloro complexes show absorption spectra characteristic of a *trans*-$[CoCl_2N_4]^+$-type complex in the ligand field region (Fig. 3). Under D_{4h} approximation the band around 16000 cm^{-1} can be assigned to the Ia($^1E_g \leftarrow {}^1A_{1g}$), and broad bands around 20000—25000 cm^{-1} to the Ib($^1A_{2g} \leftarrow {}^1A_{1g}$), and IIa($^1B_{2g} \leftarrow {}^1A_{1g}$) transitions.[12] For all the complexes, the C_1 isomer shows the bands at a little smaller energy than the corresponding bands of the C_2 isomer. To estimate ligand field parameters of nitrogen (Δ(N)=3$e\sigma$(N), $e\pi$(N) is assumed to be zero) and chloride donors (Δ(Cl)=3$e\sigma$(Cl) −4$e\pi$(Cl)) based on the AOM model,[17,18] maximum positions of the Ia(= 1/2[Δ(N)+Δ(Cl)]−C, C: Racah's parameter) and the Ib(=Δ(N)−C) bands were determined by Gaussian curve fitting analysis (Table 3). With these data and the assumption of C=2000 cm^{-1},[12] the estimated values are given in Table 3 together with those for the N46—N49 complexes. In Fig. 4 the parameter values are plotted vs. the number of members of large chelate rings (x in N4x). Figure 4 shows two features; 1) the Δ(N) value decreases sharply from x=6 to 7,8,9, and then increases slowly with the increasing x showing some irregularity, and 2) the Δ(Cl) value increases from x=6 to 9 or 10, and then shows a decreasing tendency, the variation being complementary with the Δ(N) values. The reduction of Δ(N) from x=7 to 9 or 10 in feature 1) would indicate that medium-sized chelate rings are unstable owing to the strain arising from repulsions among atoms of the ring to form larger N-Co-N bite angles than 90° and longer Co-N bonds. The N-Co-N bite angle and the average Co-N distance are 104.0(1)° and 2.017(4) Å in the green isomer of *trans*-$[CoCl_2(N48)]BF_4$, 107.2(3)° and 2.040(8) Å in it's brown isomer,[11] and 105.4(1)° and 2.023(3) Å in *trans*-$[Co(NO_2)_2(N410)]BF_4$,[14] whereas the Co-N distances for the five-membered chelate rings in

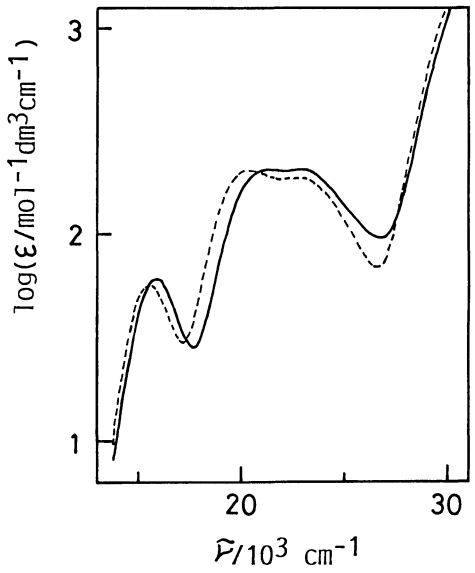

Fig. 3. Electronic spectra of the C_2 isomer (—) and the C_1 isomer (····) of *trans*-$[CoCl_2(N414)]^+$ in acetonitrile.

Table 3. Band Positions Obtained by Gaussian Curve Fitting Analysis and Ligand Field Parameters for *trans*-$[CoCl_2(N4x)]^+$

Complex	$\tilde{\nu}/10^3$ cm^{-1} (log (ε/mol^{-1} dm^3 cm^{-1}))				
	1st band		2nd band	ΔN	ΔCl
trans-$[CoCl_2(N46)]^+$	16.67 (1.52)	23.70 (2.16)[a]		25.70	11.64
trans-$[CoCl_2(N47)]^+$ (C_2)	15.9 (1.80)	21.2 (2.10)	23.5 (2.08)[b] 26.8 (1.94)	23.2	12.6
trans-$[CoCl_2(N47)]^+$ (C_1)	16.0 (1.70)	21.2 (2.11)	23.7 (2.14)[c]	23.2	12.8
trans-$[CoCl_2(N48)]^+$ (C_2)	15.9 (1.64)	20.6 (2.22)	23.7 (2.12)[c]	22.6	13.2
trans-$[CoCl_2(N49)]^+$ (C_2)	15.7 (1.71)	20.1 (2.23)	23.4 (2.18)[c]	22.1	13.3
trans-$[CoCl_2(N410)]^+$ (C_2)	15.8 (1.61)	20.2 (2.20)	23.5 (2.15)	22.2	13.4
trans-$[CoCl_2(N411)]^+$ (C_2)	15.9 (1.77)	20.7 (2.17)	23.7 (2.18)	22.7	13.1
trans-$[CoCl_2(N412)]^+$ (C_2)	15.9 (1.74)	20.7 (2.17)	23.7 (2.17)	22.7	13.1
trans-$[CoCl_2(N412)]^+$ (C_1)	15.6 (1.78)	19.9 (2.32)	23.3 (2.28)	21.9	13.3
trans-$[CoCl_2(N413)]^+$ (C_2)	15.9 (1.75)	20.3 (2.12)	23.4 (2.24)	22.3	13.5
trans-$[CoCl_2(N413)]^+$ (C_1)	15.7 (1.77)	20.1 (2.28)	23.5 (2.22)	22.1	13.3
trans-$[CoCl_2(N414)]^+$ (C_2)	15.9 (1.77)	20.7 (2.23)	23.8 (2.21)	22.7	13.1
trans-$[CoCl_2(N414)]^+$ (C_1)	15.6 (1.74)	20.1 (2.28)	23.5 (2.21)	22.1	13.1
trans-$[CoCl_2(N415)]^+$ (C_2)	15.9 (1.76)	20.6 (2.18)	23.7 (2.19)	22.6	13.2
trans-$[CoCl_2(N415)]^+$ (C_1)	15.7 (1.77)	20.0 (2.28)	23.4 (2.24)	22.0	13.4

a) From Ref. 13. b) From Ref. 12. Splitting of the 2nd d-d band is observed in the spectra of this complex.
c) From Ref. 10.

these complexes are in the range 1.930—1.952 Å. Feature 2) that shows a complementary relation between the Δ(Cl) and Δ(N) values; the smaller the Δ(N) value, the larger the Δ(Cl) value, would correspond to the cis effect of N_4x ligands on coordinate bonds of chloride ligands in the cis positions. A nearly constant position of the Ia bands should be related with this cis effect. Such a clear cis effect was not observed when compared with one another for many dichloro complexes of other amines such as ammonia or diamines.[12]

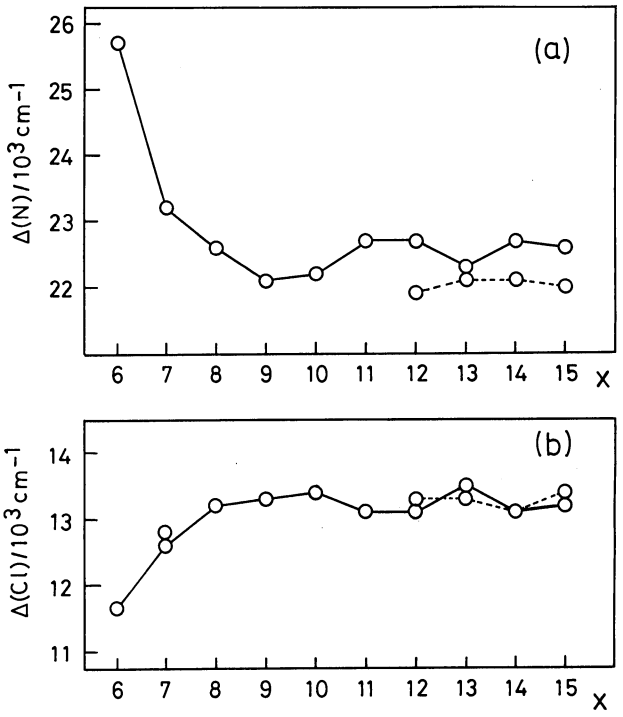

Fig. 4. The variations of the ligand field parameters of Δ(N) (a) and Δ(Cl) (b) with the chelate ring size of C_2 (–O–O–) and C_1 (··O··O··) isomers of *trans*-$[CoCl_2(N_4x)]^+$.

Electrochemistry. Table 4 lists the data of redox potentials for the Co(III)/Co(II) couples of the N_4x complexes. Figure 5 shows the variation of potentials ($E_{1/2}$/V) obtained by the RDE method as the ring size of N_4x increases. The $E_{1/2}$ value shows a positive shift from x=6 to 9, and then becomes nearly constant, although the values of the larger N_4x complexes (x>13) fluctuate to some extent. The variation of $E_{1/2}$ values indicates that the stability (free energy) difference between the Co(II) and Co(III) complexes decreases with an increase in the ring member of N_4x. The larger N_4x ligand would favor the complex formation with a larger Co(II) ion than Co(III). In Fig. 5 is also plotted the ΔE_p (=[$E_{pa}-E_{pc}$]/mV) values obtained by the CV method under a given condition. The cathodic and anodic peaks are well defined, but the peak values depend on the scan rate. In addition, the i_{pa}/i_{pc} ratio is always less than unity (0.69—0.87). These results indicate that the redox reactions may involve a slow electron transfer process and/or a following chemical reaction of the reduced Co(II) species. To make clear the mechanism of these reactions, further studies will be needed.[13] However, the ΔE_p values, which can be a measure of reversibility, show an interesting variation as the number of ring members is changed. The values are fairly large from x=8 to 11, at x=9 the reaction is irreversible (the anodic peak disappears), and then become small gradually with a further increase in ring members. The N414 and N415 complexes recover reversibility to show a ΔE_p value similar to those of the N46 and N47 complexes, although the $E_{1/2}$ values of the complexes with larger ring members than 9 do not change largely. The variations of the $E_{1/2}$ and ΔE_p values seem to be in accord with those of the ligand field parameters, Δ(N) and Δ(Cl) shown Fig. 4, and it can be concluded that medium-sized (8 to 10 or 11) chelate rings are less stable than other sized ones.

Table 4. Electrochemical Data of the Redox Potential of Co(III)/Co(II)[a]

Complex	Cyclic voltammetry				RDE Voltammetry[b]	
	E_{pc}/V	E_{pa}/V	ΔE_p/mV[c]	($E_{pc}+E_{pa}$)/2/V	$E_{1/2}$/V	$E_{1/4}-E_{3/4}$/mV
trans-$[CoCl_2(N_46)]BF_4$	−0.68	−0.59	90	−0.64	−0.63	90
trans-$[CoCl_2(N_47)]ClO_4$ (C_2)	−0.52	−0.43	90	−0.48	−0.48	90
trans-$[CoCl_2(N_47)]ClO_4$ (C_1)	−0.50	−0.34	155	−0.42	−0.47	100
trans-$[CoCl_2(N_48)]ClO_4$ (C_2)	−0.42	−0.19	230	−0.31	−0.42	115
trans-$[CoCl_2(N_49)]BF_4$ (C_2)	−0.37	—	—	—[d]	−0.39	135
trans-$[CoCl_2(N_410)]ClO_4$ (C_2)	−0.40	−0.15	245	−0.28	−0.39	115
trans-$[CoCl_2(N_411)]ClO_4$ (C_2)	−0.38	−0.15	230	−0.27	−0.39	125
trans-$[CoCl_2(N_412)]ClO_4$ (C_2)	−0.39	−0.25	140	−0.32	−0.40	110
trans-$[CoCl_2(N_412)]ClO_4 \cdot CH_3NO_2$ (C_1)	−0.42	−0.24	155	−0.32	−0.35	105
trans-$[CoCl_2(N_413)]ClO_4$ (C_2)	−0.39	−0.23	135	−0.31	−0.38	110
trans-$[CoCl_2(N_414)]ClO_4$ (C_2)	−0.42	−0.31	110	−0.37	−0.44	115
trans-$[CoCl_2(N_414)]ClO_4$ (C_1)	−0.42	−0.32	100	−0.37	−0.39	100
trans-$[CoCl_2(N_415)]ClO_4$ (C_2)	−0.39	−0.29	105	−0.34	−0.38	100

a) The data for 1 mmol dm^{-3} ferrocene: ($E_{pc}+E_{pa}$)/2=0.09 V, $E_{1/2}$=0.10 V. b) 1500 rpm, scan rate: 10 mV s^{-1}. c) $\Delta E_p=E_{pa}-E_{pc}$. d) Irreversible.

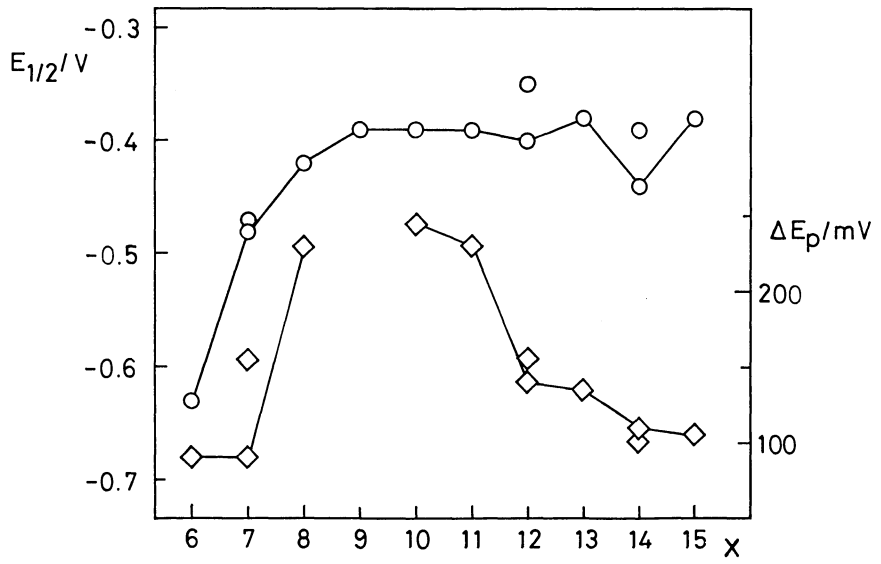

Fig. 5. The variations of the $E_{1/2}$ value (—○—) and the ΔE_p value (—◇—) with the chelate ring size of *trans*-$[CoCl_2(N_4x)]^+$.

References

1) O. Stelzer and E. Unger, *Chem. Ber.*, **108**, 2232 (1975).

2) W. E. Hill, D. M. A. Minahan, J. G. Tayler, and C. A. McAuliffe, *J. Am. Chem. Soc.*, **104**, 6001 (1982).

3) W. E. Hill, J. G. Taylor, C. P. Falshaw, T. J. King, B. Beagley, D. M. Tonge, R. G. Pritchard, and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, **1986**, 2289.

4) H. -P. Klein, U. Thewalt, H. Zettlmeissl, and H. A. Brune, *Z. Naturforsch., B,* **36**, 1125 (1981).

5) M. Sugimoto, M. Nonoyama, T. Ito, and J. Fujita, *Inorg. Chem.*, **22**, 950 (1983).

6) M. Sugimoto, J. Fujita, H. Ito, K. Toriumi, and T. Ito, *Inorg. Chem.*, **22**, 955 (1983).

7) R. D. Hancock and M. P. Ngwenya, *J. Chem. Soc., Dalton Trans.*, **1987**, 2911.

8) R. Bembi, V. K. Bhardwarj, R. Singh, R. Singh, K. Taneja, and S. Aftab, *Inorg. Chem.*, **23**, 4153 (1984).

9) R. Bembi, R. Singh, S. Aftab, T. G. Roy, and A. K. Jhanjee, *J. Coord. Chem.*, **14**, 119 (1985).

10) M. Tsuchimoto, M. Kita, M. Nonoyama, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 227 (1990).

11) M. Tsuchimoto, H. Takazawa, M. Kita, M. Nonoyama, S. Ohba, Y. Saito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 785 (1990).

12) M. Tsuchimoto, M. Kita, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 3410 (1990).

13) Y. Hung, L. Y. Martin, S. C. Jackels, A. M. Tait, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 4029 (1977).

14) M. Tsuchimoto, M. Kita, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **64**, 2554 (1991).

15) B. K. Vriesema, J. Buter, and R. M. Kellog, *J. Org. Chem.*, **49**, 110 (1984).

16) M. Mori, M. Shibata, E. Kyuno, and T. Adachi, *Bull. Chem. Soc. Jpn.*, **29**, 883 (1956).

17) C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, **9**, 401 (1965).

18) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).