Synthesis and Characterization of *trans*[$CoCl_2(232N_4x)$]$^+$ ($232N_4x$=1,4,8,11Tetraazacyclopentadecane, -cyclohexadecane, -cycloheptadecane, -cyclooctadecane, -cyclononadecane, -cycloicosane, -cyclohenicosane, and -cyclotricosane)

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Five new macrocyclic ligands which form a large (10—15) chelate ring upon coordination (1,4,8,11-tetraazacyclooctadecane($232N_410$), -cyclononadecane($232N_411$), -cycloicosane ($232N_412$), -cyclohenicosane-($232N_413$), and -cyclotricosane($232N_415$)), and the Co(III) complexes, *trans*-[$CoCl_2(232N_4x)$]$^+$ (x=7—13, 15) were prepared and characterized. Of six isomers arising from the combination of four chiral nitrogen donor atoms in this type of complex, three and two isomers were obtained, respectively, for complexes with x=7 and 8, and x=9—13 and 15. The ligand field parameter of the nitrogen donor atom (Δ(N)) of $232N_4x$ decreases largely from x=6 to 7, and then shows a small fluctuation with a small decrease at x=even-numbers and a small increase at x=odd-numbers, while a smaller change is observed for the parameter of the chloride ion (Δ(Cl)). The reduction potential for the Co(III)/Co(II) couple ($E_{1/2}$) shifts to the positive side from the complex with x=6 to those with x=7 and 8, and then shows a small change depending on the ring members. The $\Delta E_p(E_{pa}-E_{pc})$ values of complexes with x=8—11 are large, indicating an instability of the medium-sized chelate Co(II) complexes.

In previous papers[1—6] we reported that in a series of the *trans*-[$CoCl_2(222N_4x)$]$^+$-type complexes ($222N_4x$=1,4,7,10-tetraazacycloalkane) (Fig. 1) containing a x (7 to 15)-membered chelate ring, the complexes with a medium-sized chelate ring (x=8—10 or 11) are less stable than those with other ring members. The medium-sized chelate complexes have a strained structure,[2,4] give d–d absorption bands in the low-energy region,[1,3,5] and are electrochemically easily reduced to Co(II),[5] compared with complexes of other membered chelate rings. The $222N_4x$ ligand in the *trans*-dichloro-Co(III) complex forms a puckered plane with three five- and one x-membered chelate rings. In addition to the strained medium-sized chelate ring, the three five-membered chelate rings of the 1,4,7,10-tetraamine moiety around the CoN_4 plane are also largely strained to cause a distortion of the octahedral coordination and a lengthening or weakening of the Co–N bonds.[1] The spectral and electrochemical properties obtained for *trans*-[$CoCl_2(222N_4x)$]$^+$ would be influenced by the strained structure of these three linking five-membered chelate rings. To reduce such strain, we prepared a series of *trans*-dichlorocobalt(III) complexes with 1,4,8,11-tetraazacycloalkane ($232N_4x$) (Fig. 1) which form five-, six-, five-, and x-membered chelate rings upon coordination, and compared their spectral and electrochemical properties with those of the $222N_4x$ complexes. The five-, six-, and five-membered chelate rings of the 1,4,8,11-tetraamine moiety in the mer-coordination seem to have a less-strained structure. The abbreviations $232N_47$, $232N_48$, $232N_49$, $232N_410$, $232N_411$, $232N_412$, $232N_413$, and $232N_415$ are used for 1,4,8,11-tetraazacyclopentadecane, -cyclohexadecane, -cycloheptadecane, -cyclooctadecane, -cyclononadecane, -cycloicosane, -cyclohenicosane, and

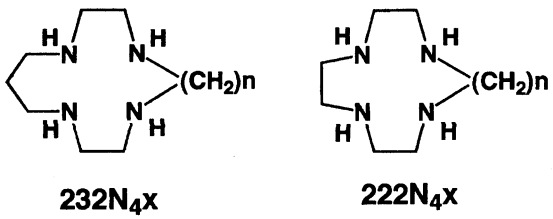

Fig. 1. Ligands $232N_4x$ ($x(n)$=7(4)—13(10), and 15(12)) and $222N_4x$.

-cyclotricosane, respectively.

Bembi et at.[7] reported on the preparation of *trans*-$[CoCl_2(232N_4x)]^+$ ($x=8$ and 9) without detailed characterization. The present paper includes the preparation, separation, and characterization of isomers of these $232N_48$ and $232N_49$ complexes.

Experimental

Measurements. ^{13}C NMR spectra were recorded on a Hitachi R-90HS NMR spectrometer. Dioxane ($\delta=67.4$) was used as an internal standard in D_2O solutions. Absorption spectra in CH_3CN solutions were obtained on a Hitachi U-3400 spectrophotometer. Gaussian curve fitting analyses of absorption spectra were performed using a modified LGNS program.[1] Electrochemical measurements were carried out on CH_3CN solutions (1 mmol dm^{-3} complex, 0.1 mol dm^{-3} $N(C_4H_9)_4BF_4$) at 24 °C with instruments of FUSO.[5] For both cyclic and RDE voltammetric measurements, an $Ag/AgNO_3$ electrode (Ag/0.01 mol dm^{-3} Ag NO_3) and a platinum wire were employed as the reference and auxiliary electrodes, respectively.

Materials. 1,4,8,11-Tetraazacyclopentadecane,[8] -cyclohexadacane,[7], and -cycloheptadecane[7] were prepared by the reported methods. The *trans*-$[CoCl_2(232N_46)]BF_4$ complex was obtained by the addition of $LiBF_4$ to an ethanol solution of the corresponding chloride salt.[9]

1,4,8,11-Tetrakis(*p*-tolylsulfonyl)-1,4,8,11-tetraazacyclooctadecane (1), -cyclononadecane (2), -cycloicosane (3), -cyclohenicosane (4), and -cyclotricosane (5). Compounds (**1**) and (**2**) were prepared from disodium 1,4,8,11-tetrakis(*p*-tolylsulfonyl)-1,4,8,11-tetraazaundecane and hepta- and octamethylene bis(*p*-toluenesulfonate), respectively, by a method similar to that used for the 1,4,7,10-analogs.[10] For (**1**), yield: 37.1%. ^{13}C NMR ($CDCl_3$) $\delta=21.5$ (C–Ts–), 25.8, 27.9, 28.3, 28.7 (C–C–C), 48.6, 49.5, 49.8, 51.2, (N–C–C), 127.4, 129.6, 129.7, 134.7, 134.8, 143.3, 143.5 (phenyl). For (**2**), the gummy product obtained in a yield of 44.1% was dried under reduced pressure and used for the following reaction. Compounds (**3**), (**4**), and (**5**) were prepared from dicaesium 1,4,8,11-tetrakis(*p*-tolylsulfonyl)-1,4,8,11-tetraazaundecane and the corresponding 1,ω-dibromoalkane by a method similar to that used for the 1,4,7,10-analogs.[5,11] For (**3**), yield: 39.5%. ^{13}C NMR ($CDCl_3$) $\delta=21.4$ (C–Ts–), 25.5, 27.1, 27.8, 28.3, 28.8 (C–C–C), 48.3, 48.4, 49.8, 50.6 (N–C–C), 127.1, 129.5, 135.1, 135.3, 143.1, 143.3 (phenyl). For (**4**), yield: 30.6%. ^{13}C NMR ($CDCl_3$) $\delta=21.4$ (C–Ts–), 25.6, 27.5, 27.7, 28.2, 28.5 (C–C–C), 47.7, 49.0, 50.0 (N–C–C), 127.1, 129.5, 129.6, 135.2, 135.6, 143.1, 143.4 (phenyl). For (**5**), yield: 30.2%. ^{13}C NMR ($CDCl_3$) $\delta=21.4_2$, 21.4_5 (C–Ts–), 25.9, 28.0, 28.1, 28.5 (C–C–C), 47.6, 48.1, 48.9, 50.1 (N–C–C), 127.2, 127.3, 129.6, 129.7, 135.5, 135.8, 143.1, 143.4 (phenyl).

1,4,8,11-Tetraazacycloalkane Tetrahydrobromides ($232N_4x$·4HBr, x=10—13, and 15). Each product of finely powdered (**1**)—(**5**) of 12.5 mmol ((**1**): 10.9 g, (**2**): 11.1 g, (**3**): 11.3 g, (**4**): 11.4 g, (**5**): 11.8 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**) and (**2**)), for 5 d ((**3**)), and 7d ((**4**) and (**5**)). The resulting red-black solutions were worked up in a similar manner to that for the previously reported 1,4,7,10-tetraazacycloalkane hydrobromides.[5] Yield of $232N_410$·4HBr·$1/2C_2H_5OH$: 6.7 g (89%). Found: C, 29.94; H, 6.65; N, 9.54%. Calcd for $C_{15}H_{39}N_4O_{0.5}Br_4$: C, 29.87; H, 6.52; N, 9.29%. The presence of ethanol of crystallization was confirmed by the ^{13}C NMR spectrum in D_2O. ^{13}C NMR (D_2O) $\delta=22.2$, 25.1, 25.2, 26.9 (C–C–C), 43.0, 44.9, 48.0 (C–C–N). Yield of $232N_411$·4HBr·H_2O: 6.4 g (83%). Found: C, 29.20; H, 6.50; N, 9.00%. Calcd for $C_{15}H_{40}N_4OBr_4$: C, 29.43; H, 6.59; N, 9.15%. ^{13}C NMR (D_2O) $\delta=22.7$, 25.6, 27.3 (C–C–C), 43.8, 44.0, 45.4, 48.8 (C–C–N). Yield of $232N_412$·4HBr: 6.4 g (84%). Found: C, 31.51; H, 6.79; N, 9.41%. Calcd for $C_{16}H_{40}N_4Br_4$: C, 31.60; H, 6.63; N, 9.21%. ^{13}C NMR (D_2O) $\delta=22.8$, 25.8, 27.8 (C–C–C), 43.8, 44.0, 45.2, 49.0 (C–C–N). Yield of $232N_413$·4HBr·H_2O: 7.2 g (90%). Found: C, 31.94; H, 6.80; N, 8.74%. Calcd for $C_{17}H_{44}N_4OBr_4$: C, 31.89; H, 6.93; N, 8.75%. ^{13}C NMR (D_2O) $\delta=23.1$, 25.8, 25.9, 28.2 (C–C–C), 43.8, 44.1, 45.3, 49.1 (C–C–N). Yield of $232N_415$·4HBr: 6.1 g (75%). Found: C, 34.93; H, 7.34; N, 8.80%. Calcd for $C_{19}H_{46}N_4Br_4$: C, 35.10; H, 7.13; N, 8.62%. ^{13}C NMR (D_2O) $\delta=23.1$, 25.9, 26.1, 28.5, 28.9, 29.1 (C–C–C), 43.6, 43.8, 45.4, 49.0 (C–C–N).

***trans*-[$CoCl_2(232N_4x)$]X (x=7—13, 15; X=BF_4^-, or ClO_4^-). Method 1.** The $232N_4x$ ligands ($x=7$—13, 15) were extracted from aqueous NaOH solutions of $232N_4x$·4HBr with $CHCl_3$,[10] and the complexes were obtained by the oxidation of methanol solutions containing $232N_4x$ (1 mmol) and $CoCl_2$·$6H_2O$ (1 mmol) with air according to the same method as Method 1 for *trans*-$[CoCl_2(222N_4x)]ClO_4$ ($x=9$—15).[5] Yield of *trans*-$[CoCl_2(232N_47)]BF_4$ (a mixture of C_1 and C_s isomer): 0.14 g (39%). Found: C, 30.69; H, 6.02; N, 13.16%. Calcd for $C_{11}H_{26}N_4BCl_2CoF_4$: C, 30.66; H, 6.08; N, 13.00%. ^{13}C NMR of the C_s isomer (CD_3CN) $\delta=24.4$, 27.9 (C–C–C), 49.2, 49.5, 53.5, 54.6 (C–C–N). ^{13}C NMR of the C_1 isomer (CD_3CN) $\delta=25.3$, 26.0, 28.4 (C–C–C), 48.7_6, 48.8_0, 52.4, 53.6, 54.6, 55.1, 55.2_6, 55.3_1 (C–C–N). Yield of *trans*-$[CoCl_2(232N_48)]BF_4$ (a mixture of C_1 and C_s isomer): 0.22 g (48%). Found: C, 32.54; H, 6.41; N, 12.49%. Calcd for $C_{12}H_{28}N_4BCl_2CoF_4$: C, 32.39; H, 6.34; N, 12.59%. ^{13}C NMR of the C_s isomer (CD_3CN) $\delta=19.1$, 27.6, 28.8 (C–C–C), 49.9, 51.9, 53.4, 56.1 (C–C–N). ^{13}C NMR of the C_1 isomer (CD_3CN) $\delta=$ 24.8, 26.5, 28.2, 29.6 (C–C–C), 48.3, 48.7, 53.7, 54.8, 55.2, 55.3, 56.4, 56.8 (C–C–N). Yield of *trans*-$[CoCl_2(232N_49)]$-BF_4 (C_1 isomer): 0.26 g (57%). Found: C, 34.15; H, 6.82; N, 12.19%. Cacld for $C_{13}H_{30}N_4BCl_2CoF_4$: C, 34.01; H, 6.59; N, 12.21%. ^{13}C NMR (CD_3CN) $\delta=18.7$, 23.0, 26.0, 28.3, 28.5 (C–C–C), 48.8, 49.2, 51.4, 52.2, 53.4, 53.6, 55.9, 56.1 (C–C–N). Yield of *trans*-$[CoCl_2(232N_410)]BF_4$ (C_1 isomer): 0.16 g (34%). Found: C, 35.71; H, 7.05; N, 11.74%. Calcd for $C_{14}H_{32}N_4BCl_2CoF_4$: C, 35.55; H, 6.82; N, 11.84%. ^{13}C NMR (CD_3NO_2) $\delta=23.3$, 24.5, 27.8, 29.1, 29.5, 30.5 (C–C–C), 49.5, 49.8, 52.2, 54.4, 55.0, 55.9, 56.1 (C–C–N). Yield of *trans*-$[CoCl_2(232N_411)]ClO_4$ (C_1 isomer): 0.23 g (46%). Found: C, 35.97; H, 7.07; N, 11.10%. Calcd for $C_{15}H_{34}N_4O_4Cl_3Co$: C, 36.05; H, 6.86; N, 11.21%. ^{13}C NMR (CD_3NO_2) $\delta=21.8$, 22.5, 22.9, 25.1, 26.5, 26.6, 29.2 (C–C–C), 49.5, 49.8, 50.4, 50.7, 52.2, 52.9, 54.9, 56.4 (C–C–N). Yield of *trans*-$[CoCl_2(232N_412)]BF_4$ (C_1 isomer): 0.23 g (46%). Found: C, 38.39; H, 7.48; N, 11.27%. Calcd for $C_{16}H_{36}N_4BCl_2CoF_4$: C, 38.35; H, 7.24; N, 11.18%. ^{13}C NMR (CD_3NO_2) $\delta=25.0$, 25.3, 25.8, 25.9, 26.8, 26.9,

28.2, 29.0 (C–C–C), 49.2, 49.5, 49.8, 51.7, 52.3, 53.6, 54.7, 56.1 (C–C–N). Yield of *trans*-[$CoCl_2$(232N$_4$13)]BF_4 (C_1 isomer): 0.23 g (45%). Found: C, 39.49; H, 7.70; N, 10.92%. Calcd for $C_{17}H_{38}N_4BCl_2CoF_4$: C, 39.64; H, 7.44; N, 10.88%. ^{13}C NMR (CD_3NO_2) δ=24.1, 25.0, 25.6, 26.1, 26.7, 27.2, 27.3, 29.0 (C–C–C), 49.4, 49.7, 49.9, 51.2, 52.6, 53.4, 54.7, 56.1 (C–C–N). Yield of *trans*-[$CoCl_2$(232N$_4$15)]ClO_4 (C_1 isomer): 0.24 g (43%). Found: C, 41.16; H, 7.65; N, 10.02%. Calcd for $C_{19}H_{42}N_4O_4Cl_3Co$: C, 41.06; H, 7.62; N, 10.08%. ^{13}C NMR (CD_3NO_2) δ=24.2, 24.5, 24.8, 26.7, 27.0, 27.3, 27.5, 27.7, 27.8, 28.5, 29.0 (C–C–C), 49.3, 49.6, 50.2, 50.6, 52.1, 54.6, 54.7, 55.9 (C–C–N).

Method 2. To an aqueous solution of $K_3[Co(CO_3)_3]$[12] in a 2 mmol scale was added 232N$_4$*x*·4HBr (2 mmol); the mixture was heated on a steam bath until the color of the solution became deep red. While the solution was heating, hydrochloric acid (0.05 mol dm^{-3}) was added dropwise to keep the pH of the solution at ca. 9. The resulting solution was filtered, the filtrate was evaporated to dryness under reduced pressure, and the residue was mixed with ethanol to extract the complex. The ethanol solution was evaporated again to dryness under reduced pressure to give a red oily product. It was dissolved in a small amount of water and poured onto a small column (ϕ 2.5 cm×10 cm) of SP-Sephadex C-25. A red-purple product was adsorbed on the column, and a purple effluent was obtained. Although the complex contained in the effluent was unknown, the effluent gave the same trans-dichloro complexes (C_1 or a mixture of C_1 and C_s) as those obtained by Method 1 upon heating with hydrochloric acid. The Sephadex which adsorbed the red-purple product was transferred on the top of a column (ϕ 2.5 cm×40 cm) of SP-Sephadex C-25. By elution with an aqueous 0.1 mol dm^{-3} LiCl solution (pH ca. 4, HCl), a red-purple eluate was obtained. It was mixed with 0.5 cm^3 of concd hydrochloric acid, and evaporated to dryness under reduced pressure to give an oily green (x=7, 8) or purple (x=9—13, 15) residue. The product was dissolved in a small amount of ethanol acidified with hydrochloric acid, and the solution was filtered. Upon the addition of LiX (X=BF_4^- or ClO_4^-) with stirring, green *trans*-[$CoCl_2$(232N$_4x$)]X (X=BF_4^- or ClO_4^-) was precipitated from the filtrate, collected by filtration, washed well with ethanol, and dried in air. For the 232N$_4x$ (x=9—13, 15) complexes, the second crop was obtained by evaporating the filtrate to dryness under reduced pressure and by washing the residue with ethanol. The complex was recrystallized from CH_3NO_2 (weakly acidified with HBF_4 or $HClO_4$) and diethyl ether. Yield of *trans*-[$CoCl_2$(232N$_4$7)]ClO_4 (C_2 isomer): 0.20 g (22%). Found: C, 29.91; H, 5.75; N, 12.64%. Calcd for $C_{11}H_{26}N_4O_4Cl_3Co$: C, 29.78; H, 5.91; N, 12.63%. ^{13}C NMR (CD_3CN) δ=23.1, 30.0 (C–C–C), 45.6, 53.0, 55.4, 55.6 (C–C–N). Yield of *trans*-[$CoCl_2$(232N$_4$8)]BF_4 (C_1' isomer): 0.24 g (27%). Found: C, 32.17; H, 6.36; N, 12.47%. Calcd for $C_{12}H_{28}N_4BCl_2CoF_4$: C, 32.39; H, 6.34; N, 12.59%. ^{13}C NMR (CD_3CN weakly acidified with HBF_4) δ=21.1, 23.1, 27.0, 27.7 (C–C–C), 45.5, 45.6, 51.8, 52.6, 54.2, 55.0, 55.6, 57.3 (C–C–N). Yield of *trans*-[$CoCl_2$(232N$_4$9)]BF_4 (C_1' isomer): 0.33 g (36%). Found: C, 34.34; H, 6.88; N, 12.41%. Calcd for $C_{13}H_{30}N_4BCl_2CoF_4$: C, 34.01; H, 6.59; N, 12.21%. ^{13}C NMR (CD_3CN) δ=23.2, 24.5, 26.0, 28.7, 30.3 (C–C–C), 45.2, 45.3, 52.3, 52.6, 53.3, 53.4, 54.0, 54.3 (C–C–N). Yield of *trans*-[$CoCl_2$(232N$_4$10)]BF_4 (C_1' isomer): 0.17 g (18%). Found: C, 35.76; H, 7.06; N, 11.97%. Calcd for $C_{14}H_{32}N_4BCl_2CoF_4$: C, 35.55; H, 6.82; N, 11.84%. ^{13}C NMR (CD_3NO_2) δ=21.3, 22.7, 23.4, 25.5, 25.8, 26.7 (C–C–C), 45.6, 45.9, 50.0, 51.3, 51.8, 53.2, 54.3, 54.8 (C–C–N). Yield of *trans*-[$CoCl_2$(232N$_4$11)]BF_4 (C_1' isomer): 0.26 g (27%). Found: C, 37.34; H, 7.33; N, 11.58%. Calcd for $C_{15}H_{34}N_4BCl_2CoF_4$: C, 36.99; H, 7.04; N, 11.50%. ^{13}C NMR (CD_3NO_2 weakly acidified with HBF_4) δ=23.7, 24.7, 26.5, 27.0$_0$, 27.0$_3$, 27.5, 28.2 (C–C–C), 45.1, 46.3, 50.4, 52.4, 52.9, 53.9, 54.4, 54.8 (C–C–N). Yield of *trans*-[$CoCl_2$(232N$_4$12)]BF_4 (C_1' isomer): 0.47 g (47%). Found: C, 38.58; H, 7.45; N, 11.09%. Calcd for $C_{16}H_{36}N_4BCl_2CoF_4$: C, 38.55; H, 7.24; N, 11.18%. ^{13}C NMR (CD_3NO_2 weakly acidified with HBF_4) δ=23.6, 23.8, 24.1, 24.3, 25.7, 26.6, 27.9, 29.0 (C–C–C), 45.1, 46.1, 50.0, 50.7, 51.8, 54.0, 54.2, 54.4 (C–C–N). Yield of *trans*-[$CoCl_2$(232N$_4$13)]BF_4 (C_1' isomer): 0.29 g (29%). Found: C, 39.90; H, 7.62; N, 11.11%. Calcd for $C_{17}H_{38}N_4BCl_2CoF_4$: C, 39.64; H, 7.44; N, 10.88%. ^{13}C NMR (CD_3NO_2 weakly acidified with HBF_4) δ=23.6, 24.3, 24.9, 25.1, 25.6, 25.7, 26.5, 27.5, 27.9 (C–C–C), 45.1, 46.1, 50.5, 51.8, 54.0, 54.5, 54.7 (C–C–N). Yield of *trans*-[$CoCl_2$(232N$_4$15)]BF_4 (C_1' isomer): 0.27 g (25%). Found: C, 42.34; H, 8.15; N, 10.30%. Calcd for $C_{19}H_{42}N_4BCl_2CoF_4$: C, 42.01; H, 7.79; N, 10.31%. ^{13}C NMR (CD_3NO_2) δ= 23.6, 25.5, 26.2, 26.4, 26.6, 27.0, 27.4, 27.8, 27.9, 28.5, 28.7 (C–C–C), 45.0, 46.1, 50.6, 52.0, 53.4, 53.7, 53.9, 54.5 (C–C–N).

***trans*-[$CoCl_2$(232N$_4$7)]BF_4 (C_s Isomer).** A mixture of 0.185 g (0.43 mmol) of *trans*-[$CoCl_2$(232N$_4$7)]BF_4 (C_1 and C_s isomer), which was prepared by Method 1, and ca. 1 g of SP-Sephadex C-25 (Li^+ form) was stirred in ca. 5 cm^3 of water. The Sephadex which adsorbed the complex was transferred on the top of a column (ϕ 2 cm×30 cm) of SP-Sephadex C-25, which had been washed with an eluent, an aqueous 0.1 mol dm^{-3} LiCl solution (pH ca. 2, HCl). By elution, a green band was developed, but about half of the complex remained on the column. The eluate of the green band was collected and evaporated to dryness under reduced pressure; the residue was dissolved in a small amount of methanol. The green C_s isomer of *trans*-[$CoCl_2$(232N$_4$7)]BF_4 was precipitated by the addition of $LiBF_4$ with stirring, collected by filtration, and recrystallized from CH_3CN and diethyl ether. Yield: 0.056 g (30%). Found: C, 30.76; H, 6.13; N, 12.93%. Calcd for $C_{11}H_{26}N_4BCl_2CoF_4$: C, 30.66; H, 6.08; N, 13.00%.

***trans*-[$Co(NO_2)_2$(232N$_4$8)]ClO_4.** This complex was prepared from 232N$_4$8·4HBr, $CoCl_2$·6H_2O and $NaNO_2$ according to the method for the 222N$_4x$ (x=8, 9) analogs.[1] Yield: 53%. Found: C, 30.15; H, 5.66; N, 17.15%. Calcd for $C_{12}H_{28}N_6O_8ClCo$: C, 30.10; H, 5.90; N, 17.55%.

***trans*-[$CoCl_2$(232N$_4$8)]BF_4 (C_1 Isomer).** An aqueous solution (200 cm^3) or *trans*-[$Co(NO_2)_2$(232N$_4$8)]ClO_4 (0.24 g, 0.51 mmol) was poured on a column (ϕ 2.5 cm×10 cm) of SP-Sephadex C-25. The Sephadex which adsorbed the complex was placed on the top of a column (ϕ 2.5 cm×60 cm) of SP-Sephadex C-25, and the complex was eluted with an aqueous 0.1 mol dm^{-3} KCl solution (pH 4 with HCl). The eluate of the main orange band was collected, mixed with concd hydrochloric acid (2 cm^3), and evaporated to dryness under reduced pressure. After the red product was dissolved in concd hydrochloric acid (3 cm^3), the solution was heated on a water bath until it became green. It was then evaporated to dryness under reduced pressure, and the complex

was extracted with ethanol. Upon the addition of $LiBF_4$ the extract gave a green precipitate of *trans*-$[CoCl_2(232N_48)]BF_4$ (C_1 isomer), which was collected by filtration, and recrystallized from CH_3CN and diethyl ether. Yield: 0.11 (47%). Found: C, 32.60; H, 6.54; N, 12.65%. Calcd for $C_{12}H_{28}N_4BCl_2CoF_4$: C, 32.39; H, 6.34; N, 12.59%.

Results and Discussion

Synthesis and Characterization of the Ligands and the Complexes. New tetraaza-macrocyclic ligands $232N_4x$ ($x=10$—13, 15) were prepared by methods similar to those for the $222N_4x$ ($x=10$—15) analogs.[5] Cyclization reactions were carried out with the disodium salt of 1,4,8,11-tetrakis(*p*-tolylsulfonyl)-1,4,8,11-tetraazaundecane and hepta- or octamethylene bis-(*p*-toluenesulfonate) for $232N_4x$ ($x=10$ and 11), and with the dicaesium salt of the same 1,4,8,11-tetraazaundecane and a 1,ω-dibromoalkane for $232N_4x$ ($x=12$, 13, and 15). The cyclization products were obtained in moderate yields (30—40%), and detosylated by refluxing in a mixture of hydrobromic acid and acetic acid for 3—7 d, the reaction taking a longer time with an increase in the ring members. The ligands were isolated as the tetrahydrobromide salt.

The green $[CoCl_2(232N_4x)]^+$ ($x=7$—13, 15) complexes were prepared by two methods similar to those for the corresponding $222N_4x$ complexes: one was the oxidation of $CoCl_2 \cdot 6H_2O$ in methanol in the presence of $232N_4x$ with air (Method 1); the other was the reaction of $[Co(CO_3)(232N_4x)]^+$, which was prepared from $K_3[Co(CO_3)_3]$[12] and $232N_4x \cdot 4HBr$, with hydrochloric acid (Method 2). In the reaction of $K_3[Co(CO_3)_3]$ and $232N_4x \cdot 4HBr$, it was necessary to decompose a large excess of $KHCO_3$ contained in the solution of $K_3[Co(CO_3)_3]$ with an occasional addition of hydrochloric acid. The $[Co(CO_3)(232N_4x)]^+$ complex in the reaction mixture was extracted with ethanol. The extract was diluted with water, and the aqueous solution was chromatographed with a column of SP-Sephadex C-25. The red-purple $[Co(CO_3)(232N_4x)]^+$ complex was adsorbed on the column, and a purple solution which passed through the column was obtained. The purple solution gave the same dichloro complex as that obtained by Method 1 upon heating with hydrochloric acid. Although the complex in the purple solution might have been $[Co(CO_3)_2(232N_4x)]^-$, this was not confirmed.

All of the dichloro complexes prepared by Methods 1 and 2 show absorption spectra similar to that of *trans*-$[CoCl_2(en)_2]^+$ (en: ethylenediamine), and can be assigned to the trans-isomer (Table 1). The *trans*-$[CoCl_2(232N_4x)]^+$ complex can have six isomers similar to those in the $222N_4x$ complex due to the combination of four chiral nitrogen atoms (R or S): RRRR(SSSS) (C_2 symmetry), RRRS(SSSR) (=RSSS(SRRR)) (C_1 symmetry), RSRR(SRSS)(=RRSR(SSRS)) (C_1 symmetry), RSSR(SRRS) (C_2 symmetry), RRSS(SSRR) (C_s symmetry), and RSRS(SRSR) (C_s symmetry), where symbols R and S are given in the order of N(1)N(4)N(8)-N(11) (Fig. 2). On the basis of ^{13}C NMR spectra, it is concluded that the $232N_4x$ complexes prepared by Method 1 are a mixture of the C_1 and the C_2 or C_s isomers (ca. 2 : 1) for $x=7$ and 8, and the C_1 isomer for $x=9$—13 and 15, and that the complexes prepared by Method 2 are the C_2 or C_s isomer for $x=7$, and the different C_1 isomer from that prepared by Method 1 for $x=8$—13 and 15. The structures of these trans-dichloro complexes can be assigned based on a structural relationship with $[Co(CO_3)(232N_4x)]^+$. For $[Co(CO_3)(232N_4x)]^+$, there are $16(2^4)$ different combinations for the configurations of four chiral nitrogen atoms. However, molecular models indicate that only two of 16 isomers, RRRR(SSSS) and RRRS(SSSR), are possible (Fig. 3). In these two isomers the six-membered chelate ring takes a stable chair conformation. Since the chirality of nitrogen atoms would be retained in a strong acidic solution, the trans-dichloro complexes derived from the carbonato complexes upon a reaction with hydrochloric acid would be the RRRR(SSSS) (C_2) or RRRS(SSSR) (C_1) isomer. Thus, the complexes obtained by Method 2 can be assigned to the RRRR-(SSSS) (C_2) isomer for $232N_47$, and to the RRRS-(SSSR) (C_1) isomer for $232N_4x$ ($x=8$—13, 15). There are only two kinds of C_1 isomers for the trans-dichloro complex, and the C_1 isomers of the $232N_4x$ ($x=8$—13, 15) complexes obtained by Method 1 can be assigned

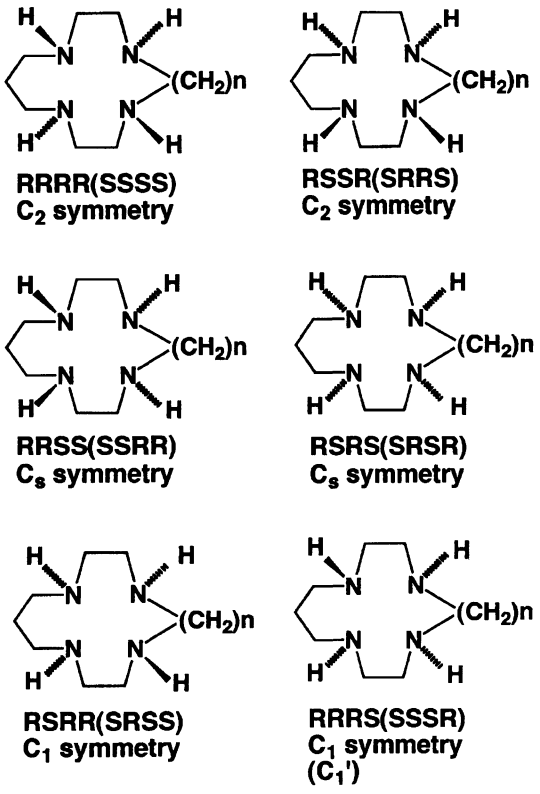

Fig. 2. Six isomers arising from the combination of four chiral nitrogen donor atoms in *trans*-$[CoCl_2(232N_4x)]^+$.

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$_2$(232N$_4$7)]BF$_4$ (C_2)	15.8 (1.55)	20.9 (1.66)	24.6 (1.81)	32.6 (sh) 39.3 (4.29)
trans-[CoCl$_2$(232N$_4$7)]ClO$_4$ (C_s)	15.7 (1.61)	20.5 (1.66)	24.5 (1.87)	32.2 (sh) 38.8 (4.42)
trans-[CoCl$_2$(232N$_4$8)]BF$_4$ (C_1)	15.6 (1.55)	20.3 (1.51)	24.5 (1.80)	31.5 (sh) 38.6 (4.41)
trans-[CoCl$_2$(232N$_4$8)]BF$_4$ (C_1')[b)]	15.5 (1.57)	20.0 (1.75)	24.0 (1.87)	31.0 (sh) 38.9 (4.47)
trans-[CoCl$_2$(232N$_4$9)]ClO$_4$ (C_1)	15.6 (1.60)	20.7 (1.54)	24.7 (1.83)	31.5 (sh) 38.9 (4.40)
trans-[CoCl$_2$(232N$_4$9)]BF$_4$ (C_1')[b)]	15.6 (1.57)	20.3 (1.77)	24.2 (1.88)	31.3 (sh) 38.9 (4.43)
trans-[CoCl$_2$(232N$_4$10)]BF$_4$ (C_1)	15.6 (1.56)	20.3 (1.54)	24.4 (1.82)	31.5 (sh) 38.9 (4.40)
trans-[CoCl$_2$(232N$_4$10)]BF$_4$ (C_1')[b)]	15.5 (1.58)	19.8 (1.85)	23.9 (1.94)	31.3 (sh) 39.1 (4.47)
trans-[CoCl$_2$(232N$_4$11)]ClO$_4$ (C_1)	15.7 (1.58)	20.7 (1.53)	24.7 (1.83)	31.7 (sh) 39.1 (4.43)
trans-[CoCl$_2$(232N$_4$11)]BF$_4$ (C_1')[b)]	15.5 (1.60)	20.1 (1.78)	24.1 (1.92)	31.6 (sh) 39.0 (4.44)
trans-[CoCl$_2$(232N$_4$12)]BF$_4$ (C_1)	15.7 (1.59)	20.6 (1.56)	24.6 (1.84)	31.5 (sh) 39.1 (4.43)
trans-[CoCl$_2$(232N$_4$12)]BF$_4$ (C_1')[b)]	15.5 (1.62)	20.1 (1.82)	24.2 (1.94)	31.3 (sh) 38.9 (4.47)
trans-[CoCl$_2$(232N$_4$13)]BF$_4$ (C_1)	15.7 (1.56)	20.5 (1.58)	24.5 (1.83)	31.2 (sh) 38.9 (4.41)
trans-[CoCl$_2$(232N$_4$13)]BF$_4$ (C_1')[b)]	15.5 (1.62)	20.2 (1.81)	24.2 (1.94)	31.4 (sh) 38.9 (4.45)
trans-[CoCl$_2$(232N$_4$15)]ClO$_4$ (C_1)	15.7 (1.58)	20.6 (1.57)	24.7 (1.85)	31.6 (sh) 39.1 (4.43)
trans-[CoCl$_2$(232N$_4$15)]BF$_4$ (C_1')[b)]	15.6 (1.62)	20.3 (1.79)	24.2 (1.93)	31.4 (sh) 38.9 (4.45)

a) In CH_3CN. b) In CH_3CN weakly acidified with HBF_4.

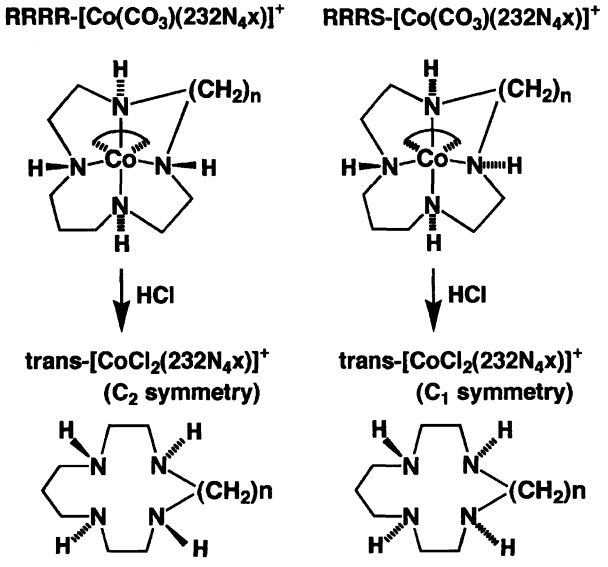

Fig. 3. Two possible structures of [Co(CO$_3$)(232N$_4x$)]$^+$.

to the RSRR(SRSS) (C_1) isomer (Fig. 2). Although no assignment can be given for the C_1 isomer contained in the 232N$_4$7 complex prepared by Method 1, the isomer is supposed to be the same C_1 (RSRR(SRSS)) isomer as those of other 232N$_4x$ complexes obtained by Method 1. The two isomers of *trans*-[CoCl$_2$(232N$_4$15)]ClO$_4$ obtained by Methods 1 and 2 have been determined to have the RSRR(SRSS) and RRRS(SSSR) combinations, respectively, by an X-ray diffraction method.[6)] In the present paper the RSRR(SRSS) and RRRS(SSSR) isomers are denoted by C_1 and C_1', respectively. By Method 1 *trans*-[CoCl$_2$(232N$_4x$)]$^+$ (x=7 and 8) yielded a different C_2 or C_s isomer from that prepared by Method 2, together with the C_1 isomer. These isomers may be assigned to the RRSS(SSRR) (C_s) isomer, since an analogous *trans*-[CoCl$_2$(232N$_4$6)]$^+$ forms the RRSS(SSRR) isomer by a similar preparative method to Method 1.[9)]

Molecular models indicate that the six-membered chelate rings in the C_1 (RSRR(SRSS)) and C_s (RRSS-(SSRR)) isomers prepared by Method 1 take a chair conformation, while those in the C_1' (RRRS(SSSR)) and C_2 (RRRR(SSSS)) isomers prepared by Method 2 are forced to take a skewboat form. To examine which iso-

mer is more stable, isomerization reactions were followed by ^{13}C NMR spectra. The C_1' isomers of the 232N$_4x$ (x=11—13) complexes in CD_3CN or CD_3NO_2 solutions isomerized rapidly to the C_1 isomer unless the solutions were made acidic. The C_2 isomer of the 232N$_4$7 and the C_1' isomers of the 232N$_4x$ (x=9, 10, 15) complexes were stable in neutral CD_3CN, but isomerized to a mixture of the C_1 and C_s isomers (x=7) or to the C_1 isomer (x=9, 10, 15) when made weakly basic with $N(C_2H_5)_3$ or NaOD. The C_1' isomer of the 232N$_4$8 complex in neutral CD_3CN isomerized to a mixture of the C_1 and C_s isomers together with the formation of a new complex. The new complex was shown to have C_2 or C_s symmetry on the ^{13}C NMR spectrum (δ=22.9, 25.7, 26.3, (C–C–C), 45.4, 53.4, 56.0, 56.3 (N–C–C)), and may be assigned to another isomer of *trans*-[$CoCl_2$(232N$_4$8)]$^+$. However, the complex disappeared upon the addition of $N(C_2H_5)_3$, the solution giving a mixture of the C_1 and C_s isomers. It is thus concluded that the C_1 and C_s isomers prepared by Method 1 are more stable than the C_1' and C_2 isomers prepared by Method 2. The X-ray structure analysis of *trans*-[$CoCl_2$(232N$_4$15)]$^+$ revealed that the C_1 isomer has a six-membered chelate ring in a chair form, and is less strained than the C_1' isomer, in which the six-membered chelate ring is in a skew-boat form.[6]

The 232N$_4x$ (x=7, 8) complexes yield a mixture of the C_1 and C_s isomers, while those of x=9—13, and 15 yielded only the C_1 isomer by Method 1. In the C_s isomer of *trans*-[$CoCl_2$(232N$_4x$)]$^+$ the two N–C bonds of the large chelate ring are disposed towards the same direction from the CoN_4 plane, but point in different directions from each other in the C_1 isomer. Repulsions among atoms of the large chelate ring would be larger in the C_s isomer than in the C_1 isomer. The difference in stability between the C_s and C_1 isomers arising from such steric conditions would increase along with an increase in the members of the large chelate ring; those complexes with a chelate ring of ring members larger than nine might yield only the C_1 isomer by Method 1.

The C_s isomer in a mixture of C_1 and C_s isomers of the 232N$_4$7 complex obtained by Method 1 was separated by SP-Sephadex C-25 column chromatography. By elution with an aqeuous 0.1 mol dm^{-3} LiCl solution (pH ca. 2, HCl), a green band containing the C_s isomer was eluted, while the C_1 isomer remained at the top of the column. From the eluate the C_s isomer was obtained. For the 232N$_4$8 complex, the C_1 isomer was derived from [$Co(NO_2)_2$(232N$_4$8)]ClO_4 by a reaction with hydrochloric acid. The main product of the dinitro complex was a trans isomer (^{13}C NMR (DMSO-d^6) δ=23.5, 25.6, 28.5 (C–C–C), 47.4, 49.0, 50.20, 51.7, 52.9, 54.0, 55.7 (N–C–C)), which was purified by SP-Sephadex C-25 column chromatography with an aqueous 0.1 mol dm^{-3} KCl solution as an eluent. By reacting this purified product with hydrochloric acid, the C_1 isomer of *trans*-[$CoCl_2$(232N$_4$8)]$^+$ was obtained.

Ligand Field Spectra. All of *trans*-[$CoCl_2$(232N$_4x$)]$^+$ prepared in this study show ligand field spectra characteristic of the [$CoCl_2N_4$]-type complex (Table 1). Under a D_{4h} approximation the band at around 16000 cm^{-1} can be assigned to the Ia ($^1E_g \leftarrow {}^1A_{1g}$), the band at around 20000 cm^{-1} to the Ib ($^1A_{2g} \leftarrow {}^1A_{1g}$), and the band at around 24000 cm^{-1} to the II ($^1E_g + {}^1B_{2g} \leftarrow {}^1A_{1g}$) bands.[3] All of the C_1' isomers show these d–d bands at a slightly lower energy with a slightly stronger intensity than those of the corresponding C_1 isomers.

On the basis of the AOM model,[13] the ligand field parameters of the nitrogen (Δ(N)=3$e\sigma$(N)) and the chlorine (Δ(Cl)=3$e\sigma$(Cl)−4$e\pi$(Cl)) donor atoms in these complexes were estimated based on the maximum positions of the Ia and Ib bands determined by a Gaussian curve-fitting analysis. The parameters were obtained based on the assumption of C=2000 cm^{-1}[13] for the Racah's parameter.[14] Figure 4 shows the variation of the parameter values, Δ(N) and Δ(Cl), with the number of ring members (x) in *trans*-[$CoCl_2$(232N$_4x$)]$^+$. The Δ(N) value decreases largely from x=6 to 7, and then becomes nearly constant showing a small decrease at x=even-numbers and a small increase at x=odd-numbers. The smallest Δ(N) value is seen at x=10. On the other hand, the Δ(Cl) values change slightly over all the x's, though the largest value is seen at x=10. The changes in the Δ(N) and Δ(Cl) values are small, but seem to indicate an instability of the complexes containing a medium-sized chelate ring with an x of around 10. Similar and more clear variations of the Δ(N) and

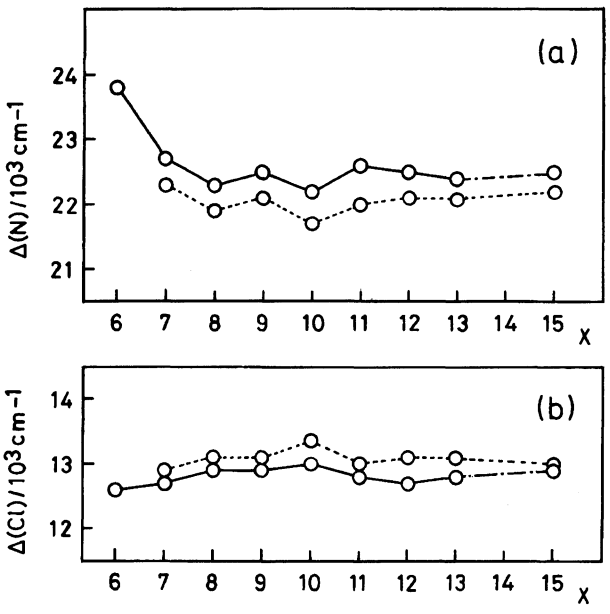

Fig. 4. Variations of the ligand field parameters of Δ(N) (a) and Δ(Cl) (b) with the chelate ring size of *trans*-[$CoCl_2$(232N$_4x$)]$^+$; the C_1 (x=8—13, and 15) and C_2 (x=7) isomers {-O-}, the C_1' (x=8—13, and 15) and C_s (x=7) isomers {--O--}.

Table 2. Electrochemical Data of the Redox Potential of Co(III)/Co(II) vs. Ag/Ag$^+$ [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$_2$(232N$_4$6)]BF$_4$	−0.67	−0.60	75	−0.63	−0.62	75
trans-[CoCl$_2$(232N$_4$7)]ClO$_4$ (C$_2$)	−0.54	−0.46	80	−0.50	−0.51	80
trans-[CoCl$_2$(232N$_4$7)]BF$_4$ (C$_s$)	−0.52	−0.44	75	−0.48	−0.48	75
trans-[CoCl$_2$(232N$_4$8)]BF$_4$ (C$_1$)	−0.42	−0.27	160	−0.35	−0.42	105
trans-[CoCl$_2$(232N$_4$9)]ClO$_4$ (C$_1$)	−0.42	−0.24	180	−0.33	−0.44	115
trans-[CoCl$_2$(232N$_4$9)]BF$_4$ (C$_1'$)	−0.40	−0.22	180	−0.31	−0.39	120
trans-[CoCl$_2$(232N$_4$10)]BF$_4$ (C$_1$)	−0.40	−0.26	145	−0.33	−0.40	105
trans-[CoCl$_2$(232N$_4$10)]BF$_4$ (C$_1'$)	−0.39	−0.25	140	−0.32	−0.37	110
trans-[CoCl$_2$(232N$_4$11)]ClO$_4$ (C$_1$)	−0.43	−0.32	110	−0.38	−0.45	110
trans-[CoCl$_2$(232N$_4$12)]BF$_4$ (C$_1$)	−0.44	−0.34	100	−0.39	−0.42	85
trans-[CoCl$_2$(232N$_4$13)]BF$_4$ (C$_1$)	−0.44	−0.35	90	−0.40	−0.44	100
trans-[CoCl$_2$(232N$_4$15)]ClO$_4$ (C$_1$)	−0.48	−0.40	80	−0.44	−0.44	75
trans-[CoCl$_2$(232N$_4$15)]ClO$_4$ (C$_1'$)	−0.48	−0.40	75	−0.44	−0.42	85

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. c) $\Delta E_p=E_{pa}-E_{pc}$.

the Δ(Cl) values with the x's were observed for the corresponding 222N$_4x$ complexes.[5] No clear explanation can presently be given for the small changes in these parameter values of the 232N$_4x$ complexes.

Electrochemistry. Table 2 lists the data of the redox potentials for the Co(III)/Co(II) couples of *trans*-[CoCl$_2$(232N$_4x$)]$^+$. Figure 5 shows the variation in the reduction potentials ($E_{1/2}$/V) obtained by the RDE method with the size of the chelate rings. The $E_{1/2}$ value shifts to the positive side (easier to reduce) from x=6 through 7 to 8, and then becomes nearly constant, showing a small negative shift at x=odd-numbers and a small positive shift at x=even-numbers. The pattern of the variation with the x's is similar to that for the Δ(N) values obtained from the electronic spectra. From these variations, it may be concluded that the complexes containing a medium-sized chelate ring of even-numbers are more strained and reduced more easily, though the differences are slight, compared to those of odd-numbers. A similar variation of the $E_{1/2}$ values with the size of chelate rings has been observed for the corresponding 222N$_4x$ complexes.[5] The difference in stability (free energy) between the Co(III) and Co(II) complexes of the present N$_4x$-type ligand decreases along with an increase in the size (x) of the chelate rings.

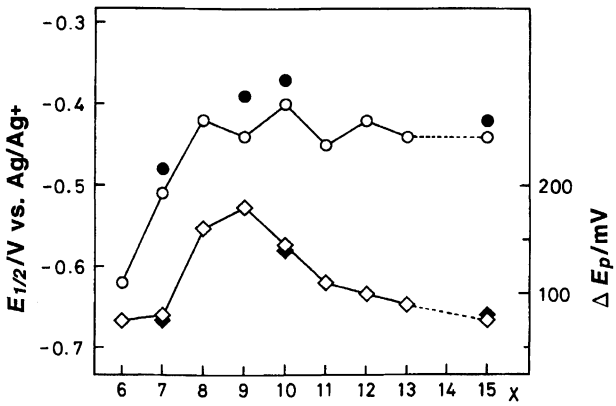

Fig. 5. Variations of the $E_{1/2}$ value (-○-) and the ΔE_p value (-◇-) with the chelate ring size of *trans*-[CoCl$_2$(232N$_4x$)]$^+$; the C_1 (x=8—13, and 15) and C_2 (x=7) isomers {○, ◇}, the C_1' (x=9, 10, and 15) and C_s (x=7) isomers {●, ◆}.

In Fig. 5 is also shown the variation of the ΔE_p(=[$E_{pa}-E_{pc}$]/mV) value obtained by the CV method under a given condition.[5] The cathodic and anodic peak values were dependent on the scan rate, and the i_{pa}/i_{pc} ratio was always less than unity (0.71—0.97). A slow electron-transfer process and a following chemical reaction for the reduced Co(II) species are suggested to be involved in the redox reactions. The 232N$_4x$ (x=6 and 7) complexes show a small ΔE_p value (75 and 80 mV), and the reactions can be regarded as beig quasi-reversible. The ΔE_p value increases largely from x=7 to 8, shows the maximum (180 mV) at x=9, and then decreases along with a further increase in the x's to become as small as those for x=6 and 7 at x=15. The large ΔE_p values for the medium-sized chelate ring complexes would indicate the instability of these complexes in the Co(II) oxidation state. A similar variation for ΔE_p with the size of chelate rings has been observed for the corresponding 222N$_4x$ complexes.[5] However, the ΔE_p values of the 232N$_4x$ complexes are generally smaller than those of the 222N$_4x$ complexes, indicating that the 232N$_4x$ complexes have better reversibility than the 222N$_4x$ complexes in the Co(III)/Co(II) redox reaction. The Co(II)–232N$_4x$ complex, in which the ligand has a larger cavity than the corresponding 222N$_4x$ ligand, might be more stable than the Co(II)–222N$_4x$ complex.

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