Bull. Chem. Soc. Jpn., ***63***, *227—234 (1990)*

Synthesis and Characterization of Co(III) Complexes with 1,4,7,10-Tetraazacyclotetradecane, -pentadecane, and -hexadecane

Masanobu Tsuchimoto, Masakazu Kita, Matsuo Nonoyama, and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

(Received July 5, 1989)

New cobalt(III)-1,4,7,10-tetraazacyclotetradecane (N_47), -pentadecane (N_48), and -hexadecane (N_49) complexes, *trans*-$[CoCl_2(N_4x)]^+$ (x=7 (two isomers), 8 (two isomers), 9 (one isomer)), *trans*-$[Co(NO_2)_2(N_4x)]^+$ (x=7, 8, 9, one isomer), *cis*-$[Co(NO_2)_2(N_47)]^+$ (one isomer), and $[Co(en)(N_4x)]^{3+}$ (x=7, 8, one isomer) were synthesized and characterized. For analogous 1,4,7,10-tetraazacycloundecane (N_46) complexes, two isomers for each of *cis*-$[Co(NO_2)_2(N_46)]^+$ and $[Co(en)(N_46)]^{3+}$ were also obtained and were found to isomerize to each other in acetonitrile. The ligand field parameters of nitrogen Δ(N) and chlorine Δ(Cl) estimated from the observed ligand field bands of *trans*-$[CoCl_2(N_4x)]^+$ show a correlation between them; with an increase in ring size of N_4x, the Δ(N) value decreases, while the Δ(Cl) value increases. The reduction potentials for each series of the dichloro, dinitro, and en complexes become less negative with an increase in ring size of N_4x.

Metal complexes of tetraazamacrocycles involving chelate rings larger than six-membered (seven to nine) have been prepared and their structures, spectra, and stabilities have been compared with those of extensively studied metal macrocycles comprising five- and/or six-membered chelate rings.[1—11] However, most of the investigations are concerned with relatively labile complexes formed with Ni(II),[1—10] Cu(II),[4—6,8—11] Zn(II),[9] Cd(II),[9] and Pb(II),[9] and more inert complexes are limited to a few Co(III) complexes with a tetraazamacrocycle forming 5,6,5,8- or 5,6,5,9-membered chelate rings.[4] For such inert metal macrocycles, it is expected to obtain geometrical or diastereomeric isomers, which have not been reported so far, by appropriate synthetic routes.

This paper reports the synthesis, stereochemistry, and spectral and electrochemical properties of the dichloro, dinitro, and ethylenediamine (en) Co(III) complexes with 1,4,7,10-tetraazacycloalkanes. The abbreviations, N_45, N_46, N_47, N_48, and N_49 are used for 1,4,7,10-tetraazacyclododecane, -tridecane, -tetradecane, -pentadecane, and -hexadecane, respectively (see Fig. 1).

Experimental

Measurements. Electronic spectra were obtained on HITACHI U-3400 and JASCO UVIDEC 610B spectrophotometers. ^{13}C NMR spectra were obtained on a HITACHI R-90HS NMR spectrometer. Electrochemical measurements were carried out on solutions in acetonitrile at 24 °C by using a HECS 321B potential sweep unit and a HECS 317B potentiostat of Huso electrochemical system, and a GRAPHTEC WX1000 recorder. A glassy carbon electrode and it attached to a Yanaco P10-RE Mark II head were used for cyclic and RDE voltammetric measurements, respectively. For both measurements an Ag/AgNO$_3$ electrode (Ag/0.01 mol dm^{-3} AgNO$_3$) and a platinum wire were employed as the reference and auxiliary electrodes, respectively. $N(C_4H_9)_4ClO_4$ was used as the supporting electrolyte at 0.1 mol dm^{-3} concentration. Sample solutions were degassed with nitrogen for 20 min prior to measurements.

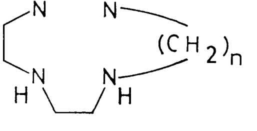

Fig. 1. Ligands N_4x (x(n)=7(4), 8(5), 9(6)).

Materials. Macrocyclic ligands, N_47, N_48, and N_49,[1] and complexes $[Co(en)(N_45)](ClO_4)_3$,[12] *cis*-$[Co(NO_2)_2(N_45)]BF_4$,[13] *trans*-$[CoCl_2(N_46)]BF_4$,[14] and *trans*-$[CoCl_2(trien)]ClO_4$[15] were prepared by methods previously described, where trien denotes 3,6-diazaoctane-1,8-diamine.

***trans*-$[CoCl_2(N_47)]Cl$ (C_2 Isomer):** $CoCl_2\cdot6H_2O$ (2.21 g, 5 mmol) was added to a solution of an equimolar amount of N_47 in methanol (200 cm^3). Air was bubbled through the solution for 2 h and then concd hydrochloric acid (1 cm^3) was added dropwise to the solution. Air-bubbling was continued for another 1 h and the solution was evaporated to dryness under reduced pressure. The residue was dissolved in methanol (50 cm^3) and an undissolved material was removed by filtration. The filtrate was applied on a column (ϕ 6.5 cm×35 cm) of Sephadex LH-20. By elution with methanol, a green main band was obtained and the eluate was evaporated to dryness under reduced pressure. The product was recrystallized from methanol and ether. Yield: 0.915 g (48.8%). Found: C, 32.84; H, 6.66; N, 15.36%. Calcd for $C_{10}H_{24}N_4CoCl_3$=*trans*-$[CoCl_2(N_47)]Cl$: C, 32.85; H, 6.62; N, 15.32%.

***trans*-$[CoCl_2(N_47)]ClO_4$ (C_2 Isomer):** A methanolic solution (200 cm^3) containing N_47 (5 mmol) and $CoCl_2\cdot6H_2O$ (5 mmol) was bubbled with air by the same method as the above chloride. On addition of 70% perchloric acid (1 cm^3) the solution gave a green precipitate, which was filtered, washed with methanol, and recrystallized from acetonitrile and ether. Yield: 1.16 g (54.1%). Found: C, 28.12; H, 5.55; N, 13.33%. Calcd for $C_{10}H_{24}N_4CoCl_3O_4$=*trans*-$[CoCl_2(N_47)]ClO_4$: C, 27.96; H, 5.63; N, 13.04%.

***trans*-$[CoCl_2(N_47)]ClO_4$ (C_1 Isomer):** *trans*-$[CoCl_2(N_47)]Cl$ (C_2) (0.731 g, 2 mmol) was dissolved in a mixture of ethanol and water (4:1, 200 cm^3). To the solution was added dropwise an aqueous solution (10 cm^3) of potassium carbonate (0.42 g, 3 mmol). After stirring for 1 h, the solution was evaporated to dryness under reduced pressure, the residue was dissolved in ethanol, and the solution was filtered. The filtrate was evaporated again to dryness under reduced pressure to give a reddish oily product, which was dissolved in water and poured onto a short column (ϕ 2.5 cm×10 cm) of SP-Sephadex C-25. The Sephadex adsorbed the product was transferred 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 adjusted its pH at ca. 5 with hydrochloric acid. Two purple bands, A and B in the order of elution were developed and the eluates were collected separately. To each eluate 1 cm^3 of concd hydrochloric acid was added and then the solution was evaporated to dryness under reduced pressure to give an oily residue. The purple solutions from bands A and B became reddish brown and green respectively, during concentration. Each oily residue was dissolved in ethanol (20 cm^3) and filtered. Lithium perchlorate (0.32 g, 2 mmol) was added to the solution and the mixture was stirred. Green *trans*-$[\mathrm{CoCl_2(N_47)}]\mathrm{ClO_4}$ ($\mathrm{C_1}$) was precipitated from the brown solution of band A and green *trans*-$[\mathrm{CoCl_2(N_47)}]\mathrm{ClO_4}$ ($\mathrm{C_2}$) from the green solution of band B. They were filtered and washed with ethanol. Yield of *trans*-$[\mathrm{CoCl_2(N_47)}]\mathrm{ClO_4}$ ($\mathrm{C_1}$): 0.070 g (8.2%). Found: C, 27.72; H, 5.52; N, 12.97%. Calcd for $\mathrm{C_{10}H_{24}N_4CoCl_3O_4}$=*trans*-$[\mathrm{CoCl_2(N_47)}]\mathrm{ClO_4}$: C, 27.96; H, 5.63; N, 13.04%. Yield of *trans*-$[\mathrm{CoCl_2(N_47)}]\mathrm{ClO_4}$ ($\mathrm{C_2}$): 0.217 g (25.3%).

***trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{X}$ ($\mathrm{C_2}$ and $\mathrm{C_S}$ Isomers) X=Cl, $\mathrm{ClO_4}$:** A mixture of isomers $\mathrm{C_2}$ and $\mathrm{C_S}$ of *trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{X}$ (X=Cl or $\mathrm{ClO_4}$) was obtained by an air-oxidation method similar to that for *trans*-$[\mathrm{CoCl_2(N_47)}]\mathrm{X}$ ($\mathrm{C_2}$) (X=Cl or $\mathrm{ClO_4}$). Yield of *trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{Cl}$ ($\mathrm{C_2+C_S}$): 71.9%. Found: C, 34.75; H, 7.04; N, 14.68%. Calcd for $\mathrm{C_{11}H_{26}N_4CoCl_3}$=*trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{Cl}$: C, 34.80; H, 6.90; N, 14.76%. Yield of *trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{ClO_4}$ ($\mathrm{C_2+C_S}$): 53.3%. Found: C, 29.98; H, 5.95; N, 12.62%. Calcd for $\mathrm{C_{11}H_{26}N_4CoCl_3O_4}$=*trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{ClO_4}$: C, 29.78; H, 5.91; N, 12.63%.

***trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{ClO_4}$ ($\mathrm{C_2}$ Isomer):** A mixture of isomers $\mathrm{C_2}$ and $\mathrm{C_S}$ of *trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{Cl}$ was treated with potassium carbonate and the product was chromatographed by a method similar to that for *trans*-$[\mathrm{CoCl_2(N_47)}]\mathrm{ClO_4}$ ($\mathrm{C_1}$ isomer). By elution with 0.1 mol dm^{-3} LiCl (pH ca. 5 with hydrochloric acid), two purple bands appeared. By treating each eluate with concd hydrochloric acid in a similar manner to *trans*-$[\mathrm{CoCl_2(N_47)}]\mathrm{ClO_4}$ ($\mathrm{C_1}$ isomer), the eluate of the slower-moving band gave brown *trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{ClO_4}$ ($\mathrm{C_2}$ isomer), while a mixture of the $\mathrm{C_2}$ and $\mathrm{C_S}$ isomers of *trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{ClO_4}$ was obtained together with other unknown complexes from the eluate of the faster-moving band. The $\mathrm{C_1}$ isomer (see below) seems to be unstable even in acidic solution. Yield of *trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{ClO_4}$ ($\mathrm{C_2}$): 28.2%. Found: C, 29.96; H, 5.89; N, 12.79%. Calcd for $\mathrm{C_{11}N_4H_{26}CoCl_3O_4}$=*trans*-$[\mathrm{CoCl_2(N_48)}]\mathrm{ClO_4}$: C, 29.78; H, 5.91; N, 12.63%.

***trans*-$[\mathrm{CoCl_2(N_49)}]\mathrm{BF_4}$ ($\mathrm{C_2}$ Isomer):** The complex was prepared by an air-oxidation method similar to that for *trans*-$[\mathrm{CoCl_2(N_47)}]\mathrm{Cl}$ ($\mathrm{C_2}$ isomer). Column chromatography of the crude product on Sephdex LH-20 gave a brown main band. The eluate of the band was concentrated to ca. 20 cm^3 under reduced pressure. On addition of $\mathrm{LiBF_4}$ with stirring, the concentrate yielded a brown precipitate, which was filtered, washed with methanol, and recrystallized from acetonitrile and ether. Yield: 16.3%. Found: C, 32.22; H, 6.26; N, 12.69%. Calcd for $\mathrm{C_{12}H_{28}N_4CoCl_2BF_4}$=*trans*-$[\mathrm{CoCl_2(N_49)}]\mathrm{BF_4}$: C, 32.39; H, 6.34; N, 12.59%. To obtain other isomers, the complex was treated with $\mathrm{K_2CO_3}$ and then with concd hydrochloric acid according to the method for the $\mathrm{N_47}$ complex. However, only the same $\mathrm{C_2}$ isomer was yielded. No fraction indicative of other isomers was obtained on column chromatography.

$[\mathrm{Co(en)(N_46)}](\mathrm{ClO_4})_3$ ((1) and (2) Isomer): To a suspension of *trans*-$[\mathrm{CoCl_2(N_46)}]\mathrm{BF_4}$ (0.403 g, 1 mmol) in DMSO (50 cm^3) was added dropwise with stirring a DMSO solution (50 cm^3) of ethylenediamine (0.06 g, 1 mmol). After stirring for 6 h, the solution was diluted with 1 dm^3 of 0.01 mol dm^{-3} hydrochloric acid, and applied on a short column (ϕ 2.5 cm×10 cm) of SP-Sephadex C-25. The Sephadex adsorbed the product was transferred 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 0.2 mol dm^{-3} $\mathrm{K_2SO_4}$ solution adjusted its pH at ca. 2 with sulfuric acid. A yellowish orange band (1) and a reddish orange one (2) were eluted successively. Each eluate was diluted ten times with water, and the solution was applied on a short column (ϕ 2.5 cm×10 cm) of SP-Sephadex C-25. The column was washed thoroughly with an aqueous 0.05 mol dm^{-3} $\mathrm{LiClO_4}$ solution (ca. pH 2, $\mathrm{HClO_4}$). The complex was eluted with an aqueous 1 mol dm^{-3} $\mathrm{LiClO_4}$ solution (pH 2, $\mathrm{HClO_4}$), and the eluate was concentrated to a small volume under reduced pressure. On addition of ethanol the concentrate from band (1) yielded a yellowish orange precipitate and that from band (2) a reddish orange one. Yield of $[\mathrm{Co(en)(N_46)}](\mathrm{ClO_4})_3$ (Isomer (1)): 0.095 g (15.7%). Found: C, 22.06; H, 5.00; N, 14.03%. Calcd for $\mathrm{C_{11}H_{30}N_6CoCl_3O_{12}}$=$[\mathrm{Co(en)(N_46)}](\mathrm{ClO_4})_3$: C, 21.89; H, 5.01; N, 13.92%. Yield of $[\mathrm{Co(en)(N_46)}](\mathrm{ClO_4})_3$ (Isomer (2)): 0.135 g (22.4%). Found: C, 21.94; H, 4.96; N, 14.15%. Calcd for $\mathrm{C_{11}H_{30}N_6CoCl_3O_{12}}$=$[\mathrm{Co(en)(N_46)}](\mathrm{ClO_4})_3$: C, 21.89; H, 5.01; N, 13.92%.

$[\mathrm{Co(en)(N_4}x)](\mathrm{ClO_4})_3$ (x=7 and 8): These complexes were prepared from the corresponding dichloro complexes and en by a method similar to that for $[\mathrm{Co(en)(N_46)}](\mathrm{ClO_4})_3$. Both the $\mathrm{N_47}$ and $\mathrm{N_48}$ complexes yielded only one isomer and isolated as orange and red perchlorates, respectively. Yield of $[\mathrm{Co(en)(N_47)}](\mathrm{ClO_4})_3$: 55.0%. Found: C, 23.33; H, 5.18; N, 13.66%. Calcd for $\mathrm{C_{12}H_{32}N_6CoCl_3O_{12}}$=$[\mathrm{Co(en)(N_47)}](\mathrm{ClO_4})_3$: C, 23.33; H, 5.22; N, 13.61%. Yield of $[\mathrm{Co(en)(N_48)}](\mathrm{ClO_4})_3$: 5.2%. Found: C, 24.69; H, 5.37; N, 13.34%. Calcd for $\mathrm{C_{13}H_{34}N_6CoCl_3O_{12}}$=$[\mathrm{Co(en)(N_48)}](\mathrm{ClO_4})_3$: C, 24.72; H, 5.42; N, 13.30%.

***cis*-$[\mathrm{Co(NO_2)_2(N_46)}]\mathrm{PF_6}$ ((1) and (2) Isomers):** To an aqueous solution (100 cm^3) containing NaOH (0.12 g, 3 mmol) and $\mathrm{N_46 \cdot 3HBr}$ (0.858 g, 2 mmol) was added an aqueous solution (50 cm^3) containing $\mathrm{CoCl_2 \cdot 6H_2O}$ (0.476 g, 2 mmol) and $\mathrm{NaNO_2}$ (0.210 g, 3 mmol). Air was bubbled through the solution overnight, and the resulting brown solution was applied on a short column (ϕ 2.5 cm×10 cm) of SP-Sephadex C-25. The Sephadex adsorbed the product was transferred on the top of a column (ϕ 4.5 cm×35 cm) of SP-Sephadex C-25 and the product was eluted with an aqueous 0.05 mol dm^{-3} $\mathrm{K_2SO_4}$ solution adjusted its pH at ca. 4 with sulfuric acid. Two orange bands, (1) and (2) in the order of elution were developed. The eluate of each band was concentrated under reduced pressure to one-tenth of its orignal volume. On addition of $\mathrm{NH_4PF_6}$ with stirring, the concentrate yielded a yellow-orange precipitate of *cis*-$[Co(NO_2)_2(N46)]PF_6$, which was filtered, washed with water, and recrystallized from nitromethane and ether. Yield of *cis*-$[Co(NO_2)_2(N46)]PF_6$ Isomer (1): 0.130 g (13.5%). Found: C, 22.19; H, 4.46; N, 17.65%. Calcd for $C_9H_{22}N_6CoO_4PF_6$=*cis*-$[Co(NO_2)_2(N46)]PF_6$: C, 22.42; H, 4.60; N, 17.43%. Yield of *cis*-$[Co(NO_2)_2(N46)]PF_6$ Isomer (2): 0.29 g (30.1%). Found: C, 22.44; H, 4.51; N, 17.63%. Calcd for $C_9H_{22}N_6CoO_4PF_6$=*cis*-$[Co(NO_2)_2(N46)]PF_6$: C, 22.42; H, 4.60; N, 17.43%.

***trans*- and *cis*-$[Co(NO_2)_2(N47)]BF_4$:** To a solution of *trans*-$[CoCl_2(N47)]Cl$ (C_2) (0.365 g, 1 mmol) in a mixture of ethanol and water (4:1, 100 cm^3) was added dropwise an aqueous solution (5 cm^3) of $NaNO_2$ (0.214 g, 3 mmol). The solution was stirred for 1 h and then evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of methanol and the solution was filtered. The filtrate was evaporated to give an oily residue, which was dissolved again in a small amount of water and poured onto a short column (ϕ 2.5 cm×10 cm) of SP-Sephadex C-25 equipped with a cooling jacket (ca. 0 °C).[16] The Sephadex adsorbed the product was transferred on the top of a cold column (ϕ 3 cm×70 cm, 0 °C) of SP-Sephadex C-25 and the product was eluted with an aqueous 0.05 mol dm^{-3} potassium sulfate solution. Orange *trans*-$[Co(NO_2)_2(N47)]^+$ and then orange *cis*-$[Co(NO_2)_2(N47)]^+$ were developed separately. The eluate of each band was collected and evaporated to dryness below 20 °C under reduced pressure. The product was extracted with methanol, and the extract was mixed with $LiBF_4$ (0.094 g, 1 mmol) with stirring to yield orange $[Co(NO_2)_2(N47)]BF_4$, which was filtered, washed with ethanol and recrystallized from acetonitrile and ether. Yield of *trans*-$[Co(NO_2)_2(N47)]BF_4$: 0.33 g (37.7%). Found: C, 27.42; H, 5.67; N, 19.28%. Calcd for $C_{10}H_{24}N_6CoO_4BF_4$=*trans*-$[Co(NO_2)_2(N47)]BF_4$: C, 27.42; H, 5.52; N, 19.18%. Yield of *cis*-$[Co(NO_2)_2(N47)]BF_4$: 0.16 g (18.3%). Found: C, 27.41; H, 5.51; N, 19.23%. Calcd for $C_{10}H_{24}N_6CoO_4BF_4$=*cis*-$[Co(NO_2)_2(N47)]BF_4$: C, 27.42; H, 5.52; N, 19.18%.

Reactions of *trans*- and *cis*-$[Co(NO_2)_2(N47)]BF_4$ with Hydrochloric Acid: Solutions of *trans*- and *cis*-$[Co(NO_2)_2(N47)]BF_4$ (0.16 mmol) in concd hydrochloric acid (2 cm^3) were allowed to stand for a day at room temperature. Both orange solutions turned brown gradually. To the solutions was added $LiClO_4$ (0.16 g, 1 mmol) in ethanol (5 cm^3), yielding precipitates of *trans*-$[CoCl_2(N47)]ClO_4$ (C_2 isomer) from *trans*-$[Co(NO_2)_2(N47)]BF_4$ and *trans*-$[CoCl_2(N47)]ClO_4$ (C_1 isomer) from *cis*-$[Co(NO_2)_2(N47)]BF_4$. They were filtered and washed with ethanol. Yield of *trans*-$[CoCl_2(N47)]ClO_4$ (C_2 isomer): 0.044 g (64.0%). Yield of *trans*-$[CoCl_2(N47)]ClO_4$ (C_1 isomer): 0.037 g (53.8%).

***trans*-$[Co(NO_2)_2(N4x)]BF_4$ (x=8 and 9) Method 1:** These complexes were prepared by an air-oxidation method similar to that for *cis*-$[Co(NO_2)_2(N46)]PF_6$. Both complexes yielded only a trans isomer. The eluate obtained by column chromatography was evaporated to dryness under reduced pressure, and the complex was extracted with methanol. On addition of $LiBF_4$ the extract gave an orange precipitate of the complex, which was filtered, washed with ethanol, and recrystallized from acetonitrile and ether. Yield of *trans*-$[Co(NO_2)_2(N48)]BF_4$: 52.3%. Found: C, 29.21; H, 5.79; N, 18.42%. Calcd for $C_{11}H_{26}N_6CoO_4BF_4$=*trans*-$[Co(NO_2)_2(N48)]BF_4$: C, 29.22; H, 5.80; N, 18.59%. Yield of *trans*-$[Co(NO_2)_2(N49)]BF_4$: 47.9%. Found: C, 30.92; H, 6.02; N, 18.22%. Calcd for $C_{12}H_{28}N_6CoO_4BF_4$=*trans*-$[Co(NO_2)_2(N49)]BF_4$: C, 30.92; H, 6.05; N, 18.03%.

Method 2. The reaction product obtained from the corresponding trans dichloro complex and $NaNO_2$ according to a method similar to that for $[Co(NO_2)_2(N47)]BF_4$ was chromatographed and the complex was isolated as the tetrafluoroborate by a method similar to the above Method 1. Yield of *trans*-$[Co(NO_2)_2(N48)]BF_4$: 78.8%. Yield of *trans*-$[Co(NO_2)_2(N49)]BF_4$: 80.1%.

Reactions of *trans*-$[Co(NO_2)_2(N4x)]BF_4$ (x=8 and 9) with Hydrochloric Acid: *trans*-$[Co(NO_2)_2(N48)]BF_4$ (0.226 g, 0.5 mmol) was dissolved in concd hydrochloric acid (2 cm^3) and the solution was heated on a steam bath. The resulting yellow-green solution was cooled, mixed with methanol (10 cm^3), and filtered. To the filtrate was added $LiClO_4$ (0.160 g, 1.0 mmol) with stirring. After a while *trans*-$[CoCl_2(N48)]ClO_4$ (C_2 isomer) was precipitated, filtered and washed with methanol and then with ether. The yield was 0.15 g (67.6%).

A similar reaction of *trans*-$[Co(NO_2)_2(N49)]BF_4$ with concd hydrochloric acid resulted in decomposition of the complex to give cobalt(II) species.

Results and Discussion

Synthesis and Characterization of the Complexes. Two kinds of green $[CoCl_2(N47)]^+$ were obtained; one was yielded by oxidizing a methanol solution containing $CoCl_2\cdot6H_2O$ and N47 with air, and the other was obtained by reaction of one of two isomers of $[Co(CO_3)(N47)]^+$ with hydrochloric acid. The same reaction of the other isomer of the carbonate complex yielded the same dichloro complex as the one obtained by the air-oxidation method. Both complexes show electronic spectra similar to that of *trans*-$[CoCl_2(en)_2]^+$ (Fig. 2 and Table 1) and can be assigned to the isomers

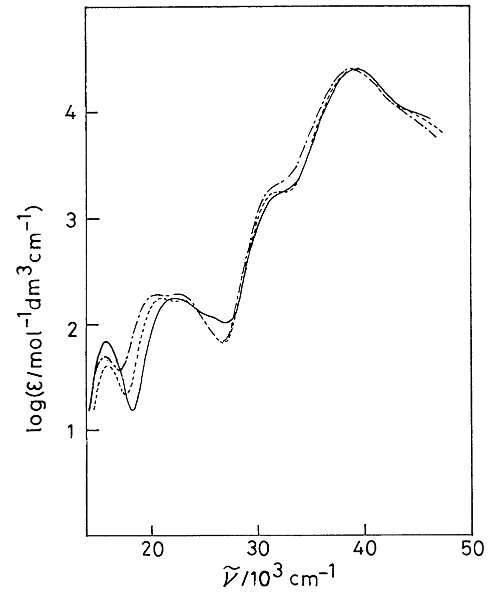

Fig. 2. Electronic spectra of the C_2 isomers of *trans*-$[CoCl_2(N4x)]^+$; x=7 (—), x=8 (---), x=9 (-·-) in acetonitrile.

Table 1. Electronic Spectral Data

Complex	$\tilde{\nu}/10^3$ cm^{-1} (log(ε/mol^{-1} dm^3 cm^{-1})) 1st band		2nd band	CT
trans-[CoCl$_2$(N$_4$6)]ClO$_4$$^{a)}$	16.67(1.52)	23.70(2.15)		
trans-[CoCl$_2$(N$_4$7)]ClO$_4$(C$_2$)$^{b)}$	15.8 (1.84)	22.2 (2.25)	25.8(2.07)	32.4(sh) 39.3(4.40)
trans-[CoCl$_2$(N$_4$7)]ClO$_4$(C$_1$)$^{b)}$	16.0(1.70)	21.6 (2.22)	22.7(2.25)	32.0(sh) 39.5(4.41)
trans-[CoCl$_2$(N$_4$8)]ClO$_4$(C$_2$)$^{b)}$	15.8(1.64)	20.9 (2.25)	22.7(2.23)	31.9(3.25) 39.1(4.39)
trans-[CoCl$_2$(N$_4$9)]BF$_4$$^{b)}$	15.7(1.71)	20.5 (2.27)	22.6(2.27)	32.1(sh) 39.0(4.42)
trans-[CoCl$_2$(trien)]ClO$_4$$^{c)}$	16.2(1.79)	22.1 (2.09)	23.8(2.07)	
cis-[Co(NO$_2$)$_2$(N$_4$5)]BF$_4$$^{b)}$	22.4(2.50)			30.8(3.74) 40.3(4.37)
cis-[Co(NO$_2$)$_2$(N$_4$6)]PF$_6$ (1)$^{d)}$	22.0(2.51)			30.1(3.74) 39.7(4.35)
cis-[Co(NO$_2$)$_2$(N$_4$6)]PF$_6$ (2)$^{d)}$	21.9(2.51)			30.2(3.74) 39.6(4.33)
cis-[Co(NO$_2$)$_2$(N$_4$7)]BF$_4$$^{b)}$	21.7(2.47)			29.5(3.75) 39.5(4.37)
trans-[Co(NO$_2$)$_2$(N$_4$7)]BF$_4$$^{b)}$	22.2(2.43)			28.1(3.49) 38.7(4.25)
trans-[Co(NO$_2$)$_2$(N$_4$8)]BF$_4$$^{b)}$	21.7(2.48)			28.0(3.56) 38.9(4.31)
trans-[Co(NO$_2$)$_2$(N$_4$9)]PF$_4$$^{b)}$	21.5(2.51)			28.1(3.56) 38.6(4.35)
[Co(en)(N$_4$5)]Cl$_3$·1.25 H$_2$O$^{e)}$	20.5(2.30)		29.3(2.20)	44.0(4.32)
[Co(en)(N$_4$6)](ClO$_4$)$_3$ (1)$^{f)}$	21.0(2.21)		29.0(2.14)	43.8(4.33)
[Co(en)(N$_4$6)](ClO$_4$)$_3$ (2)$^{f)}$	20.6(2.26)		28.7(2.17)	43.4(4.32)
[Co(en)(N$_4$7)](ClO$_4$)$_3$$^{f)}$	20.6(2.26)		28.4(2.15)	42.6(4.30)
[Co(en)(N$_4$8)](ClO$_4$)$_3$$^{f)}$	20.2(2.25)		28.1(2.16)	42.1(4.28)

a) From Ref. 14. b) In CH$_3$CN. c) In CH$_3$NO$_2$. d) In CH$_3$CN weakly acidified with HClO$_4$. e) From Ref. 12. f) In water acidified with HClO$_4$ (pH 2).

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

Complex	δ(C-$\underline{C}$-C)	δ(C-$\underline{C}$-N)
trans-[CoCl$_2$(N$_4$7)]ClO$_4$(C$_2$)$^{a)}$	29.8	49.9, 53.4, 54.5, 58.3
trans-[CoCl$_2$(N$_4$7)]ClO$_4$(C$_1$)$^{a)}$	23.3, 25.5	48.7, 48.9, 49.2, 50.1, 53.7, 55.8, 56.1, 58.2
trans-[CoCl$_2$(N$_4$8)]ClO$_4$(C$_2$)$^{a)}$	26.2, 27.2	50.0, 53.4, 55.6, 60.1
trans-[CoCl$_2$(N$_4$8)]ClO$_4$(Cs)$^{a)}$	19.5, 28.8	51.2, 51.8, 52.2, 59.9
trans-[CoCl$_2$(N$_4$9)]BF$_4$(C$_2$)$^{a)}$	23.8, 28.3	49.9, 53.7, 53.7, 59.7
cis-[Co(NO$_2$)$_2$(N$_4$6)]PF$_6$ (1)$^{b)}$	22.8	45.8, 48.5, 49.5, 49.5, 51.8, 52.3, 52.7 53.6
cis-[Co(NO$_2$)$_2$(N$_4$6)]PF$_6$ (2)$^{b)}$	24.4	46.7, 47.9, 49.9, 50.3, 50.7, 54.9, 55.5, 56.5
trans-[Co(NO$_2$)$_2$(N$_4$7)]BF$_4$$^{a)}$	29.1	50.3, 53.2, 55.0, 57.7
cis-[Co(NO$_2$)$_2$(N$_4$7)]BF$_4$$^{a)}$	22.7, 28.9	50.4, 51.9, 52.1, 52.1, 53.1, 53.7, 54.7, 55.4
trans-[Co(NO$_2$)$_2$(N$_4$8)]BF$_4$$^{a)}$	24.8, 27.0	50.0, 53.7, 56.0, 59.0
trans-[Co(NO$_2$)$_2$(N$_4$9)]BF$_4$$^{c)}$	21.8, 25.9	49.4, 51.9, 52.2, 57.9
[Co(en)(N$_4$6)](ClO$_4$)$_3$ (1)$^{d)}$	23.0	45.2, 45.4, 45.8, 48.0, 50.4, 52.3, 52.4, 54.0, 54.4, 54.5
[Co(en)(N$_4$6)](ClO$_4$)$_3$ (2)$^{d)}$	23.6	45.7, 45.8, 47.0, 49.8, 50.0, 50.9, 51.7, 56.5, 56.9, 58.8
[Co(en)(N$_4$7)](ClO$_4$)$_3$$^{a)}$	22.4, 28.1	44.6, 46.7, 51.5, 52.1, 52.3, 53.3, 53.9, 54.0, 54.2, 55.2
[Co(en)(N$_4$8)](ClO$_4$)$_3$$^{a)}$	20.2, 23.8, 26.6	44.7, 46.7, 51.3, 53.1, 53.2, 53.7, 53.8, 54.6

a) In CD$_3$CN, CD$_3$CN (1.3 ppm) reference. b) In DMSO-*d*$_6$ weakly acidified with DCl, TMS reference. c) In DMSO-*d*$_6$. d) In D$_2$O acidified with DCl, dioxane (67.4 ppm) reference.

of the *trans*-dichloro complex. In ^{13}C NMR spectra the isomer yielded by the air-oxidation method show five signals and has either a C$_2$ axis or a mirror plane, while the other isomer gives ten signals and has C$_1$ symmetry (Table 2). For *trans*-[CoCl$_2$(N$_4$*x*)]$^+$, 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*-

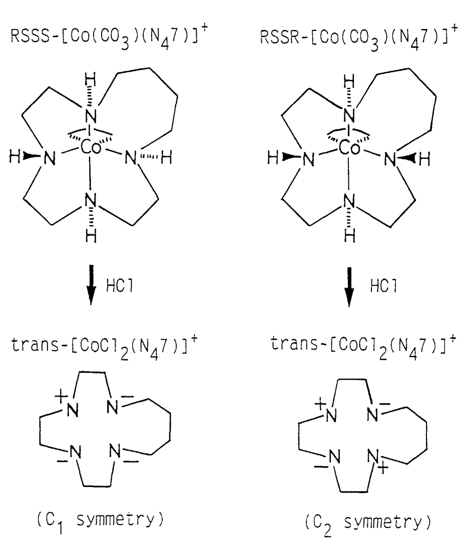

Fig. 3. Possible structures of $[Co(CO_3)(N_47)]^+$. The signs + and − represent amine protons disposed above and below from the CoN_4 plane, respectively.

(*SRRS*)(C_2 symmetry), and two meso isomers with C_s symmetry, *RRSS*(=*SSRR*) and *RSRS*(=*SRSR*), where the four symbols (*R* or *S*) denote chirality of nitrogen in the order of N(1)N(4)N(7)N(10). No assignment can be given for the structures of two isomers from absorption and NMR spectra. The structures were assigned on the basis of the structures of two isomers of $[Co(CO_3)(N_47)]^+$. The carbonato complex yielded two isomers by reaction of *trans*-$[CoCl_2(N_47)]^+$ with K_2CO_3, although these isomers were not isolated because of their decomposition under the acidic conditions. For $[Co(CO_3)(N_4x)]^+$, there are $16(=2^4)$ geometrical isomers, and all of which have their antipodes. However, molecular models indicate that structually possible, less strained isomers of $[Co(CO_3)(N_47)]^+$ are only two of these isomers, *RSSR*(*SRRS*) and *RSSS*(*SRRR*) as shown in Fig. 3. These carbonato complexes yielded *trans*-dichloro complexes by reaction with hydrochloric acid. Since the chilarity of nitrogen atoms will be retained in reactions in acidic solution, the *trans*-dichloro complex with C_2 or C_s symmetry can be assigned to the *RSSR*(*SRRS*) isomer(C_2), and that with C_1 symmetry to the *RSSS*(*SRRR*) one.

The C_2 isomer has the same chilarities of nitrogen atoms as those found in X-ray structure analysis of *trans*-$[NiCl_2(N_47)]$[2] and $[Cu(N_47)](ClO_4)_2$.[8] The structure involves three five-membered chelate rings of a gauche form ($\delta\lambda\delta$ for *RSSR*) and a seven-membered chelate ring of a skew form (λ for *RSSR*) which corresponds to the most stable twist-chair form of cycloheptane.[17] The skew form has been found in $[Co(tmd)_3]^{3+}$ [18] and *cis*-$[Co(NO_2)_2(tmd)_2]^+$ [19] (tmd: 1,4-butanediamine), in which the two methylene carbons adjacent to the nitrogen atoms are disposed on the opposite sides of the plane formed by the cobalt and two nitrogen atoms. In the C_1 isomer, on the other hand, these methylene carbons are forced to be on the same side of the CoN_2 plane of the seven-membered chelate ring, although other rings can take similar conformations to those in the C_2 isomer. Such a structure seems to involve more strain than that of the C_2 isomer. The ^{13}C NMR spectrum of a CD_3CN solution of the C_1 isomer completely changed to that of the C_2 isomer when made weakly basic with triethylamine or NaOD. The less stability of the C_1 isomer is reflected on absorption spectra and electrochemical properties described later.

For *trans*-$[CoCl_2(N_48)]^+$, a mixture of two isomers was obtained by an air-oxidation method similar to that for the N_47 complex. The ^{13}C NMR spectrum of the product shows twelve signals consisting of two sets of six signals with similar intensities (Table 2), indicating formation of two isomers with C_2 or C_s symmetry in similar amounts. Attempts to separate them were unsuccessful. To obtain pure isomers, the mixture was converted to the carbonato complex by the same method as that for the N_47 complex. The carbonato complex yielded two isomers which might have the same *RSSR*(*SRRS*) and *RSSS*(*SRRR*) structures as those of two isomers of the N_47 complex. By reaction with hydrochloric acid, one isomer gave one of two isomers found in the mixture, while the other isomer gave the same mixture with other unknown complexes. The formation of the mixture from $[Co(CO_3)(N_48)]^+$ indicates that configurational inversion at the nitrogen atom takes place and that the inversion under acidic conditions should involve clevelage of the Co–N bond. The stability of metal macrocycles seems to decrease with an increasing ring memberes of the ligand as also seen in the N_49 complex described later.

The pure isomer of *trans*-$[CoCl_2(N_48)]^+$ was tentatively assigned to the *RSSR*(*SRRS*) isomer (C_2) corresponding to the more stable C_2 isomer of *trans*-$[CoCl_2(N_47)]^+$. The assignment has been confirmed by preliminary X-ray analysis on its nitrate and tetrafluoroborate salts.[20] The other isomer contained in the mixture may be assigned to the *RSRS* isomer (C_s) from analogy with the planar $[Ni(N_48)](ClO_4)_2$ complex whose structure has been determined by X-ray analysis.[2] In the *RSRS* structure, the central five-membered chelate ring cannot adopt a gauche conformation, but is forced to take an eclipsed form. Thus the complex seems to be more strained than the C_2 isomer. However, the C_2 isomer in a weakly basic ($N(C_2H_5)_3$) CD_3CN solution isomerizes to the C_s isomer to give a mixture containing similar amounts of these two isomers. The results indicates that the energy difference is very small between the C_2 and C_s isomers.

A single brown isomer of *trans*-$[CoCl_2(N_49)]^+$ was yielded by an air-oxidation method similar to that for the $N_4 7$ complex. The complex shows six signals in the ^{13}C NMR spectrum, and has either C_2 or C_S symmetry. By reaction with K_2CO_3, the complex yielded only one isomer of $[Co(CO_3)(N_4 9)]^+$, from which the same isomer of *trans*-dichloro complex as above was formed by reaction with hydrochloric acid. The complex is presumed to have the *RSSR*(*SRRS*)(C_2) configuration from the previous discussion on isomers of the $N_4 7$ and $N_4 8$ complexes. The *RSSR*(*SRRS*) configuration has been found in *trans*-$[NiCl_2(N_4 9)]$ by X-ray analysis.[2)] This complex forms a largely distorted octahedron with the large bite angle (119.14(4)°) of the nine-membered chelate ring. The Co(III) complex will also involve similar large distortion. The complex decomposed slowly in acidic solution to give Co(II) species. No reduction was observed for the $N_4 7$ and $N_4 8$ complexes under the same conditions.

Two isomers of $[Co(en)(N_4 6)]^{3+}$ were yielded by reaction of *trans*-$[CoCl_2(N_4 6)]^+$ with en in DMSO, and separated by SP-Sephadex C-25 column chromatography. The two isomers are yellow-orange and red-orange in color, and show similar absorption and ^{13}C NMR spectra. The isomers are stable in acidic solution, but easily isomerize to each other in neutral water and acetonitrile, similar amounts of the isomers being observed at equilibrium by ^{13}C NMR spectra. Most probable structures of these two isomers are indicated by molecular models to have those with the same *RSSR*(*SRRS*) and *RSSS*(*SRRR*) configurations as those of $[Co(CO_3)(N_4 x)]^+$. However, no assignment can be made for each complex.

For $[Co(en)(N_4 x)]^{3+}$ (x=7, 8) only one isomer was obtained by similar reactions to that for the $N_4 6$ complex. The yield of the $N_4 8$ complex was very low (5.2%), and no en complex with $N_4 9$ was obtained. The en complex with $N_4 x$ seems to become unstable when x exceeds 8 probably because of steric crowding due to the increasing methylene and amine protons. Both the $N_4 7$ and $N_4 8$ complexes will be either the *RSSR*(*SRRS*) or *RSSS*(*SRRR*) isomer, but the structures remain unknown.

The $[Co(NO_2)_2(N_4 6)]^+$ complex yielded two isomers by oxidation of an aqueous solution containing $CoCl_2 \cdot 6H_2O$, $N_4 6$, and $NaNO_2$ with air, and the isomers were separated by SP-Sephadex C-25 column chromatography. Both isomers are shown to have C_1 symmetry by appearance of nine signals in the ^{13}C NMR spectra. The absorption spectra of the isomers are similar. The bands around 30000 cm^{-1} are stronger than those of *trans*-$[Co(NO_2)_2(N_4 x)]^+$ (x=7, 8, 9) with C_2 symmetry described below and similar to that of *cis*-$[Co(NO_2)_2(N_4 5)]^+$.[13)] The two isomers easily isomerize to each other in CD_3CN. These results indicate that both isomers are a cis form. Hung et al.[14)] obtained $[Co(NO_2)_2(N_4 6)]^+$ by reaction of *trans*-$[CoCl_2(N_4 6)]^+$ with $NaNO_2$ and assumed it to be a trans isomer. Attempts to prepare the trans isomer by their method were unsuccessful to give one of the present two cis isomers. No structual assignment can be given for the two isomers, although only two with the *RSSR*(*SRRS*) and *RSSS*(*SRRR*) configurations are possible for a cis isomer.

Two isomers of $[Co(NO_2)_2(N_4 7)]^+$ were obtained by reaction of *trans*-$[CoCl_2(N_4 7)]^+$ with $NaNO_2$ and by SP-Sephadex C-25 column chromatography. The ^{13}C NMR spectra indicate that one has C_1 symmetry, and the other C_2 or C_S symmetry. The absorption band of the C_1 isomer at 29500 cm^{-1} is stronger than that of the other C_2 or C_S isomer, indicating the cis isomer for the former and the trans one for the latter. The C_1 and C_2 or C_S isomers yielded the C_1 and C_2 isomers of *trans*-$[CoCl_2(N_4 7)]^+$, respectively by reaction with hydrochloric acid. Thus the C_2 or C_S and C_1 dinitro complexes can be assigned to the *trans-RSSR*(*SRRS*) (C_2) and the *cis-RSSS*(*SRRR*) (C_1) isomers, respectively. The same *cis-RSSS*(*SRRR*) structure is found in X-ray structure analysis of *cis*-$[Ni(NCS)_2(N_4 7)]$.[3)]

The $[Co(NO_2)_2(N_4 x)]^+$ (x=8, 9) complexes yielded only one isomer by two methods similar to those for the $N_4 6$ and $N_4 7$ complexes, an air-oxidation method and reaction of *trans*-$[CoCl_2(N_4 x)]^+$ with $NaNO_2$. The two complexes can be assigned to a trans isomer by the ^{13}C NMR spectra. The absorption spectra support the assignment; the intensities of bands around 28000 cm^{-1} are similar to that of *trans*-$[Co(NO_2)_2(N_4 7)]^+$. The *trans*-$N_4 8$ complex yields the C_2 isomer of *trans*-$[CoCl_2(N_4 8)]^+$ by reaction with hydrochloric acid, indicating the *RSSR*(*SRRS*) isomer. The same reaction of the *trans*-$N_4 9$ complex resulted in decomposition to cobalt(II) species.

Electronic Spectra. The *trans*-dichloro complexes show absorption spectra similar to that of *trans*-$[CoCl_2(en)_2]^+$, except intensity enhancement of the bands in the region of 18000 to 25000 cm^{-1} (Fig. 2). The bands are assigned as shown in Table 1 according to the assignment for *trans*-$[CoCl_2(en)_2]^+$ (D_{4h} approximation);[21)] the first d–d band split into two components, $I_a(^1E_g \leftarrow {}^1A_{1g})$ and $I_b(^1A_{2g} \leftarrow {}^1A_{1g})$, the second d–d band, $II(^1E_g + {}^1B_{2g} \leftarrow {}^1A_{1g})$, and two charge-transfer bands. The intensity enhancements of the I_b band will be attributed to the distortion of the square CoN_4 coordination, since the I_b band originates mainly from the transition in the CoN_4 plane. The distortion will arise from both strains due to the planar arrangement of three five-membered chelate rings and the relatively large chelate ring. As a result the bite angle of the large chelate ring widens largely as seen in $[NiCl_2(N_4 7)]$ (109.6°)[2)] and $[NiCl_2(N_4 9)]$ (119.14°).[2)] The *trans*-$[CoCl_2(trien)]^+$ complex also shows a fairly strong I_b band (log ε: 2.09), the I_b band intensity of *trans*-$[CoCl_2(en)_2]^+$ being 1.38.[21)] X-Ray structure analyses of *trans*-$[CoX_2(trien)]^+$ (X=CN,[22)] NCS,[23)] NO_2[24)]) reveal that three bite angles of trien are in the range of 85°—88°, while the other N–Co–N

Table 3. Band Positions Obtained by Gaussian Curve Fitting Analysis and Ligand Field Parameters for *trans*-$[CoCl_2(N_4x)]^+$

Complex	$\tilde{\nu}/10^3\ cm^{-1}$			$\Delta/10^3\ cm^{-1}$	
	1st band		2nd band	Δ(N)	Δ(Cl)
trans-$[CoCl_2(N_46)]ClO_4$[a]	16.67	23.70		27.50	13.45
trans-$[CoCl_2(N_47)]ClO_4(C_2)$	15.8	21.6	25.8	25.4	13.7
trans-$[CoCl_2(N_47)]ClO_4(C_1)$	16.0	21.2	23.7	25.0	14.6
trans-$[CoCl_2(N_48)]ClO_4(C_2)$	15.9	20.6	23.7	24.4	15.0
trans-$[CoCl_2(N_49)]BF_4$	15.7	20.1	23.4	23.9	15.2

a) From Ref. 14.

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

Complex	Cyclic voltammetry				RDE voltammetry[b]	
	E_{pc}/V	E_{pa}/V	ΔE_p[c]/mV	$(E_{pc}+E_{pa})/2$/V	$E_{1/2}$/V	$E_{1/4}-E_{3/4}$/mV
trans-$[CoCl_2(N_46)]BF_4$	−0.69	−0.59	100	−0.64	−0.65	90
trans-$[CoCl_2(N_47)]ClO_4(C_2)$	−0.52	−0.42	100	−0.47	−0.51	90
trans-$[CoCl_2(N_47)]ClO_4(C_1)$	−0.50	−0.32	180	−0.41	−0.50	75
trans-$[CoCl_2(N_48)]ClO_4(C_2)$	−0.43	−0.14	295	−0.29	−0.44	115
trans-$[CoCl_2(N_49)]BF_4$	−0.38	IRREV	—	—	−0.41	135
cis-$[Co(NO_2)_2(N_45)]BF_4$[d]	−0.89	IRREV	—	—	−0.86	100
cis-$[Co(NO_2)_2(N_47)]BF_4$	−0.81	−0.68	130	−0.75	−0.76	120
trans-$[Co(NO_2)_2(N_47)]BF_4$	−0.81	−0.72	90	−0.77	−0.76	85
trans-$[Co(NO_2)_2(N_48)]BF_4$	−0.72	−0.57	150	−0.65	−0.72	110
trans-$[Co(NO_2)_2(N_49)]BF_4$	−0.67	−0.37	295	−0.52	−0.68	130
$[Co(en)(N_45)](ClO_4)_3$	−0.57	−0.38	190	−0.48	−0.55	85
$[Co(en)(N_47)](ClO_4)_3$	−0.45	−0.22	230	−0.34	−0.44	90
$[Co(en)(N_48)](ClO_4)_3$	−0.37	IRREV	—	—	−0.33	85

a) The data for 1 mmol dm^{-3} ferrocene; $(E_{pc}+E_{pa})/2=0.08$ V, $E_{1/2}=0.09$ V. b) 1500 rpm, scan rate: 10 mV s^{-1}. c) $\Delta E_p=E_{pa}-E_{pc}$. d) Supporting electrolyte: 0.1 mol dm^{-3} $(C_4H_9)_4NBF_4$.

angle is widened to 99°—102°.

The ligand field parameters of nitrogen (Δ(N)) and chlorine (Δ(Cl)) for *trans*-$[CoCl_2(N_4x)]^+$ were estimated from the observed I_a and I_b bands on the basis of the AOM model.[25] The band positions were obtained by Gaussian curve fitting analysis using the program LGNS[26] modified by Dr. T. Komorita of Osaka University. The Racah's parameter C is approximated to be a constant value of 3800 cm^{-1}.[27] Table 3 lists the parameter values. The values indicate the following two features; 1) the Δ(N) value decreases as the ring size of macrocycles increases, and 2) the Δ(Cl) value increases with the decreasing Δ(N) values. Feature 1) suggests the best fitness of N_46 to the Co(III) ion among the present N_4x ligands. The reduction of Δ(N) occured by the increasing ring size of N_4x will be attributable to lengthening of the Co–N bond and increasing distortion of the N–Co–N bond angle from 90°. The average Ni–N distances of $[NiCl_2(N_47)]$[2] and $[NiCl_2(N_49)]$[2] are 2.07 and 2.16 Å, respectively, and the large bite angle are observed as described above. Between the two isomers of the N_47 complex, the C_2 isomer has a larger Δ(N) value than that of the C_1 isomer, indicating better fitness of N_47 in the C_2 structure. This result seems to be compatible with the fact that the C_2 isomer is more stable than the C_1 isomer. Feature 2) will correspond to the cis effect, the electronic effect of a ligand on the coordinate bonds of other ligands in the cis positions. A complementary relation is seen between the Δ(N) and Δ(Cl) values; the larger the Δ(N) value, the smaller the Δ(Cl) value. A similar cis effect has been found for Ni(II) macrocycles.[28]

The $[Co(en)(N_4x)]^{3+}$ complexes show two clear d–d bands, $I(^1T_{1g} \leftarrow {}^1A_{1g}(O_h))$ and $II(^1T_{2g} \leftarrow {}^1A_{1g}(O_h))$. All the bands are in lower energy and have stronger intensity than the corresponding bands of $[Co(en)_3]^{3+}$. Except the II band of the N_45 complex, these bands shift to the lower energy side in the order of the N_46(isomer 1)$>N_46$(isomer 2)$\gtrsim N_47 > N_45 > N_48$ complexes. The II band of the N_45 complex is at the highest energy among those of the complexes. The reason for the band positions of the N_45 complex remains unknown.

The dinitro complexes exhibit only the first d–d band, the second d–d band being hidden by a strong charge transfer band. For both cis and trans isomers, the energy of the first d–d band decreases with an increase in ring size of N_4x. The relation of the first d–d band position between the cis and trans isomers is the same as that for the isomers of $[Co(NO_2)_2(en)_2]^+$; the band of the trans isomer is at higher energy than that of the cis isomer.

Electrochemistry. Table 4 lists the data of redox potentials for the Co(III)/Co(II) couples of the N_4x complexes. For each series of the complexes, a positive shift of $E_{1/2}$ and an increase in $\Delta E_p(=E_{pa}-E_{pc})$ are observed as the ring size of N_4x increases. The ratio of I_{pa}/I_{pc} is always less than one, indicating that a chemical reaction of the Co(II) species follows the reduction process. The range of $E_{1/2}$ is small in each series of the complexes. The variation of $E_{1/2}$ with the ring size indicates that the larger N_4x ligand favors the formation of a Co(II) complex. The sequence of $E_{1/2}$ becoming more positive (less negative) in each series of the complexes is the same as that of the decreasing first d–d transition energy except for $[Co(en)(N_45)]^{3+}$. The increase in ΔE_p indicates that the chemical irreversibility in the reduction reaction increases with an increase in ring size of N_4x. The reactions of the largest ligand dichloro and en complexes, *trans*-$[CoCl_2(N_49)]^+$ and $[Co(en)(N_48)]^{3+}$ are irreversible.

The $E_{1/2}$ value for isomer C_2 of *trans*-$[CoCl_2(N_47)]^+$ is more negative than isomer C_1, although the difference is small. This result is consistent with the more stability of the C_2 isomer discussed previously.

No data for *cis*-$[Co(NO_2)_2(N_46)]^+$ and $[Co(en)(N_46)]^{3+}$ were obtained because of their isomerization in acetonitrile.

This work was supported by Grant-in-Aid for Scientific Research No. 61430013 from the Ministry of Education, Science and Culture.

References

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

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

3) M. Sugimoto, H. Ito, K. Toriumi, and T. Ito, *Acta Crystallogr., Sect. B*, **38**, 2453 (1982).

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

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

6) M. Micheloni, P. Paoletti, A. Poggi, and L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, **1982**, 61.

7) M. Micheloni, P. Paoletti, and A. Sabatini, *J. Chem. Soc., Dalton Trans.*, **1983**, 1189.

8) A. Bianchi, L. Bologni, P. Dapport, M. Micheloni, and P. Paoletti, *Inorg. Chem.*, **23**, 1201 (1984).

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

10) J. W. L. Martin, J. H. Timmons, A. E. Martell, and C. J. Willis, *Inorg. Chem.*, **19**, 2328 (1980).

11) J. H. Timmons, P. Rudolf, A. E. Martell, J. W. L. Martin, and A. Clearfield, *Inorg. Chem.*, **19**, 2331 (1980).

12) M. Nonoyama and T. Kurimoto, *Polyhedron*, **4**, 471 (1985).

13) J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5**, 1380 (1966).

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

15) A. M. Seargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

16) Decomposition of $[Co(NO_2)_2(N_47)]^+$ occured when it was eluted at room temperature.

17) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

18) S. Saito and Y. Saito, *Acta Crystallogr., Sect. B*, **31**, 1378 (1975).

19) M. Shiomi, Y. Fujinawa, H. Ogino, K. Kanamori, and K. Kawai, *Bull. Chem. Soc. Jpn.*, **61**, 3491 (1988).

20) M. Tsuchimoto, M. Kita, M. Nonoyama, and J. Fujita, Symposium on Coordination Chemistry, 37th, Tokyo, 3A07 (1987).

21) A. B. P. Lever, "Inorganic Electronic Spectroscopy," 2nd ed, Elsevier, Amsterdam (1984), p. 469.

22) R. K. Wismer and R. A. Jacobson, *Inorg. Chim. Acta*, **7**, 477 (1973).

23) Y. Kushi, M. Kuramoto, S. Utsuno, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **56**, 2742 (1983).

24) M. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect B*, **28**, 463 (1972).

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

26) D. B. Siano and D. E. Metzler, *J. Chem. Phys.*, **51**, 1856 (1969).

27) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

28) L. Y. Martin, C. R. Sperati, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 2968 (1977).