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Anomalous Stereochemistry of Pyrazolato-3,5-dicarboxylato-Bridged Dinuclear Chromate(III) Complexes Containing Ethylenediamine-*N*,*N*′-dicarboxylates with Entrapped Unstable Conformations: X-ray Structure of Na[Cr_2(eddp)(*μ*-pzdc)]·$6H_2O$

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Several new pyrazolato-3,5-dicarboxylato (pzdc) bridged dinuclear chromate(III) complexes containing linear tetradentate O−N−N−O type ligands were synthesized and structurally characterized. Among them, the X-ray structure of the eddp complex Na[Cr_2(eddp)(*μ*-pzdc)]·$6H_2O$ (eddp = ethylenediamine-*N*,*N*′-dipropionate) was determined to have a (sym-cis)−(unsym-cis) geometrical configuration with intramolecular three-center hydrogen bonds, entrapping the unfavored sym-cis configuration for the Cr(eddp) moiety as well as the favored unsym-cis one. As a pair of positional disorders, there were also found to be two conformational isomers with respect to the absolute configurations of the coordinated asymmetric nitrogen atom at the G (in-plane) ring for the unsym-cis moiety. Moreover, chiral pzdc-bridged dinuclear complexes with another type of O−N−N−O ligand, 1,2-cyclohexanediamine-*N*,*N*′-diacetate (cdda), were successfully synthesized, isolated, and characterized by column chromatographic behavior, elemental analysis, and chiroptical spectra. There were two diastereomers for Na[(*R*,*R*-cdda)Cr(*μ*-pzdc)Cr(*S*,*S*-cdda)] and only one isomer for Na[(*R*,*R*-cdda)Cr(*μ*-pzdc)Cr(*R*,*S*-cdda)] and Na[(*R*,*R*-cdda)Cr(*μ*-pzdc)Cr(edda)] (*R*,*R*- or *S*,*S*- and *R*,*S*-cdda = *R*,*R*-*trans*- or *S*,*S*-*trans*- and *R*,*S*-*cis*-1,2-cyclohexanediamine-*N*,*N*′-diacetate, and edda = ethylenediamine-*N*,*N*′-diacetate). From their circular dichroism (CD) spectra, these complexes could exhibit the Δ−Δ absolute configuration with {(sym-*cis*-*R*,*R*-cdda)−(unsym-*cis*-edda or *S*,*S*- or *R*,*S*-cdda)} geometrical configuration, indicating the abnormal eq−eq (N−C_{eq}) configuration for the *R*,*R*-cdda. The comparison among the CD spectra of the {(cdda)−(cdda)} complexes revealed that two diastereomers of the {(*R*,*R*-cdda)−(*S*,*S*-cdda)} complex correspond to the conformational isomers resulting from the difference in geometrical orientations of the secondary amine protons on two coordinated asymmetric nitrogen atoms with the opposite absolute configuration in the unsym-*cis*-*S*,*S*-cdda moiety. In a series of the pzdc-bridged Cr(III) complexes the anomalous conformations in two different geometrical configurations could be entrapped probably owing to stereognostic coordination through the intramolecular N−H···O hydrogen bond interaction.

Introduction

Our recent papers[1,2] on the syntheses and characterization of the pyrazolato-3,5-dicarboxylato (pzdc) bridged dinuclear Cr(III) complexes with acetylacetonates or linear tetradentate edda (ethylenediamine-*N*,*N*′-diacetate) type ligands promised that this type of pzdc dinuclear complexes could give more variety of stereochemistry in nonbridging ligands. It has been revealed that the edda and trdda complexes, Na[Cr_2(edda)$_2$(*μ*-pzdc)]·$5H_2O$ and Na[Cr_2(trdda)$_2$(*μ*-pzdc)]·$3H_2O$ (trdda = trimethylenediamine-*N*,*N*′-diacetate), were formed stereospecifically to take a {(sym-cis(mer))−(unsym-cis(mer))} and {(unsym-cis(mer))−(unsym-cis(mer))} geometrical configuration,[3] respectively, by the X-ray analysis. For the former edda complex, the hydrogen bond between two Cr(III) moieties gives rise to the labile (if else unstable) entrapped unsym-cis configuration. At that time, we failed to isolate the corresponding ethylenediamine-*N*,*N*′-dipropionate (eddp) dinuclear complex. However, a continuing endeavor to pursue the eddp dinuclear complex could be still important in hopes of entrapping either one or both conformations with respect to the absolute configuration of the coordinated asymmetric nitrogen atoms at the G (in-plane)-ring side within one pocket at an unsym-cis site, as found for two mononuclear diastereomers of unsym-*cis*-[Co(eddp)(en)]Cl.[4]

Other peculiar conformational isomers of linear tetradentate complexes with sym-cis configuration have been established by Yamamoto and Shimura,[5] following a chiroptical study of similar kinds of diastereomer of the *R*,*R*-*trans*-1,2-cyclohexanediamine-*N*,*N*′-diacetato (*R*,*R*-cdda) Co(III) complexes.[6] They demonstrated the stereoselective formation of a diastereomer of Δ-sym-*cis*-[$CrCl_2$(*R*,*R*-pichxn)]ClO_4 and Λ-sym-*cis*-[$CrCl_2$-

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(3) The combinations are (sym-cis)−(sym-cis), (sym-cis)−(unsym-cis), and (unsym-cis)−(unsym-cis), and each unsym-cis configuration has two geometrical isomers (*mer*- and *fac*-Cr$(N)_3(O)_3$), while sym-cis one has only mer isomer (see ref 2).

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(*S*,*S*-picbn)]ClO_4 (*R*,*R*-pichxn = 1*R*,2*R*-*N*,*N*′-bis(2-pyridylmethyl)-1,2-cyclohexanediamine, *S*,*S*-picbn = 2*S*,3*S*-*N*,*N*′-bis-(2-pyridylmethyl)-2,3-butanediamine) and Δ-sym-*cis*-[Co(*R*,*R*-chxn)(*R*,*R*-cdda)]$^+$, which have two equatorially oriented substituents at the terminal chelate rings, i.e., the abnormal form or eq−eq (N−C_{eq}) one. It is interesting to examine whether such a novel abnormal conformation could be entrapped in the above type of pzdc-bridged dinuclear complexes of the edda type complexes within a pocket of sym-cis configuration or whether there might exist appropriate orientations of the secondary amine hydrogen for the intramolecular N−H···O hydrogen bond.

On preparation of pzdc-bridged dinuclear complexes, use of eddp and cdda instead of edda and trdda could be expected to open new exceptional stereochemistry of otherwise nonexistent or unstable diastereomers in linear tetradentate ligands. In this paper, anomalous stereochemistry as well as the synthesis and the characterization of the pzdc-bridged dinuclear eddp, *R*,*R*- and *S*,*S*-, and/or *R*,*S*-cdda (*S*,*S*- and *R*,*S*-cdda = *S*,*S*-*trans*- and *R*,*S*-1,2-*cis*-cyclohexanediamine-*N*,*N*′-diacetate) or edda Cr(III) complexes by X-ray analysis or FAB (fast atom bombardment) mass spectrometry and circular dichroism (CD) will be reported.

Experimental Section

Materials. Ethylenediamine-*N*,*N*′-diacetic acid (H_2edda) and *R*,*S*-*cis*-cyclohexanediamine were purchased from Tokyo Kasei Kougyo and pyrazolate-3,5-dicarboxylic acid (H_3pzdc) from Aldrich. *R*,*R*- and *S*,*S*-*trans*-cyclohexanediamine were obtained by the literature method.[7]

Preparation of Ligands. Ethylenediamine-*N*,*N*′-dipropionic acid dihydrogen dichloride (H_2eddp·2HCl) was obtained by the reported method.[2]

Optically active *R*,*R*- and *S*,*S*-1,2-trans- and *R*,*S*-1,2-*cis*-cyclohexanediamine-*N*,*N*′-diacetates (*R*,*R*-, *S*,*S*-, and *R*,*S*-cdda) were prepared from the corresponding 1,2-cyclohexanediamines by the following method analogous to the one reported for H_2edda·2HCl.[8]

To *R*,*R*- (*S*,*S*-) or *R*,*S*-cyclohexanediamine (22.8 g) in a 500 mL flask, which was cooled in an ice bath, was added a cold aqueous solution (30 mL) containing 19.6 g of potassium cyanide. After the solution was allowed to stand for 20 min, 37% formaldehyde was added to it below 10 °C with stirring fot 30 min. After that, the stirring was continued for 4 h at room temperature. During this time, the solution changed from transparent to milky white then yellow-brown. From this reaction solution, the unreacted product was removed by a vacuum rotary evaporator at 40 °C. To the yellow-brown residue containing the corresponding 1,2-*trans*-cyclohexanediamine-*N*,*N*′-diacetonitrile (chxn$(CH_2CN)_2$) was added 50 mL of a stirred solution of 20% potassium hydroxide. Then the mixture was hydrolyzed by bubbling air at 60−70 °C. A small amount of water was added in order to make the reaction proceed effectively. The pH was adjusted to 3 by adding dilute hydrochloric acid to the reaction solution in an ice bath. The mixture was concentrated to viscous liquid at 40 °C by a rotary evaporator. This was dissolved in ethanol, and the solution was allowed to stand in a refrigerator. A white precipitate of KCl was removed by filtration. After desalting was again carried out to remove KCl by concentrating the filtrate, brown hygroscopic powder was obtained by vacuum-drying. Anal. Calcd for H_2-*R*,*R*-cdda·2.5HCl·$4H_2O$: C, 30.53; H, 7.30; N, 7.12. Found: C, 30.59; H, 7.20; N, 7.14. Anal. Calcd for H_2-*S*,*S*-cdda·HCl·$5H_2O$: C, 33.66; H, 8.19; N, 7.85. Found: C, 33.60; H, 8.08; N, 7.84.

Since H_2-*R*,*S*-cdda·2HCl could not be isolated, the elemental analysis data were not available. The aqueous reaction solution containing H_2-*R*,*S*-cdda was directly used for the preparation of the chromium(III) complex after removing KCl from the hydrolyzed solution by aqueous KOH.

Preparation of Complexes. 1. Na[Cr_2(eddp)$_2$(*μ*-pzdc)]·$6H_2O$ (0). As noted previously,[2] the same preparation method as that for the edda or trdda complex failed to produce the dinuclear eddp complex. The desired dinuclear complex was prepared by a modified method.

A solution containing 5.5 g (0.02 mol) of H_2eddp·2HCl in 20 mL of H_2O was neutralized by 4.2 g (0.04 mol) of Na_2CO_3. It was mixed with a solution containing 2.6 g (0.01 mol) of $CrCl_3$·$6H_2O$ in 10 mL of H_2O with stirring at 80 °C. To this solution was added H_3pzdc·H_2O (1.9 g, 0.01 mol) in 10 mL of H_2O neutralized by Na_2CO_3 added dropwise over a period of 30 min. This mixture was heated at 80 °C for 2 h and then allowed to stand overnight at room temperature and filtered. The QAE-Sephadex A-25 (Cl^- form) anion-exchange column chromatography of the filtrate with 0.2 M NaCl solution gave three bands. The second and third eluates were the mononuclear complexes corresponding to the two isomers obtained previously.[2] From the first eluate, red-purple powder was obtained after purification. Anal. Calcd for Na[Cr_2(eddp)$_2$(*μ*-pzdc)]·$5H_2O$·0.5NaCl: C, 29.72; H, 5.22; N, 9.90. Found: C, 29.48; H, 5.19; N, 9.82.

Red plate crystals of Na[Cr_2(eddp)$_2$(*μ*-pzdc)]·$6H_2O$ (**0**) used for X-ray measurements were obtained as minor crops during the crystallization of the mononuclear complex Na_2[Cr(eddp)(pzdc)]·$6H_2O$ in water−ethanol solution. We could not have their elemental analysis data because of the small amount. The remaining red needles (∼99%) are confirmed to be the mononuclear complex described in the previous paper[2] by the chromatographic behavior for the solution of the dissolved crystals.

2. Starting Diaqua Complexes. [Cr(edda)$(H_2O)_2$]Cl (**1**) was prepared by the literature method.[2] The reaction solution was used for the synthesis of the dinuclear complex. The concentration of the edda complex was determined by spectroscopic analysis of CrO_4^{2-} at 372 nm after oxidation of the complex with hot alkaline hydrogen peroxide.

The other complexes [Cr(*R*,*R*-cdda)$(H_2O)_2$]Cl (**2**), [Cr(*S*,*S*-cdda)-$(H_2O)_2$]Cl (**3**), and [Cr(*R*,*S*-cdda)$(H_2O)_2$]Cl (**4**) were synthesized by a method analogous to that for **1**. The pH of the solution (20 mL) containing 0.02 mol of H_2*R*,*R*-cdda·2.5HCl·$4H_2O$, H_2*S*,*S*-cdda·HCl·$5H_2O$, and H_2*R*,*S*-cdda·2HCl was adjusted to 5−6 by Na_2CO_3 in H_2O. To this solution an aqueous solution (10 mL) of $CrCl_3$·$6H_2O$ (5.2 g, 0.02 mol) was added dropwise. The pH of the solution was again adjusted to 5−6 by Na_2CO_3 in H_2O. After the reaction solution was stirred at 80 °C for 4 h, it was allowed to stand overnight. The solution was poured onto an SP-Sephadex C-25 (K^+ form) cation-exchange column. The column was washed with water and eluted with 0.1 M KCl solution. The column gave only one red-violet band. This eluate was concentrated by a rotary evaporator. After KCl was removed by repeated concentrating and Sephadex G-10 column chromatography, the solution was concentrated to dryness. Anal. Calcd for [Cr(*R*,*R*-cdda)$(H_2O)_2$]Cl·$6H_2O$·0.5KCl: C, 24.16; H, 6.49, N, 5.64. Found: C, 24.10; H, 6.55; N, 5.63. Anal. Calcd for [Cr(*S*,*S*-cdda)$(H_2O)_2$]Cl·$7H_2O$·KCl: C, 21.74; H, 6.20, N, 5.07. Found: C, 21.79; H, 6.39; N, 5.08. Anal. Calcd for [Cr(*R*,*S*-cdda)$(H_2O)_2$]Cl·$7H_2O$·KCl: C, 21.74; H, 6.20, N, 5.07. Found: C, 21.81; H, 6.35; N, 5.09.

3. Mononuclear pzdc Complexes. 3.1. K_2[Cr(edda)(pzdc)] (5). To an aqueous solution (50 mL, 0.84 mmol) of **1** was added an aqueous solution (20 mL) of H_3pzdc (0.15 g, 0.84 mmol), which was neutralized in advance by 0.17 g (1.3 mmol) of K_2CO_3 added dropwise over 30 min. After the reaction mixture was stirred at 80 °C for 2 h, it was allowed to stand at room temperature overnight. The resultant precipitate was filtered off. The filtrate was poured onto a QAE-Sephadex A-25 column. The column was washed with water, and then the elution with 0.10 M KCl solutions gave a large amount of the red dinuclear complex [Cr_2(edda)$_2$(*μ*-pzdc)]$^-$. After that, the elution with 0.2 M KCl solution gave a small amount of a reddish violet band. The identification of this eluate as the [Cr(edda)(pzdc)]$^{2-}$ complex was made by column chromatography and by judging the reaction product with the diaqua-

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(ethylenediamine-*N*,*N*′-diacetato) complex, which resulted in the formation of the dinuclear complexes as mentioned below. The yield of this complex was less than 0.5%. To prevent dinucleating, the eluate should be stored in a freezer. The concentration was determined by the spectroscopic method mentioned above.

3.2. K_2[Cr(*R*,*R*-, *S*,*S*-, or *R*,*S*-cdda)(pzdc)] Complexes (6−8). To an aqueous solution of **2** or **3** or **4** was added an aqueous solution of H_3pzdc, which was neutralized in advance with equimolar amounts of K_2CO_3 added dropwise over 30 min. After the reaction mixture was stirred at 60 °C for 2 h, it was allowed to stand at room temperature overnight. The resultant precipitate was filtered off. The filtrate was poured onto a QAE-Sephadex A-25 column. A small amount of a blue-violet band was eluted with 0.10 M KCl solution. This was identified as $[Cr(R,R\text{-}, S,S\text{-}, \text{or } R,S\text{-cdda})(OH)_2]^-$ by elemental analysis. After a reddish violet eluate with 0.2 M KCl solution was concentrated by a rotary evaporator, KCl was removed by repeated concentrations and Sephadex G-10 column chromatography.

Anal. Calcd for K_2[Cr(*R*,*R*-cdda)(pzdc)]·$7H_2O$·KCl: C, 24.04; H, 4.17, N, 7.48. Found: C, 23.95; H, 4.02; N, 7.39. Anal. Calcd for K_2[Cr(*S*,*S*-cdda)(pzdc)]·$6H_2O$·0.5KCl: C, 27.43; H, 4.45, N, 8.53. Found: C, 27.56; H, 4.52; N, 8.54. Anal. Calcd for K_2[Cr(*R*,*S*-cdda)(pzdc)]·$7H_2O$·0.5KCl: C, 26.70; H, 4.63, N, 8.30. Found: C, 26.56; H, 4.82; N, 8.29.

4. Dinuclear Complexes. 4.1. K[(*R*,*R*-cdda)Cr(*μ*-pzdc)Cr(edda)] (9 and 10). These complexes were prepared by two methods with different combinations of the diaqua complexes and the pzdc complexes; one method (I) uses $[Cr(edda)(H_2O)_2]^+$ (**1**) and $[Cr(R,R\text{-cdda})(pzdc)]^{2-}$ (**6**) and the other (II) uses $[Cr(R,R\text{-cdda})(H_2O)_2]^+$ (**2**) and $[Cr(edda)(pzdc)]^{2-}$ (**5**). The products of the *R*,*R*-cdda complex from the two methods were found to be identical with each other by spectroscopic measurements as discussed below.

An aqueous mixture of equimolar amounts of **1** (24 mL, 4.5×10^{-4} mol) and **6** (30 mL, 4.5×10^{-4} mol) or **2** (24 mL, 4.5×10^{-4} mol) and **5** (30 mL, 4.5×10^{-4} mol) was stirred at 80 °C for 2 h. After the mixture was cooled to room temperature, QAE-Sephadex A-25 column chromatography with eluting with 0.1 M KCl solution gave a reddish violet band. After it was concentrated by a rotary evaporator, desalting was performed to remove KCl by Sephadex G-10 column chromatography. The yields were 40−45%. Anal. Calcd for K[(*R*,*R*-cdda)Cr(*μ*-pzdc)Cr(edda)]·C_2H_5OH·KCl: C, 31.72; H, 4.18, N, 10.57. Found for **9** from method I: C, 31.99; H, 4.16; N, 10.65. Anal. Calcd for K[(edda)-Cr(*μ*-pzdc)Cr(*R*,*R*-cdda)]·C_2H_5OH·1.5KCl: C, 30.30; H, 4.00, N, 10.10. Found for **10** from method II: C,30.48; H, 3.98; N, 10.14. UV−vis data: 530 nm ($\epsilon = 354.0$ cm^{-1} dm^3 mol^{-1}), 389 nm ($\epsilon = 302$ cm^{-1} dm^3 mol^{-1}), 270 nm (shoulder $\epsilon \approx 14\,000$ cm^{-1} dm^3 mol^{-1}).

4.2. Two Isomers of K[(*R*,*R*-cdda)Cr(*μ*-pzdc)Cr(*S*,*S*-cdda)] (11 and 12) and K[(*S*,*S*-cdda)Cr(*μ*-pzdc)Cr(*R*,*R*-cdda)] (13 and 14). These complexes were prepared with two methods with different combinations of the diaqua complexes and the pzdc complexes; one method (III) uses $[Cr(S,S\text{-cdda})(H_2O)_2]^+$ (**3**) and $[Cr(R,R\text{-cdda})(pzdc)]^{2-}$ (**6**), and the other (IV) uses $[Cr(R,R\text{-cdda})(H_2O)_2]^+$ (**2**) and $[Cr(S,S\text{-cdda})(pzdc)]^{2-}$ (**7**). These two products obtained from two methods were confirmed to be the enantiomers by spectroscopic measurements as discussed below.

An aqueous mixture of equimolar amounts of **3** (23 mL, 8.7×10^{-4} mol) and **6** (30 mL, 8.7×10^{-4} mol) or **2** (26 mL, 8.2×10^{-4} mol) and **7** (30 mL, 8.2×10^{-4} mol) was stirred at 50 °C for 4 h. After the mixture was cooled to room temperature, QAE-Sephadex A-25 column chromatography with eluting with 0.1 M KCl solution gave two reddish violet bands in almost equal amounts (labeled E1 and E2 from method III and E3 and E4 from method IV in elution order). After they were concentrated by a rotary evaporator, desalting was performed to remove KCl by Sephadex G-10 column chromatography, and then the condensed product was finally washed with ethanol. The yields were about 35%. Anal. Calcd for K[(*R*,*R*-cdda)Cr(*μ*-pzdc)Cr(*S*,*S*-cdda)]·$8H_2O$: C, 33.48; H, 5.51, N, 9.37. Found for **11** (E1) from method III: C, 33.86; H, 5.48; N, 9.48. Anal. Calcd for K[(*R*,*R*-cdda)Cr(*μ*-pzdc)-Cr(*S*,*S*-cdda)]·$3H_2O$·$0.5C_2H_5OH$: C, 37.64; H, 5.10, N, 10.13. Found for **12** (E2) from method III: C,37.82; H, 4.98; N, 10.15. Anal. Calcd for K[(*S*,*S*-cdda)Cr(*μ*-pzdc)Cr(*R*,*R*-cdda)]·$5H_2O$·$0.5C_2H_5OH$: C, 36.07; H, 5.36, N, 9.71. Found for **13** (E3) from method IV: C,35.98; H, 5.18; N, 9.69. Anal. Calcd for K[(*S*,*S*-cdda)Cr(*μ*-pzdc)Cr(*R*,*R*-cdda)]·$2H_2O$·C_2H_5OH: C, 38.85; H, 5.19, N, 10.07. Found for **14** (E4) from method IV: C,37.99; H, 5.07; N, 9.84. UV−vis data for E1: 535 nm ($\epsilon = 355.5$ cm^{-1} dm^3 mol^{-1}); 389 nm ($\epsilon = 317.9$ cm^{-1} dm^3 mol^{-1}); 270 nm (shoulder $\epsilon \approx 14\,000$ cm^{-1} dm^3 mol^{-1}). UV−vis data for E2: 535 nm ($\epsilon = 352.1$ cm^{-1} dm^3 mol^{-1}); 391 nm ($\epsilon = 273.9$ cm^{-1} dm^3 mol^{-1}); 270 nm (shoulder $\epsilon \approx 14\,000$ cm^{-1} dm^3 mol^{-1}).

4.3. K[(*R*,*R*- or *S*,*S*-cdda)Cr(*μ*-pzdc)Cr(*R*,*S*-cdda)] (15 and 16). This complex was prepared by a method similar to that for the corresponding K[(*R*,*R*-cdda)Cr(*μ*-pzdc)Cr(*S*,*S*-cdda)] complex with use of H_2-*R*,*S*-cdda·2HCl instead of H_2-*S*,*S*- or *R*,*R*-cdda·2HCl and only by changing the reaction condition from 50 °C for 4 h to 40 °C for 6 h. QAE-Sephadex A-25 column chromatography with eluting with 0.1 M KCl solution gave a reddish violet band (E5 and E6 from *R*,*R*- and *S*,*S*-cdda, respectively). Isolation was performed by the above method. The yields were ca. 25%. Anal. Calcd for K[(*R*,*R*-cdda)Cr(*μ*-pzdc)Cr-(*R*,*S*-cdda)]·$2H_2O$·0.8KCl: C, 35.40; H, 4.40, N, 9.91. Found for **15** (E5): C, 33.81; H, 4.51; N, 10.29. Anal. Calcd for K[(*S*,*S*-cdda)Cr(*μ*-pzdc)Cr(*R*,*S*-cdda)]·$3H_2O$·$2C_2H_5OH$: C, 38.75; H, 5.72, N, 9.35. Found for **16** (E6): C, 38.65; H, 5.34; N, 19.34. UV−vis data: 538 nm ($\epsilon = 354.6$ cm^{-1} dm^3 mol^{-1}); 391 nm ($\epsilon = 338.0$ cm^{-1} dm^3 mol^{-1}); 270 nm (shoulder $\epsilon \approx 14\,000$ cm^{-1} dm^3 mol^{-1}). These dinuclear complexes are unstable and decomposed in organic solvents, especially and instantly in acetone.

4.4. [Cr(*R*,*R*-cdda)(phen)]Cl (17). This was prepared from $[CrCl_3(dmf)(phen)]$, which is obtained from a mixture of $CrCl_3$ and phen in dmf, and H_2-*R*,*R*-cdda·2HCl. After the former phen complex (3.7 mg) was aquated to $[Cr(H_2O)_4(phen)]^{3+}$ in 100 mL of H_2O, to the resulting red solution was added a 10 mL aqueous solution of H_2-*R*,*R*-cdda·2.5HCl·$4H_2O$ (2.7 g), which was adjusted to pH 5−6 with K_2CO_3. The mixture was stirred at 80−90 °C for 6 h. The reaction solution was poured onto an SP-Sephadex C-25 column. After the column was washed with water, the mixture was eluted with 0.1 M KCl solution. The obtained reddish violet band was collected and desalted by repeated concentrations. The yield was ca. 45%. Anal. Calcd for [Cr(*R*,*R*-cdda)-(phen)]Cl·$3H_2O$·0.5KCl: C, 48.47; H, 5.55; N, 10.28. Found for **17**: C, 48.37; H, 5.61; N, 10.27.

Measurements. UV−vis spectra were recorded by a Perkin-Elmer Lambda 19 spectrophotometer. CD spectra were measured by a Jasco J-720W spectropolarimeter. Negative ion FAB mass spectra were obtained in aqueous solutions by a JEOL JMS−SX102 mass spectrometer.

X-ray Structural Analysis of Na[$Cr_2(eddp)_2$(*μ*-pzdc)]·$6H_2O$ (0). A red plate crystal having approximate dimensions of 0.15 mm × 0.10 mm × 0.01 mm was mounted on a glass fiber. The intensity data were collected by a Enraf-Nonius diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) at 23 °C.

Data were collected at 23 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ of 49.9°. Of 5833 reflections collected, 5612 were unique. The intensities of three representative reflections that were measured after every 100 reflections declined by 2.7%. A linear correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient for Mo Kα is 7.8 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, and the rest were refined isotropically. Two carbon atoms (C(12) and C(16)) and four of six water oxygen atoms (O(53), O(54), O(55), and O(56)) had positional disorders and were best modeled with two or three positions for each atom. All hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1687 observed reflections ($I > 3\sigma(I)$). Crystallographic data of Na[$Cr_2(eddp)_2$(*μ*-pzdc)]·$6H_2O$ are summarized in Table 1. Selected bond distances and angles are shown in Table 2.

Results and Discussion

Molecular Structure of Na[$Cr_2(eddp)_2$(*μ*-pzdc)]·$6H_2O$ (0). The X-ray molecular structure of the complex is shown in Figure 1. This complex has a dinuclear structure in which two Cr-

Table 1. Crystallographic Data of $Na[Cr_2(eddp)_2(\mu\text{-pzdc})]\cdot 6H_2O$ (**0**)

formula	$C_{21}H_{29}N_6O_{12}Cr_2Na\cdot 6H_2O$
MW	708.36
cryst syst	monoclinic
cryst size, mm	0.15 × 0.10 × 0.01
space group	$P\bar{1}$
a, Å	9.410(4)
b, Å	11.047(6)
c, Å	15.875(8)
α, deg	92.16(3)
β, deg	101.64(3)
γ, deg	98.21(3)
Z	2
d_{calcd}, g cm^{-3}	1.624
R^a	0.065
$R_w{}^b$	0.076
no. independent reflns	4673

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

Table 2. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) of $Na[Cr_2(\mu\text{-eddp})_2(pzdc)]\cdot 6H_2O$ (**0**)

Intramolecular Data			
Cr(1)−O(1)	1.95(1)	Cr(2)−O(7)	1.94(1)
Cr(1)−O(3)	1.96(1)	Cr(2)−O(9)	1.96(1)
Cr(1)−O(L1)	1.98(1)	Cr(2)−O(L2)	1.99(1)
Cr(1)−N(1)	2.10(1)	Cr(2)−N(3)	2.06(1)
Cr(1)−N(2)	2.04(2)	Cr(2)−N(4)	2.04(2)
Cr(1)−N(L1)	2.08(1)	Cr(2)−N(L2)	2.06(2)
Cr(1)···Cr(2)	4.574(4)		
O(1)−Cr(1)−O(3)	178.7(6)	O(7)−Cr(2)−O(9)	92.8(5)
O(1)−Cr(1)−O(L1)	86.5(5)	O(7)−Cr(2)−O(11)	173.9(5)
O(1)−Cr(1)−N(1)	88.2(5)	O(7)−Cr(2)−N(3)	89.9(5)
O(1)−Cr(1)−N(2)	90.4(6)	O(7)−Cr(2)−N(4)	94.0(6)
O(1)−Cr(1)−N(L1)	90.2(5)	O(7)−Cr(2)−N(L2)	94.9(5)
O(3)−Cr(1)−O(L1)	93.7(5)	O(9)−Cr(2)−O(11)	90.9(4)
O(3)−Cr(1)−N(1)	91.7(5)	O(9)−Cr(2)−N(3)	174.3(6)
O(3)−Cr(1)−N(2)	90.9(6)	O(9)−Cr(2)−N(4)	91.0(5)
O(3)−Cr(1)−N(L1)	88.6(5)	O(9)−Cr(2)−N(L2)	92.5(5)
O(L1)−Cr(1)−N(1)	171.2(5)	O(11)−Cr(2)−N(3)	86.9(5)
O(L1)−Cr(1)−N(2)	89.3(6)	O(11)−Cr(2)−N(4)	90.8(5)
O(L1)−Cr(1)−N(L1)	80.8(5)	O(11)−Cr(2)−N(L2)	80.1(5)
N(1)−Cr(1)−N(2)	83.7(6)	N(3)−Cr(2)−N(4)	83.7(6)
N(1)−Cr(1)−N(L1)	106.3(5)	N(3)−Cr(2)−N(L2)	92.3(6)
N(2)−Cr(1)−N(L1)	170.0(6)	N(4)−Cr(2)−N(L2)	170.2(6)
N(1)−C(7)−C(8)−N(2)	49(2)	N(3)−C(15)−C(16A)−N(4)	52(2)
N(3)−C(15)−C(16B)−N(4)	4(6)	N(1)−Cr(1)−N(2)−C(8)	23(1)
N(3)−Cr(2)−N(4)−C(16A)	34(1)	N(3)−Cr(2)−N(4)−C(16B)	6(2)
N(2)−Cr(1)−N(1)−C(3)	4(1)	N(4)−Cr(2)−N(3)−C(15)	−4(1)
Intermolecular Hydrogen Bond Distances and Angles			
N(1)···O(5)	3.04(1)	N(1)···O(6)	3.06(1)
O(5)···H	2.30	O(6)···H	2.13
N(1)−H···O(5)	134.77	N(1)−H···O(6)	165.24
O(5)···H···O6	59		
C−O(5)···H	76.5	C═O(6)···H	84.4
O(5)···O(6)···H−N(1)	173	O(6)···O(5)···H−N(1)	173

(eddp) units are bridged by a didentate pzdc. In the complex, each chromium is coordinated by a linear tetradentate eddp (N_2O_2) and a pzdc (NO) producing an octahedral mer-$Cr(N)_3(O)_3$ geometry. The geometrical configurations of the eddp around Cr1 and Cr2 ions are sym-cis(mer) and unsym-cis(mer), respectively, corresponding to the same configuration as found for $[Cr_2(edda)_2(\mu\text{-pzdc})]^-$ anion.[2] The absolute configuration around a central metal ion is identical with those for Cr1 and Cr2. In Figure 1, the Δ−Δ enantiomer is illustrated.

For the unsym-cis isomer of the eddp complex, there are two possible conformational diastereomers (Chart 1) due to the chirality of the secondary nitrogen atom (R_N or S_N) of the G (in-plane) ring. In our previous study of the $[Cr(eddp)(ox)]^-$ complex, the spectroscopic evidence indicated the existence of the two conformational isomers.[9] All the geometrical and conformational isomers of the $[Co(eddp)(en)]^+$ complex has been structurally characterized by X-ray analysis.[4] Two conformational diastereomers of the unsym-cis isomer are designated as anti(N−H) and syn(N−H) with respect to the geometrical configurations for the amine protons of the R (out-of-plane) and G rings as shown in unsym-cis-1 (Chart 1a) and unsym-cis-2 (Chart 1b). In the case of the eddp dinuclear complex with the Δ−Δ absolute configuration, a pair of the positional disorders around the coordinated diamine is found with two sets (S_N*,S_N (anti(N−H)) and S_N*,R_N (syn(N−H)))[10] of the absolute configurations for the secondary nitrogen atoms in the coordinated eddp ligand for the unsym-cis moiety (Cr2) unit (Figure 1). They are separately illustrated in Figure 2. The ratio of the diastereomers (unsym-cis-1 and unsym-cis-2) is demonstrated to be almost 2:1 from the occupancies; the latter syn one is confirmed to exist for the first time, while the former anti configuration is favored as found for $[Nd\{Cr(eddp)(ox)\}_3(H_2O)_3]$ complex.[11] The bond lengths and angles around the Cr atoms (Table 2) are similar to those of other edda type Cr(III) complexes with some exceptions (vide infra). The ethylenediamine takes a normal gauche conformation with the torsion angles of N−C−C−N being +49(2)° for Cr(1) (sym-cis) and +52(2)° for Cr(2) (unsym-cis1), while the unsym-cis-2 has a considerably distorted diamine ring (N−C−C−N, +4(6)°) with the flattened envelope conformation. The ethylenediamine conformations in the eddp complexes with the Δ−Δ absolute

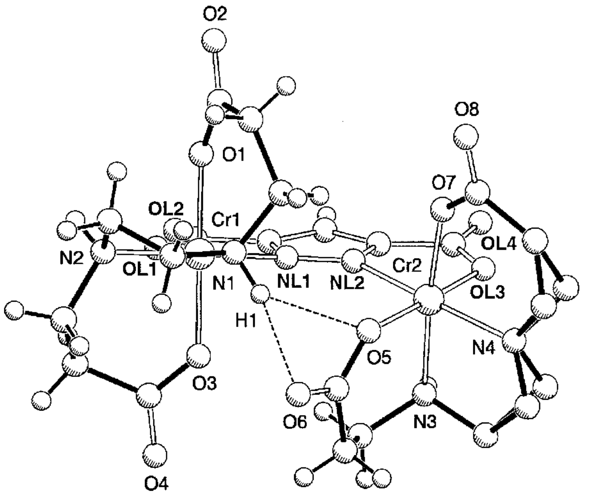
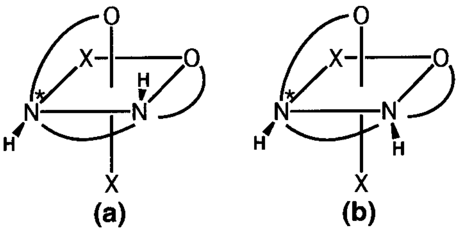


Figure 1. Molecular structure of $Na[Cr_2(eddp)_2(\mu\text{-pzdc})]\cdot 6H_2O$. The solid line shows the eddp backbone for sym- and unsym-cis configuration around the Cr(1) (left) and Cr(2) (right) ions, respectively. The broken lines refer to the three center bifurcated H···O(5) and H···O(6) hydrogen bonds.

Chart 1



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(9) Sakagami, N.; Hioki, A.; Liu, X.-L.; Konno, T.; Okamoto, K.; Kaizaki, S. 69th National Meeting of the Chemical Society of Japan, Kyoto, March 1995; Abstract 3P06.

(10) S_N,R_N and S_N*,R_N* denote the chiralities of the N and/or N* atoms in the out-of-plane (R) and in-plane (G) rings, respectively, with respect to the $Cr(N)_3(O)_1$ coordination plane.

(11) Sakagami, N.; Okamoto, K. *Chem. Lett.* **1998**, 201.

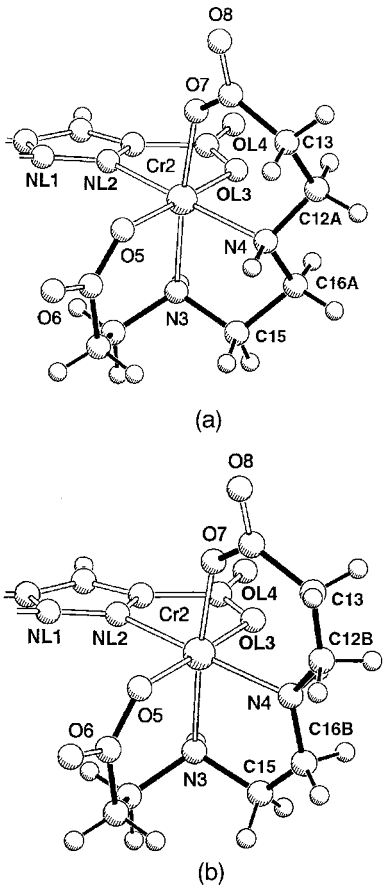

Figure 2. Two conformational diastereomeric structures around the Cr(2) unit: unsym-cis-1 (a); unsym-cis-2 (b).

configuration are δ for the sym-cis, δ for the unsym-cis-1, and an envelope for the unsym-cis-2. The unsym-cis-1 moiety is designated as $\Delta(\delta,R_N*,S_N)$, where the terminal propionate chelate ring at the R ring is formed by coordination of the unusually equatorially oriented glycinate or takes the abnormal eq (N$-$C$_{eq}$) form, leading to the δ diamine conformation as seen below in the case of the acetate for the cdda complexes. This δ conformation is opposite the λ one where the normal ax (N$-$C$_{ax}$) form occurs with the usually axially oriented coordination. The sym-cis moiety takes the $\Delta(\delta,S_N*,S_N)$ with the normal ax$-$ax form for the two β-alaninates at the terminal R rings, with one being an "ob" (λ) β-alaninate chelate ring conformation and the other a "lel" (δ) one,[12] in contrast to the "ob" conformation of both the R rings in the sym-*cis*-$[Co(eddp)(en)]^+$ complex.[4] The lack of symmetry or the formation of the lel conformation may be due to the Na$\cdots$O interaction (2.34(2) Å) between the uncoordinated carboxylate oxygen atom at the R (lel) ring (O4) and a sodium ion. Although such an ob conformation of the β-alaninate (propionate) combination at the R ring has already been claimed spectroscopically for two of the three diastereoisomers of $[Cr(edtp)]^-$ (edtp = ethylenediamine-*N*,*N*,*N*′,*N*′-tetrapropionate) type complexes[13] and structurally characterized for the β-alaninate in the R ring of Na[Cr(*u*-eddadp)]$\cdot$3H$_2$O (*u*-eddadp = ethylenediamine-*N*,*N*-diacetate-*N*′,*N*′-di-3-propionate),[14] this is the first example of the X-ray structurally determined β-alaninate ring conformations with unsymmetrical "ob$-$lel" combination in the sym-*cis*-edda type complexes.

As shown in Figure 1, there are intramolecular hydrogen bonds between the proton of the secondary amine nitrogen (N1) and both the coordinated carboxylate oxygen (O5) and uncoordinated one (O6). The angle sum around the hydrogen is α_1-(N1$-$H$\cdots$O5) + α_2(N1$-$H$\cdots$O6) + α_3(O6$\cdots$H$\cdots$O5) = 359°, and thus, the H atom is close to the plane defined by N1, O5, and O6; $\Delta = 0.092$ Å (Table 2). These structural parameters range within a rare statistical distribution, demonstrating the three-center bifurcated hydrogen bond together with the nearly symmetric location of the hydrogen in syn position with respect to the acceptor carboxylate oxygens.[15] The bond angles around the chromium(III) ions are distorted from regular octahedron. Especially the bond angle N(1)$-$Cr(1)$-$N(L1) is rather larger (106.3(5)°) compared with that (103.0(3)°) of the corresponding edda complex and the ideal angle (90°). This distortion may result from the intramolecular hydrogen bond. The Cr(1)$\cdots$Cr(2) distance is 4.574(4) Å, being longer than that (4.473(3) Å) of the edda complex but close to that (4.560(4) Å) of the trdda complex.[2]

The bond distances and bond angles of the pzdc ligand for this complex are almost the same within the error range as those for the related pzdc-bridged dinuclear complexes.[2] However, the torsion angle of N(L1)$-$Cr(1)$\cdots$Cr(2)$-$N(L2) is 9.42°, which is larger than that of the edda (5.84°) and trdda (1.89°) complexes, indicating that even the pzdc ligand structure in the eddp complex is forced to be twisted from its original plane by the insertion of the hydrogen bond between two planes. This may be in line with the fact that the preparative method for the dinuclear edda and trdda complexes is not always applicable to the corresponding eddp complex.

Although the eddp complex seems to prefer the unsym-cis configuration in general,[9,16] the (sym-cis)$-$(unsym-cis) configuration is found to form stereoselectively, the less stable sym-cis configuration being trapped by the intramolecular three-center bifurcated hydrogen bond in a reverse way for the corresponding edda complex.

Synthesis and Characterization of the cdda Complexes. In view of the synthetic course, the chromatographic behavior, elemental analysis, and the similarity in position and intensity of the UV$-$vis spectra as described in the Experimental Section, the pzdc complexes **9$-$15** are formulated as K[Cr$_2$(cdda)(cdda or edda)(pzdc)]$\cdot n$H$_2$O$\cdot m$C$_2$H$_5$OH$\cdot x$KCl and are assumed to have dinuclear structures with the same *mer*-[Cr(N)$_3$(O)$_3$] type chromophore. In fact, the respective negative FAB mass spectra of the complexes exhibited a uninegative quasi-molecular ion peak at $m/z = 663$ for $[M + 4H]^-$, with the mass of M being 659 for [Cr$_2$(cdda)(edda)(μ-pzdc)]$^-$, and two kinds of uninegative quasi-molecular ion peaks at $m/z = 713$ and 717 for $[M]^-$ and $[M + 4H]^-$, respectively, with the mass of M being 713 for [Cr$_2$(cdda)$_2$(μ-pzdc)]$^-$. These results substantiate the dinuclear structure bridged by a pzdc for these complexes, similar to that found for the corresponding edda complex.[2]

QAE-Sephadex column chromatography for the reaction solutions of equimolar mixtures of K$_2$[Cr(*R*,*R*-cdda)(pzdc)] and [CrL(H$_2$O)$_2$]Cl (L = *S*,*S*-cdda or *R*,*S*-cdda) with 0.1 M KCl

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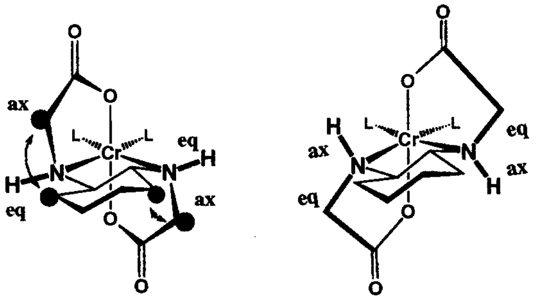
(12) The "ob" (λ) means that the ethylenic C$-$C bond of the β-alaninate ring is oblique to the pseudo-C_2 axis bisecting the N$-$Cr$-$N angle with the ethylenic gauche λ conformation. For the "lel" (δ), the C$-$C bond is parallel to the C_2 axis with the ethylenic gauche δ conformation. This notation is discussed in ref 13.

(13) (a) Kaizaki, S.; Hayashi, M. *J. Chem. Soc., Chem. Commun.* **1988**, 613. (b) Sakagami, N.; Kaizaki, S.; Hayashi, M. *J. Chem. Soc., Dalton Trans.* **1992**, 28.

(14) Radanović, D. J.; Sakagami, N.; Ristanović, V. M.; Kaizaki, S. *Inorg. Chim. Acta* **1999**, *292*, 16.

(15) Görbitz, C. H.; Etter, M. C. *J. Chem. Soc., Perkin Trans. 2*, **1992**, 131.

(16) Radanović, D. J.; Duran, M. I.; Stamenović, D. C.; Grujić, S. *Bull. Chim. Soc. Beograd* **1984**, *49*, 315.



Normal
ax-ax (NC_{ax}-NC_{ax})
$\Lambda(R_N, R_N; \lambda)$
(a)

Abnormal
eq-eq (NC_{eq}-NC_{eq})
$\Delta(S_N, S_N; \lambda)$
(b)

Figure 3. Molecular models showing diastereomers of the Δ-sym-cis-*R*,*R*-cdda complex with respect to the absolute configurations of the coordinated asymmetric nitrogens and the normal axial (a) and abnormal equatorial (b) orientations of the terminal acetate rings. The solid circles in (a) refer to the acetate and cyclohexane methylene of which the protons suffer severe steric contact as shown by arrows.

solution gave red eluates; two for the former *R*,*R*-cdda and *S*,*S*-cdda pair or one for the latter *R*,*R*-cdda and *R*,*S*-cdda pair. On the other hand, there was no indication of the dinuclear complex formation from a mixture of $K_2[Cr(R,R\text{-cdda})(pzdc)]$ and $[Cr(R,R\text{-cdda})(H_2O)_2]Cl$ and from a mixture of $K_2[Cr(R,S\text{-cdda})(pzdc)]$ and $[Cr(R,S\text{-cdda})(H_2O)_2]Cl$. Instead, precipitates with the constitution of $[Cr(pzdc)(H_2O)_2]_n$ were obtained. These findings reject any possibility of forming a Δ−Δ or Λ−Λ (sym-cis)−(sym-cis) configuration with close N−H contact or a Δ−Λ or Λ−Δ (sym-cis)−(unsym-cis) one with close glycinate chelates contact but suggest the formation of a Δ−Δ or Λ−Λ (sym-cis)−(unsym-cis) one by molecular model consideration as well as evidenced by the above result for the eddp complex and our previous result for the edda complex.[2] We will come back to this point later.

Circular Dichroism and Stereochemistry. The mononuclear *R*,*R*-cdda complexes such as $[Cr(R,R\text{-cdda})(H_2O)_2]^+$, $[Cr(R,R\text{-cdda})(pzdc)]^+$, and $[Cr(R,R\text{-cdda})(phen)]^+$ give a negative major CD component in the first ${}^4A_2-{}^4T_2$ magnetic-dipole-allowed transition region. Thus, this diastereomer may take a Δ absolute configuration. This assignment is confirmed by observing a positive CD band around 282 nm corresponding to the $\pi-\pi^*$ transition of 1,10-phenanthroline for $[Cr(R,R\text{-cdda})(phen)]^+$ as empirically established for the other trischelate mono(phen) complexes.[17] Of two sym-cis and unsym-cis geometrical isomers for Cr(III) complexes containing tetradentate O−N−N−O ligands with only the five-membered chelate rings, the cdda type ligand prefers a sym-cis configuration to a unsym-cis one on coordination, as discussed for the edda type complexes previously.[2] The sym-cis configuration for the *R*,*R*-cdda complexes is found to be more favorable than that for the edda complex in connection with the formation of {(*R*,*R*-cdda)−(edda)} complexes as examined below. Therefore, the most probable configuration of the *R*,*R*-cdda mononuclear complexes is Δ-sym-cis but not Δ-unsym-cis. If the *R*,*R*-cdda takes a sym-cis configuration with an axial orientation (normal) of two glycinates ($N-C_{ax}$ or ax−ax), the absolute configuration around chromium(III) ion is Λ, as depicted in Figure 3a. The stereoselective formation of such a Δ-sym-cis configuration means that the terminal chelate rings are formed by coordination of the equatorially oriented glycinates (abnormal; $N-C_{eq}$ or eq−eq) (Figure 3b). Thus, these sym-*cis*-*R*,*R*-cdda mononuclear complexes take the abnormal eq−eq form in the *R*,*R*-cdda coordination rather than the normal ax−ax one as found for sym-*cis*-$[CrCl_2(R,R\text{-pichxn})]ClO_4$, $-[CrCl_2(S,S\text{-picbn})]ClO_4$, and $-[Co(R,R\text{-chxn})(R,R\text{-cdda})]^+$.[5,6] This is because in the reverse Λ configuration of the normal ax−ax form there is a steric repulsion between one of the methylene protons of the terminal acetate chelate ring and the methylene proton attached to the cyclohexane carbon atom adjacent to the asymmetric carbon one as shown in Figure 3a.[5] It is also noted that the abnormal eq form can exist in the cdda complexes, notwithstanding that the five-membered glycinate chelates are more strained than relaxed six-membered β-alaninate chelates at the R-ring site in the unsym-*cis*-eddp complex where a similar eq form is found as mentioned above.

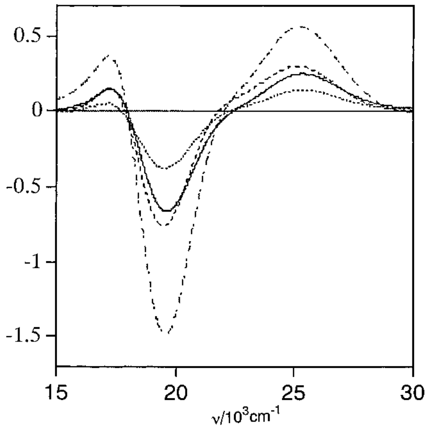


Figure 4. Circular dichroism spectra of two diasteromers of $[(R,R\text{-cdda})Cr(\mu\text{-pzdc})Cr(S,S\text{-cdda})]^-$ [E1 (**11**) (−); E2 (**12**) (-•-)] and $[(R,R\text{-cdda})Cr(\mu\text{-pzdc})Cr(R,S\text{-cdda})]^-$ [E5 (**15**) (- - -)], and $[(R,R\text{-cdda})Cr(\mu\text{-pzdc})Cr(edda)]^-$ (**9** and **10**) (•••).

The {(*R*,*R*-cdda)-(edda)} dinuclear complexes **9** from method I and **10** from method II exhibit identical CD patterns showing a negative major component in the first band region as shown in Figure 4. The CD behavior lends support to configurational chirality, leading to the assignment to the Δ absolute configuration. As mentioned above, the Δ absolute configuration originates from the sym-cis geometrical structure with the abnormal eq−eq form in the *R*,*R*-cdda coordination. Thus, both the **9** and **10** complexes have a {(Δ-sym-*cis*-*R*,*R*-cdda)}−(Δ-unsym-*cis*-edda)} configuration. This indicates that the *R*,*R*- or *S*,*S*-cdda favors the sym-cis configuration compared to the edda, since it is apparent that the formation of complex **9** or **10** from the edda(diaqua) and the edda(pzdc) complexes accompanies the isomerization from sym-cis to unsym-cis configuration and the epimerization from *R* to *S* absolute configuration of the asymmetric nitrogen atom in the edda complexes as discussed below in detail.

On the other hand, the {(*R*,*R*-cdda)−(*S*,*S*-cdda)} complexes **11** and **12** from method III and {(*S*,*S*-cdda)−(*R*,*R*-cdda)} complexes **13** and **14** from method IV gave enantiomeric CD spectra. This fact suggests that the dinuclear complexes contain one each of *R*,*R*-cdda and *S*,*S*-cdda ligands. If both the mononuclear sym-*cis*-$[Cr(R,R\text{-cdda or }S,S\text{-cdda})(pzdc)]^+$ and sym-*cis*-$[Cr(S,S\text{-cdda or }R,R\text{-cdda})(H_2O)_2]^+$ underwent isomerization to the unsym-cis configuration with comparable ease, the resultant complexes would be only a racemic one, equal amounts of (Δ−Δ)-{(*R*,*R*-cdda)−(*S*,*S*-cdda)} and (Λ−Λ)-{(*S*,*S*-cdda)−(*R*,*R*-cdda)} complexes. This is not the finding. Since a negative major CD component was observed for complexes **11**

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(17) Kaizaki, S.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 988.

Table 3. Summary of Stereochemistry for the Dinuclear Complexes with Combinations of Δ-sym-*cis*-edda and -*R*,*R*-cdda Unit in Left Column and Δ-unsym-cis Unit

	Δ-unsym-cis unit		
	edda	*S*,*S*-cdda	*R*,*S*-cdda
Δ-sym-*cis*-edda δ (ax−ax)[g] R_N,R_N[h]	syn (N−H)[a]) λ (ax)[g] R_N,S_N[h]	*b*	*b*
Δ-sym-*cis*-*R*,*R*-cdda λ (eq−eq)[g] S_N,S_N[h]	syn (N−H)[c] λ (ax)[1)] $R_N{*},S_N$[h]	syn (N−H)[d] δ (eq)[g] $R_N{*},S_N$[h] anti (N−H)[e] δ (eq)[g] $R_N{*},R_N$[h]	syn (N−H)[f] (eq) $R_N{*},S_N$[h]

[a] From ref 2 in which the notation for the coordinated asymmetric nitorgen atoms was wrong. This should be R_N,R_N and R_N,S_N. [b] Not detected. [c] Complexes **9** and **10**. [d] Complex **11**. [e] Complex **12**. [f] Complex **15**. [g] Ethylenediamine conformations (axially or equatorially oriented coordination of N−C). [h] Absolute configurations of coordinated asymmetric nitrogen.

and **12** in the first absorption band region (Figure 4), they have a configurational chirality leading to the assignment to the Δ absolute configuration. Thus, dinucleating between Δ-(sym-*cis*-*R*,*R*-cdda) and Δ-(unsym-*cis*-*S*,*S*-cdda) is confirmed from the viewpoint of the CD behavior leading to the Δ absolute configuration for **11** and **12**. This indicates that the configuration of the mononuclear sym-*cis*-[Cr(*R*,*R*-cdda)(pzdc)]$^+$ moiety tends to be retained on dinucleating and governs the whole structure of the dinuclear complexes stereoselectively probably because the trischelated pzdc complex would be more robust toward isomerization than the bischelated diaqua complex. It is intriguing that the configurational chiral dinuclear complexes are produced even though they consist of an enantiomeric pair of *R*,*R*- and *S*,*S*-cdda. These dinuclear complexes could be formed from the reaction of the pzdc with the racemic cdda (*R*,*R*- and *S*,*S*-cdda) complex but not with the same two of each enantiomer ((*R*,*R*-cdda)$_2$ or (*S*,*S*-cdda)$_2$), in accordance with the fact that the ring conformations of two diamines are found to be opposite each other (δ and λ) in Na[Cr$_2$(edda)$_2$(μ-pzdc)]·5H$_2$O,[2] as summarized in Table 3.

There are two possible conformational isomers (diastereomers) for the unsym-*cis*-Cr(*S*,*S*-cdda) moiety with respect to the coordinated asymmetric nitrogen atoms of the secondary amine as revealed above by the X-ray structural analysis for Na[Cr$_2$(eddp)$_2$(μ-pzdc)]·6H$_2$O (**0**) and unsym-*cis*-[Co(eddp)(en)]-Cl[4] as depicted in Chart 1. That is, the glycinate chelate in the R-ring is equatorially oriented or takes the abnormal *eq* form with the *R* absolute configuration of the coordinated asymmetric nitrogen in the unsym-cis isomer, whereas the asymmetric nitrogen in the G-ring could take the S_N or R_N configuration. With respect to the relative orientational (geometrical) relation of two amine protons in the asymmetric nitrogens, the diastereomers are designated as syn and anti configurations for the combination of the (R_N*,S_N) and (R_N*,R_N), respectively, as described above. The X-ray structures of the Na[Cr$_2$(edda)$_2$(μ-pzdc)]·5H$_2$O[2] and unsym-*cis*-[Cr(edda)(tzdp)] (Htzdp = 1,2,4-triazole-3,5-dipyridine)[18] revealed that the unsym-cis configuration belongs to syn. Thus, it is likely that one of the two diastereomers of the {(*R*,*R*-cdda)−(*S*,*S*-cdda)} complex (E1 (**11**) and E2 (**12**)) as well as the {(*R*,*R*-cdda)−(edda)} diastereomer (**9** and **10**) should have a syn configuration and that the other belongs to an anti one as shown in parts a and b of Figure 5.

In the case of the *R*,*S*-cdda complexes, on the other hand, only one of two possible geometrical isomers with respect to the relative position of the cyclohexane ring could be stereospecifically formed with the syn−unsym-cis configuration for the N−H positions; i.e., the glycinates near the *R* and *S* asymmetric carbon atom are coordinated at the G and R ring sites, respectively, for the Δ absolute configuration and vice versa as shown in Figure 5c. This stereospecificity results from preventing steric contact between the cyclohexane ring and the R ring for this combination, whereas the severe steric hindrance occurs for the reverse combination, *S*(C$_{\text{cyclohexane}}$) near the G ring and *R*(C$_{\text{cyclohexane}}$) near the R ring for the Δ absolute configuration from molecular model considerations. Compared with the geometrical structures of three kinds of complexes, the *R*,*R*-cdda (*S*,*S*-cdda) complexes isomerize to the unsym-cis configuration with the most difficulty; the steric strain in the unsym-cis isomer decreases in the order of *R*,*R*-cdda (*S*,*S*-cdda) > edda ≫ *R*,*S*-cdda.

Definitive structural assignments of the two {(*R*,*R*-cdda)−(*S*,*S*-cdda)} diastereomers will be examined on the basis of the CD spectra as follows. In these complexes, there are four kinds of chirality, which are due to configurations around the central metal ion (Δ and Λ), the conformation in the diamine chelate (λ and δ), and the atomic asymmetry of carbon (S_C, R_C) and coordinated nitrogen (S_N, R_N). On this basis, possible chiral contributions for the diastereomers are summarized as in Table 3, where the undefinable diamine chelate conformation in *R*,*S*-cdda is not cited. The entire CD intensity of the {*R*,*R*-cdda-*S*,*S*-cdda} complex (either **11** or **12**) may be given by linear combinations of each CD contribution as in the following equations (either eq 1 or eq 2), and that of the {*R*,*R*-cdda-*R*,*S*-cdda} complex **15** is represented by eq 3, assuming the additivity of the CD contributions as demonstrated for the CD spectra of three diastereomers of [Cr(*R*-pdtp)]$^-$ (*R*-pdtp = *R*-propylenediamine-*N*,*N*,*N'*,*N'*-tetrapropionate) and [Cr(*R*,*R*-cdtp)]$^-$ (*R*,*R*-cdtp = *R*,*R*-*trans*-1,2-cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetrapropionate).[13]

$$\Delta\epsilon(\text{i}) = \{\Delta\epsilon(\Delta) + 2\Delta\epsilon(R_C) + 2\Delta\epsilon(S_N) + \Delta\epsilon(\lambda)\}_{\text{sym}} + \{\Delta\epsilon(\Delta) + 2\Delta\epsilon(S_C) + \Delta\epsilon(R_N{*}) + \Delta\epsilon(S_N) + \Delta\epsilon(\delta)\}_{\text{unsym}} \quad (1)$$

$$\Delta\epsilon(\text{ii}) = \{\Delta\epsilon(\Delta) + 2\Delta\epsilon(R_C) + 2\Delta\epsilon(S_N) + \Delta\epsilon(\lambda)\}_{\text{sym}} + \{\Delta\epsilon(\Delta) + 2\Delta\epsilon(S_C) + \Delta\epsilon(R_N{*}) + \Delta\epsilon(R_N) + \Delta\epsilon(\delta)\}_{\text{unsym}} \quad (2)$$

$$\Delta\epsilon(\text{iii}) = \{\Delta\epsilon(\Delta) + 2\Delta\epsilon(R_C) + 2\Delta\epsilon(S_N) + \Delta\epsilon(\lambda)\}_{\text{sym}} + \{\Delta\epsilon(\Delta) + \Delta\epsilon(S_C) + \Delta\epsilon(R_C) + \Delta\epsilon(R_N{*}) + \Delta\epsilon(S_N)\}_{\text{unsym}} \quad (3)$$

According to the equations, the major difference in CD intensity among the diastereomers results from the absolute configuration of the asymmetric nitrogen at the G-ring site ($\Delta\epsilon(R_N)$ or $\Delta\epsilon(S_N)$) and the relation of the entire CD intensities are approximated as $\Delta\epsilon(\text{i}) \doteqdot \Delta\epsilon(\text{iii}) \neq \Delta\epsilon(\text{ii})$, since the degrees of the chiral contributions are evaluated to be $|\Delta\epsilon(\Delta)| \gg |\Delta\epsilon(R_N)| = |\Delta\epsilon(S_N)| > |\Delta\epsilon(\lambda)| = |\Delta\epsilon(\delta)| \gg |\Delta\epsilon(S_C)| = |\Delta\epsilon(R_C)|$. Thus, the {*R*,*R*-cdda-*S*,*S*-cdda} complex (**11**) has a syn(N−H) configuration with S_N because the CD intensity of this complex is similar to that of the {*R*,*R*-cdda−*R*,*S*-cdda} complex **15** as shown in Figure 4, whereas complex **12** has an anti(N−H) one with R_N. It is notable that the anti(N−H) configuration is found in even the strained five-membered glycinate chelate at the G-ring site of the unsym-*cis*-edda type complex. To our knowledge, this is the first example of two unsym-*cis*-edda type diastereomers with all being five-membered. The whole stere-

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(18) Niiya, K.; Fuyuhiro, A.; Kaizaki, S. 76th National Meeting of the Chemical Society of Japan, Yokohama, March 1999; Abstract 1PA056.

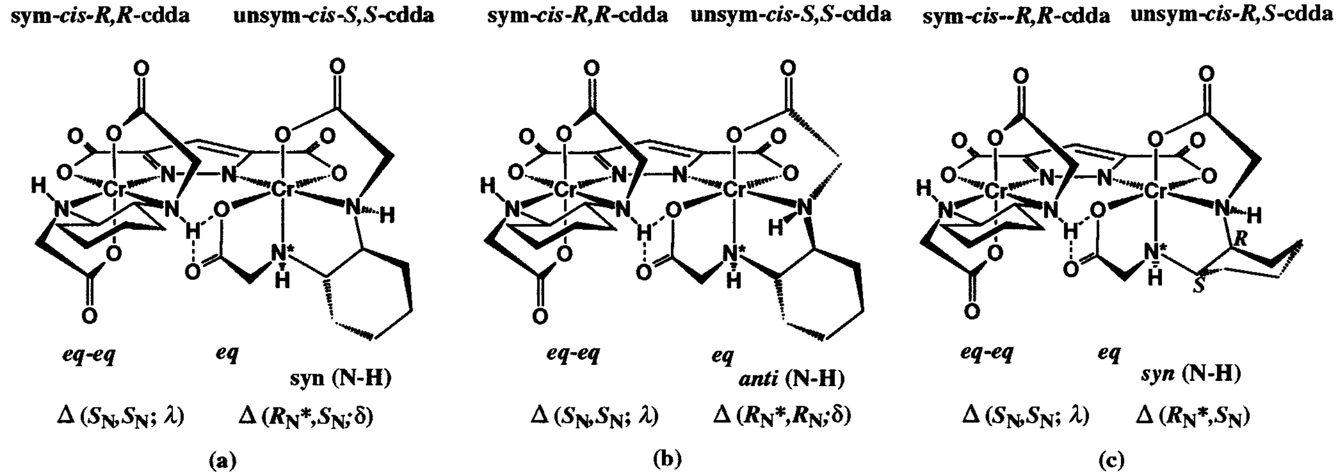

Figure 5. Proposed structures for two diasteromers of [(*R*,*R*-cdda)Cr(μ-pzdc)Cr(*S*,*S*-cdda)]$^-$ ((a, b) and [(*R*,*R*-cdda)Cr(μ-pzdc)Cr(*R*,*S*-cdda)]$^-$ (c), where the notations for the chiralities and the geometrical configurations are described under each one.

ochemistry of the present dinuclear complexes is summarized in Figure 5 and Table 3.

Conclusion

From the present experimental results, it follows that the didentate complex ligand [Cr(*R*,*R*-cdda)(pzdc)]$^{2-}$ has a stereognostically environmental pocket accommodating or entrapping edda or *S*,*S*-cdda and *R*,*S*-cdda complex units in unsym-cis configuration with thermodynamically unstable or else nonexistent conformational modes. When dinuclear complexes between the complex ligand and the mononuclear diaqua complexes are formed, the latter incoming complexes might be captured within a pocket of the former complex ligand not only by a pyrazole nitrogen and carboxylate of pzdc but also by hydrogen bonding between N−H's and coordinated carboxylate oxygen of the edda type ligands, as evidenced by the X-ray structures of the edda[2] and eddp complexes. Thus, these dinuclear complexes may be stabilized by de facto tridentate, but not didentate, coordinations including the outer-sphere coordination through the hydrogen bonds. At the same time the incoming complexes could be modified and/or undergo isomerization to an unsym-cis configuration for the edda type and sym-cis one for the eddp complex and/or epimerization of the coordinated asymmetric nitrogen atoms by adopting themselves to the surroundings within the pocket of the complex ligand. Therefore, the major factor to govern molecular recognition within such pockets is noncovalent interaction or intramolecular or intercomplex-unit hydrogen bonds to afford stereognostic coordination in dinuclear complexes as found for the edda[2] and eddp complexes (see above).

It is very interesting and promising to note that this type of complex ligand gives various possibilities for recognizing diastereomers or for realizing unique coordination modes or conformations that could not exist under normal conditions such as in mononuclear complexes or with other types of bridging ligands. Stereochemical information on entrapped conformations provides a new means to understand the reaction mechanism, including isomerization, as well as to explore how much the structures might be modified under unfamiliar conditions in relation to the electronic properties. The research in this course is under way in our laboratory.

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Supporting Information Available: Tables of all atomic coordinates, anisotropic thermal parameters, all bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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