

Syntheses and Characterization of (Diamine-*N,N'*-dicarboxylato)chromate(III) Dinuclear Complexes Bridged by Pyrazole-3,5-dicarboxylate: X-ray Structures of Na[Cr₂(edda)₂(μ -pzdc)]·5H₂O and Na[Cr₂(trdda)₂(μ -pzdc)]·3H₂O

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New pyrazole-3,5-dicarboxylato (pzdc) chromate(III) complexes containing linear tetradentate edda (ethylenediamine-*N,N'*-diacetate), trdda (trimethylenediamine-*N,N'*-diacetate), or eddp (ethylenediamine-*N,N'*-dipropionate) were synthesized and characterized by elemental analyses, column chromatography, ²H NMR, FAB mass spectra, and X-ray analyses. Crystallographic data for Na[Cr₂(edda)₂(μ -pzdc)]·5H₂O (**1**) are monoclinic with space group *P*2₁/*n*, *a* = 11.73(1) Å, *b* = 19.475(6) Å, *c* = 13.229(6) Å, β = 111.99(5)°, *Z* = 4, and a final *R* factor of 0.056 based on 4673 reflections. Na[Cr₂(trdda)₂(μ -pzdc)]·3H₂O (**2**) crystallizes in the orthorhombic space group *Fdd*2, with *a* = 16.576(4) Å, *b* = 29.235(6) Å, *c* = 12.544(5) Å, *Z* = 8, and a final *R* factor of 0.078 based on 2456 reflections. In both complexes two Cr(III) units were bridged by a pzdc. The complex **1** and **2** has a (sym-*cis*)–(unsym-*cis*) edda and (unsym-*cis*)–(unsym-*cis*) trdda geometrical configuration, respectively. Unlike the edda and trdda ligands, the eddp ligand formed mononuclear pzdc complexes, which may correspond to two geometrical isomers of unsym-*cis-mer*- and *fac*-[Cr(eddp)(pzdc)]²⁻ (**3** and **4**). The differences in the formations of the pzdc Cr(III) complexes with the edda-type ligands were demonstrated to arise from the chelate ring sizes and/or the intramolecular interaction such as hydrogen bond and van der Waals contact between two Cr(III)–edda type units. The hydrogen bond between the edda moieties following stereognostic coordination brings about the novel inert unsym-*cis* configuration in complex **1**.

Introduction

Recently we have reported¹ the magnetism and stereochemistry of some dinuclear bis(acetylacetonato)chromium(III) complexes bridged by aromatic heterocyclic compounds such as pyrazole-3,5-dicarboxylate (pzdc³⁻, Figure 1). Though two isomers (*racemic* and *meso*) were separated and isolated for the pzdc dinuclear complex, the formation ratio and stability were different probably because of the different proximity between the acac chelate rings coordinated to each Cr(III) ion. When polyamine–polycarboxylate ligands supplying hydrogen bond donor(NH)–acceptor(carboxylate) groups form the pzdc-bridged dinuclear complex instead of acac, more elaborate coordination modes and stereoselectivity will be expected to arise from the attractive as well as repulsive intramolecular interaction between these nonbridging ligands and then to result in regulating the number of possible isomers. For example, in the case of octahedral *cis*-[M(O–N–N–O)X₂] type complexes with linear tetradentate ethylenediamine-*N,N'*-diacetate- (edda-) type ligands, there are 12 possible geometrical isomers and their enantiomers, which result from pairwise combinations of geometrical isomers (sym-*cis* and unsym-*cis* in Figure 2) as shown in Figure 3. In such dinuclear complexes, the isomer distribution depends not only on the intramolecular interactions but also on the different stability of geometrical configurations in mononuclear complexes, where the stable geometrical configuration of edda Cr(III) complexes with all five-membered chelates is the sym-*cis* isomer^{2–5} and trimethylenediamine-*N,N'*-diacetate (trdda) or ethylenediamine-*N,N'*-dipropionate(eddp) with six-membered

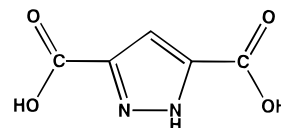


Figure 1. Pyrazole-3,5-dicarboxylic acid.

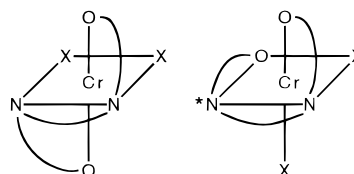


Figure 2. Two possible isomers of *cis*-[Cr(edda)X₂] type complex: sym-*cis* (left); unsym-*cis* (right).

chelate rings prefers the unsym-*cis* one.^{6–9} Therefore, the pzdc-bridged dinuclear complexes will be a suitable candidate to reveal the role of noncovalent interaction recognizing the geometrical configuration when forming dinuclear complexes.

We report here the preparation and characterization of three Cr(III)–edda-type complexes coordinated by a pzdc. The differences in geometrical configurations among the edda, trdda,

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(1) Nakahanada, M.; Ino, K.; Kaizaki, S. *J. Chem. Soc., Dalton Trans.* **1993**, 3681.
(2) Radanović, D. J.; Veselinović, D. S.; Grurić, S. A. *Bull. Chim. Soc., Beograd* **1979**, *44*, 503.

(3) Srdanov, G.; Herak, R.; Radanović, D. J.; Veselinović, D. S. *Inorg. Chim. Acta* **1980**, *38*, 37.
(4) (a) Weyh, J. A.; Pierce, R. L. *Inorg. Chem.* **1971**, *10*, 858. (b) Bianchini, R. J.; Legg, I. J. *Inorg. Chem.* **1986**, *25*, 3263.
(5) Green, C. A.; Place, H.; Willett, R. D.; Legg, J. I. *Inorg. Chem.* **1986**, *25*, 4672.
(6) Radanović, D. J.; Duran, M. I.; Stamenović, D. C.; Grujić, S. A. *Bull. Chim. Soc., Beograd* **1984**, *49*, 315.
(7) Bianchini, R. J.; Geiser, U.; Place, H.; Kaizaki, S.; Morita, Y.; Legg, J. I. *Inorg. Chem.* **1986**, *25*, 2129.
(8) Radanović, D. J.; Trifunović, S. R.; Grujić, S. A.; Maricondi, C.; Parvez, M.; Douglas, B. E. *Inorg. Chim. Acta* **1989**, *157*, 33.
(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, Abstr. No. 3P06.

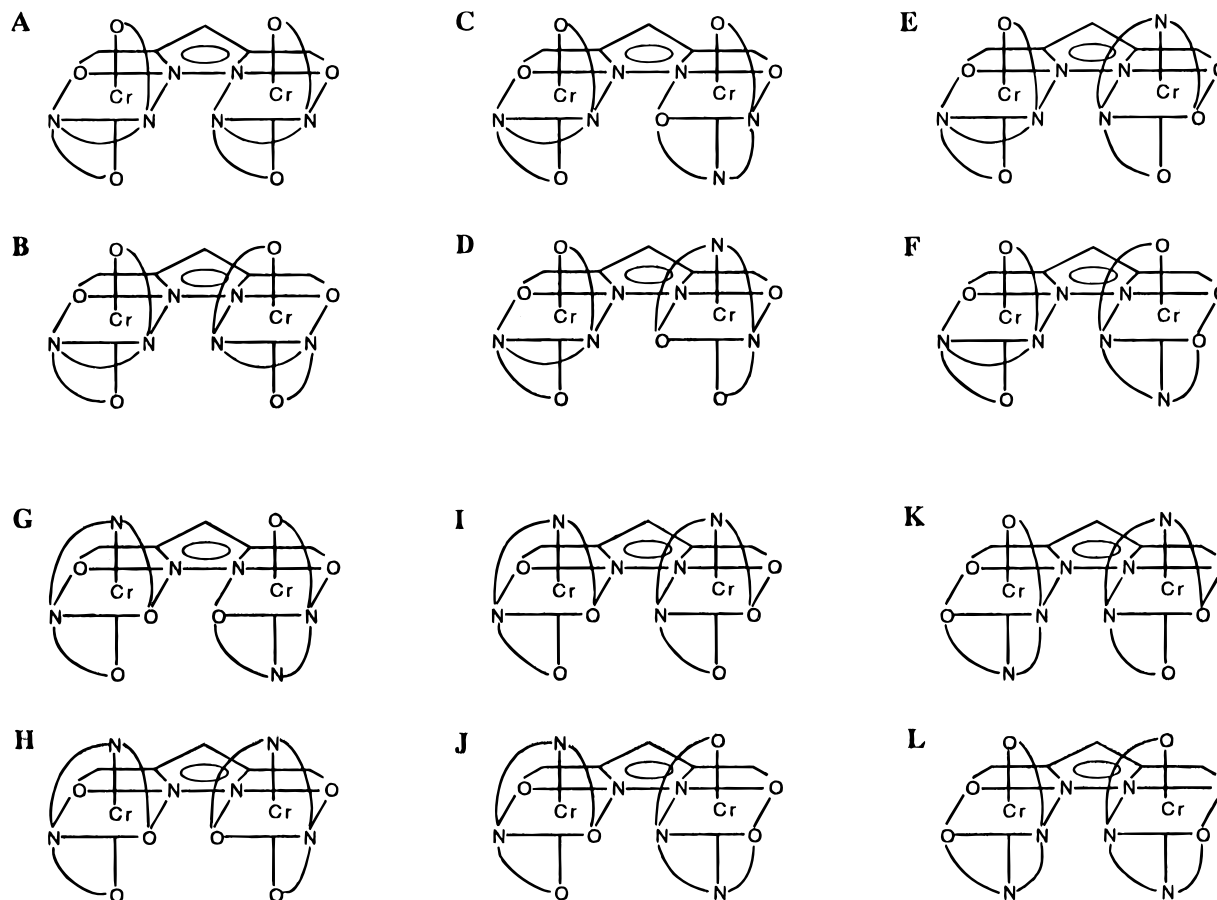


Figure 3. Twelve possible isomers of the $[\text{Cr}_2(\text{O-N-N-O})_2(\mu\text{-pzdc})]^-$ type dinuclear complex: (sym-*cis*)-(sym-*cis*) (A, B); (sym-*cis*)-(unsym-*cis*) (C–F); (unsym-*cis*)-(unsym-*cis*) (G–L).

and eddp complexes will be examined in view of not only the chelate ring sizes but also the noncovalent interaction between two Cr(III)–edda type type moieties in the dinuclear complexes.

Experimental Section

Preparation of the Ligands. H₂edda (Tokyo Kasei Kogyo Co., Ltd.) and H₃pzdc (Aldrich) were used without further purification. The trdda and eddp ligands were prepared by the literature.^{6,10} The deuteration for the acetate arms of the edda (edda-*d*₄) and for the propionate arms of the eddp (eddp-*d*₄) were performed according to the previously reported methods.^{4,11}

Preparation of the Complexes. The starting diaqua edda type complexes were obtained by heating an equimolar mixture of CrCl₃·6H₂O and the edda-type ligand neutralized by Na₂CO₃ in H₂O for 4 h. The reaction solutions were used as prepared.

Na[Cr₂(edda)₂(μ-pzdc)]·5H₂O (1). To a solution containing 2 mmol of [Cr(edda)(H₂O)₂]⁺ an aqueous solution of H₃pzdc (0.17 g, 1 mmol) neutralized by Na₂CO₃ was added. The pH of the reaction mixture was adjusted to about 4.5, and then the reaction solution was heated at 60 °C for 2 h with stirring. Only one band was eluted on a QAE-Sephadex (A-25, Cl[−] form) column with 0.05 mol dm^{−3} NaCl solution. The eluate was concentrated on a rotary evaporator and passed through a Sephadex G-10 column in order to remove NaCl. A red powder was obtained from water–acetone solution (yield 65%). Anal. Calcd for Na[Cr₂(edda)₂(μ-pzdc)]·5H₂O: C, 28.42; H, 4.35; N, 11.70. Found: C, 28.22; H, 4.27; N, 11.53.

Na[Cr₂(trdda)₂(μ-pzdc)]·3H₂O (2). This complex was prepared by a method similar to that used for the edda complex except that the reaction temperature was 80 °C. After the reaction solution was cooled

to room temperature, red crystals precipitated¹² were removed and the filtrate was poured onto a QAE-Sephadex column with the Cl[−] form. One red band was eluted with 0.05 mol dm^{−3} NaCl solution. The eluate was concentrated and desalted by G-10 column chromatography. A red powder was obtained in *ca.* 10% yield. Anal. Calcd for Na[Cr₂(trdda)₂(μ-pzdc)]·3H₂O·CH₃CH₂OH: C, 33.38; H, 4.80; N, 11.12. Found: C, 33.04; H, 4.78; N, 11.09. The analytical results were different from the chemical formula from the X-ray crystal analysis (see below).

Na₂[Cr(eddp)(pzdc)]·6H₂O (3) and Na₂[Cr(eddp)(pzdc)]·4.5H₂O (4). These complexes were obtained by the same method as that of the trdda complex. QAE-Sephadex column chromatography of the reaction solution with use of 0.05 mol dm^{−3} NaCl solution gave only minor red band. This band faded away during the elution. Additional elution with 0.2 mol dm^{−3} NaCl solution gave two major bands (3 and 4 in elution order). These reddish violet bands were collected and each eluate was desalted by G-10 Sephadex chromatography. Each sodium salt was recrystallized from a water–acetone mixture. Anal. Calcd for Na₂[Cr(eddp)(pzdc)]·6H₂O·0.5NaCl (3): C, 26.44; H, 4.61; N, 9.49. Found: C, 26.29; H, 4.58; N, 9.18. Calcd for Na₂[Cr(eddp)(pzdc)]·4.5H₂O (4): C, 29.22; H, 4.53; N, 10.49. Found: C, 29.75; H, 4.51; N, 10.42.

Measurements. Positive ion FAB mass spectra were measured in aqueous solution by a Jeol JMS-SX102 mass spectrometer. ²H NMR spectra were recorded on a Jeol JNM GSX-270 spectrometer at room temperature. Magnetic susceptibility data were obtained on powdered samples by using an automated Faraday balance in the temperature range 80–300 K. The observed susceptibilities were fitted by the theoretical expression by means of a nonlinear least-squares SIMPLEX parameter-optimization routine, minimizing the residual function $R = [\sum(\chi_{\text{obs}} - \chi_{\text{calc}})^2 / (\chi_{\text{obs}})^2]^{1/2}$.

(10) Igi, K.; Douglas, B. E. *Inorg. Chem.* **1974**, *13*, 425.

(11) (a) Sakagami, N.; Hayashi, M.; Kaizaki, S. *J. Chem. Soc., Dalton Trans.* **1992**, 285. (b) Kaizaki, S.; Byakuno, M.; Hayashi, M.; Legg, J. I.; Umakoshi, K.; Ooi, S. *Inorg. Chem.* **1987**, *26*, 2395.

(12) These red crystals were found to be [Cr₂(trdda)₂(OH)₂]₂·2H₂O by the elemental analysis.

Table 1. Crystallographic Data for Na[Cr₂(edda)₂(*μ*-pzdc)]·5H₂O (**1**) and Na[Cr₂(trdda)₂(*μ*-pzdc)]·3H₂O (**2**)

	1	2
formula	C ₁₇ H ₂₁ N ₆ O ₁₂ Cr ₂ Na·5H ₂ O	C ₁₉ H ₂₅ N ₆ O ₁₂ Cr ₂ Na·3H ₂ O
mol wt	708.36	710.47
cryst syst	monoclinic	orthorhombic
cryst size, mm	0.1 × 0.2 × 0.5	0.1 × 0.2 × 0.2
space group	<i>P2₁/n</i>	<i>Fdd2</i>
<i>a</i> , Å	11.73(1)	16.576(4)
<i>b</i> , Å	19.475(6)	29.235(6)
<i>c</i> , Å	13.229(6)	12.544(5)
β , deg	111.99(5)	
<i>Z</i>	4	8
<i>d</i> _{calcd} , g cm ⁻³	1.679	1.553
<i>R</i> ^a	0.056	0.078
<i>R</i> _w ^b	0.065	0.085
no. of independent reflns	4673	1120

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

X-ray Structural Analysis. Crystals suitable for the X-ray analyses of Na[Cr₂(edda)₂(*μ*-pzdc)]·5H₂O (**1**) and Na[Cr₂(trdda)₂(*μ*-pzdc)]·3H₂O (**2**) were grown in water–acetone and water–ethanol solutions, respectively. Though the elemental analysis of the powdered complex **2** showed the existence of one ethanol molecule as crystallization solvent, no ethanol was found in the crystal of **2** by X-ray analysis. Crystallographic data are summarized in Table 1.

The intensity data were collected by a Rigaku AFC-5R diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at 23 °C. The calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation by a VAX computer at the X-ray diffraction service of the Department of Chemistry of Osaka University.

A red plate crystal of complex **1** was mounted in a glass capillary. Data were collected at 23 ± 1 °C using the ω -2 θ scan technique to a maximum 2 θ of 50.1°. Of 4935 reflections collected, 4673 were unique. The intensities of three representative reflections which were measured after every 100 reflections declined by 0.19%. A linear correction factor was applied to the data to account for this phenomena. The linear absorption coefficient for Mo K α is 8.5 cm⁻¹. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.76 to 1.00. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in the difference-Fourier map except for those of the water molecules. The final cycle of full-matrix least-squares refinement was based on 2872 observed reflections ($I \geq 3\sigma(I)$).

A red rhombic crystal of complex **2** was loaded into a glass capillary. Data collection and structure solution were almost the same as the method of complex **1**. The maximum 2 θ value was 60.1°. A total of 2456 reflections were collected. As the intensities of three representative reflections declined by 1.64%, a linear correction factor was applied to the data. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms except for those of water molecules were calculated and not refined. The final cycle of full-matrix least-squares refinement was based on 1120 observed reflections ($I > 3\sigma(I)$).

Selected bond distances and angles are shown in Tables 2–4.

Results and Discussion

Characterization of Complexes 1 and 2. In view of the chromatographic behavior and the elemental analyses, complexes **1** and **2** are formulated as Na[Cr₂(edda)₂(pzdc)]·5H₂O and Na[Cr₂(trdda)₂(pzdc)]·3H₂O and are assumed to have dinuclear structures. The positive FAB mass spectral data of the complex **1** in aqueous solution shows three kinds of unipositive quasi-molecular ion peaks at $m/z = 651$, 629, and 607, respectively, for [M + Na]⁺, [M + H]⁺, and [M + 2H - Na]⁺, where M refers to the dinuclear entity Na[Cr₂(edda)₂(pzdc)] ($m/z = 628$). In complex **2**, two ion peaks are observed ($m/z = 657$

Table 2. Selected Bond Distances (Å) and Angles (deg) for Na[Cr₂(edda)₂(*μ*-pzdc)]·5H₂O (**1**)

Cr(1)–O(1)	1.962(4)	Cr(2)–O(5)	1.957(5)
Cr(1)–O(3)	1.939(5)	Cr(2)–O(7)	1.965(5)
Cr(1)–O(L1)	1.965(5)	Cr(2)–O(L3)	1.991(6)
Cr(1)–N(1)	2.074(6)	Cr(2)–N(3)	2.038(6)
Cr(1)–N(2)	2.067(8)	Cr(2)–N(4)	2.073(5)
Cr(1)–N(L1)	2.051(7)	Cr(2)–N(L2)	2.030(6)
Cr(1)–Cr(2)	4.473(3)		
O(1)–Cr(1)–O(3)	173.8(3)	O(5)–Cr(2)–O(7)	89.8(2)
O(1)–Cr(1)–O(L1)	88.4(2)	O(5)–Cr(2)–O(L3)	96.1(2)
O(1)–Cr(1)–N(1)	82.1(2)	O(5)–Cr(2)–N(3)	81.9(2)
O(1)–Cr(1)–N(2)	92.3(2)	O(5)–Cr(2)–N(4)	163.0(2)
O(1)–Cr(1)–N(L1)	93.9(2)	O(5)–Cr(2)–N(L2)	98.9(2)
O(3)–Cr(1)–O(L1)	96.3(2)	O(7)–Cr(2)–O(L3)	173.8(2)
O(3)–Cr(1)–N(1)	93.0(2)	O(7)–Cr(2)–N(3)	91.7(2)
O(3)–Cr(1)–N(2)	83.4(2)	O(7)–Cr(2)–N(4)	81.8(2)
O(3)–Cr(1)–N(L1)	90.9(2)	O(7)–Cr(2)–N(L2)	97.4(2)
O(L1)–Cr(1)–N(1)	170.1(2)	O(L3)–Cr(2)–N(3)	91.0(2)
O(L1)–Cr(1)–N(2)	93.9(3)	O(L3)–Cr(2)–N(4)	93.0(2)
O(L1)–Cr(1)–N(L1)	80.4(2)	O(L3)–Cr(2)–N(L2)	79.9(2)
N(1)–Cr(1)–N(2)	83.7(3)	N(3)–Cr(2)–N(4)	83.7(2)
N(1)–Cr(1)–N(L1)	103.0(3)	N(3)–Cr(2)–N(L2)	170.9(3)
N(2)–Cr(1)–N(L1)	171.4(2)	N(4)–Cr(2)–N(L2)	96.7(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Na[Cr₂(trdda)₂(*μ*-pzdc)]·3H₂O (**2**)

Cr(1)–O(1)	1.95(1)	Cr(1)–O(3)	1.93(1)
Cr(1)–O(L1)	1.933(9)		
Cr(1)–N(1)	2.06(1)	Cr(1)–N(2)	2.05(1)
Cr(1)–N(L1)	2.04(1)		
O(1)–C(2)	1.27(2)	O(2)–C(2)	1.24(2)
O(3)–C(4)	1.26(2)	O(4)–C(4)	1.24(2)
Cr(1)–Cr(1')	4.560(4)		
O(1)–Cr(1)–O(3)	91.8(4)	O(1)–Cr(1)–O(L1)	93.2(4)
O(1)–Cr(1)–N(1)	80.9(5)	O(1)–Cr(1)–N(2)	173.3(5)
O(1)–Cr(1)–N(L1)	93.6(4)	O(3)–Cr(1)–O(L1)	174.4(4)
O(3)–Cr(1)–N(1)	89.7(5)	O(3)–Cr(1)–N(2)	82.5(5)
O(3)–Cr(1)–N(L1)	101.1(5)	O(L1)–Cr(1)–N(1)	88.6(5)
O(L1)–Cr(1)–N(2)	92.4(5)	O(L1)–Cr(1)–N(L1)	81.1(4)
N(1)–Cr(1)–N(2)	95.5(5)	N(1)–Cr(1)–N(L1)	168.1(5)
N(2)–Cr(1)–N(L1)	90.9(5)		

and 635 for [M + H]⁺ and [M + 2H - Na]⁺, respectively: M = Na[Cr₂(trdda)₂(pzdc)] ($m/z = 656$). Moreover, for complex **1** the temperature dependent magnetic susceptibility shows a weak ferromagnetic interaction ($2J = +1.21$ cm⁻¹) in accordance with the observed value ($2J = +0.81$ cm⁻¹) for Na[Cr₂(acac)₄(*μ*-pzdc)]·4.5H₂O.¹ The magnetic data for complex **2** could not be obtained because of the small yield. These results support the dinuclear structure bridged by a pzdc ligand for the edda and trdda complexes.

From the fact that the sym-*cis* configuration of the Cr(III)–edda complex is more stable than the unsym-*cis* one,^{3,4} it is suggested that the (sym-*cis*)–(sym-*cis*) isomer (**A** and **B**) is formed. However, NMR spectroscopy¹³ of the edda complex causes us to reject this possibility. As in Figure 4, more than four ²H NMR signals were observed for complex **1** and the signals around -10 to -30 ppm resemble those⁴ of unsym-*cis*-[Cr(edda-d₄)(H₂O)₂]⁺. This NMR pattern suggests the existence of unsym-*cis* configuration(s) in complex **1**. On the other hand, since the Cr(III)–trdda complex favors the unsym-*cis* configuration,^{7,8} complex **2** is predicted to take the (sym-*cis*)–(unsym-*cis*) configuration.

Molecular Structures of Complexes 1 and 2. The X-ray molecular structures of complexes **1** and **2** are shown in Figures

(13) Since deuterium nuclear magnetic resonance (²H NMR) spectra give a line narrowing due to small gyromagnetic ratio as well as a large contact shift for paramagnetic chromium(III) complexes, ²H NMR is useful as a direct method to determine solution structure. Wheeler, D.; Kaizkai, S.; Legg, J. I. *Inorg. Chem.* **1982**, *21*, 3248.

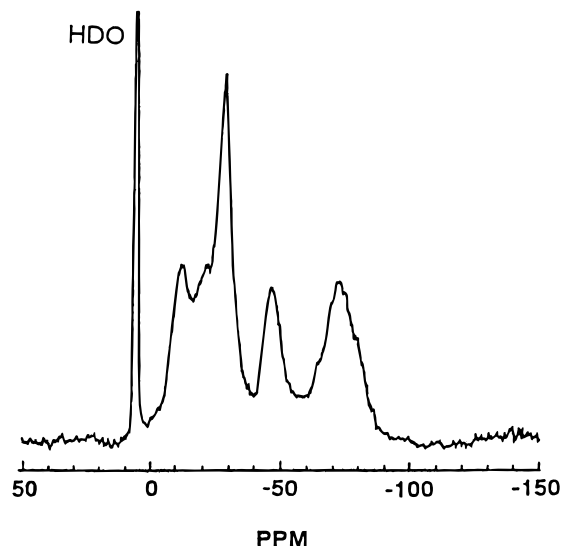
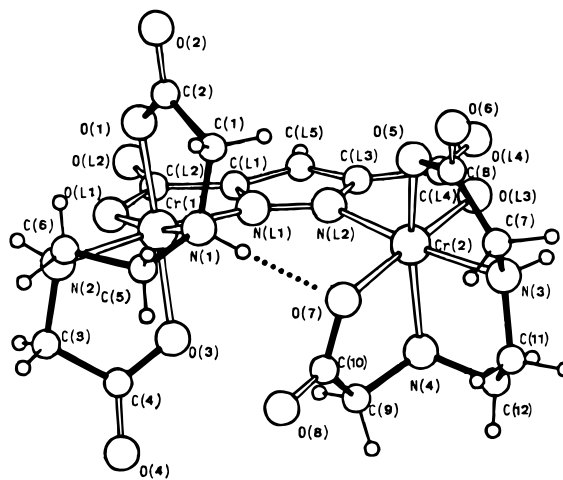
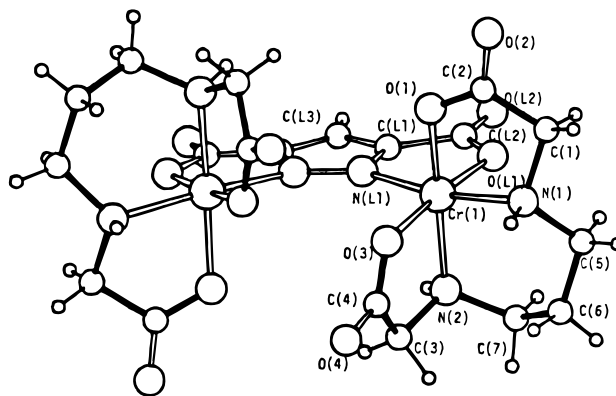
Table 4. Bond Distances (Å) and Angles (deg) for pzdc^{3-}

Compound 1			
C(L1)–C(L2)	1.46(1)	C(L3)–C(L4)	1.48(1)
C(L1)–C(L5)	1.39(1)	C(L3)–C(L5)	1.37(1)
N(L1)–C(L1)	1.36(1)	N(L2)–C(L3)	1.35(1)
O(L1)–C(L2)	1.31(1)	O(L3)–C(L4)	1.30(1)
O(L2)–C(L2)	1.23(1)	O(L4)–C(L4)	1.25(1)
N(L1)–N(L2)	1.349(8)		
C(L1)–C(L5)–C(L3)	103.3(7)	C(L4)–C(L3)–C(L5)	134.1(8)
C(L2)–C(L1)–C(L5)	134.3(8)	N(L2)–C(L3)–C(L4)	114.6(6)
N(L1)–C(L1)–C(L2)	115.8(8)	N(L2)–C(L3)–C(L5)	111.3(7)
N(L1)–C(L1)–C(L5)	109.9(6)	O(L3)–C(L4)–C(L3)	114.5(7)
O(L1)–C(L2)–C(L1)	114.2(7)	O(L4)–C(L4)–C(L3)	122.3(7)
O(L2)–C(L2)–C(L1)	121.3(9)	O(L3)–C(L4)–O(L4)	123.2(8)
O(L1)–C(L2)–O(L2)	124.5(8)	N(L2)–N(L1)–C(L1)	107.9(6)
N(L1)–N(L2)–C(L3)	107.5(6)		
Compound 2			
C(L1)–C(L2)	1.51(2)		
C(L1)–C(L3)	1.35(2)		
N(L1)–C(L1)	1.37(2)		
O(L1)–C(L2)	1.31(2)		
O(L2)–C(L2)	1.21(2)		
N(L1)–N(L1')	1.35(2)		
C(L1)–C(L3)–C(L1')	104(2)		
C(L2)–C(L1)–C(L3)	134(1)		
N(L1)–C(L1)–C(L2)	115(1)		
N(L1)–C(L2)–C(L3)	111(1)		
O(L1)–C(L2)–C(L1)	112(1)		
O(L2)–C(L2)–C(L1)	122(1)		
O(L1)–C(L2)–O(L2)	126(1)		
N(L1')–N(L1)–C(L1)	106.4(7)		

5 and 6. These complexes have dinuclear structures in which two Cr(III) ions are bridged by a pzdc. Each chromium is coordinated by a linear tetradentate diamine- N,N' -diacetate and N–O chelate of a pzdc ligand, producing an octahedral $\text{Cr}(\text{N})_3(\text{O})_3$ geometry. The bond distances and angles of pzdc ligand in **1** and **2** (Table 4) are almost the same as each other and those of the other pyrazole and/or triazole derivatives in some copper(II) complexes.¹⁴

For complex **1**, the geometrical configurations of the edda around Cr(1) and Cr(2) ions are *syn-cis* and *unsym-cis(mer)*, respectively, as supposed by the ^2H NMR spectra; corresponding to isomer C (Figure 3). The absolute configuration around a central Cr(III) ion is the same for Cr(1) and Cr(2) as in Figure 5, where only the $\Delta-\Delta^{15}$ enantiomer is illustrated. The absolute configurations of the two coordinated *sec*-amine N atoms in the edda of Cr(1) and Cr(2) are S,S and R,S^* , respectively; where S , R and S^* , R^* denote the chiralities of the N and N^* atoms in the out-of-plane (R) and in-plane (G) glycinate rings, respectively, with respect to the $\text{Cr}(\text{N})_3(\text{O})_1$ coordination plane as shown in Figure 2. The bond lengths and angles around Cr(1) and Cr(2) are rather deviated from regular octahedron as listed in Table 2. The geometry around Cr(1) is close to that of *sym-cis*- $[\text{Cr}(\text{edda})(\text{gly})]^{5-}$. Both of the diamine take a normal *gauche* conformation with the torsion angles of N–C–C–N being $+51.4(8)$ and $-54.0(8)^\circ$ for Cr(1) and Cr(2), respectively. The ethylenediamine conformations (δ or λ) in the edda are opposite to each other. The Cr(1)⋯Cr(2) distance is 4.473(3) Å.

As shown in Figure 5, there is an intramolecular hydrogen bond between the proton of the secondary amine nitrogen (N(1))

**Figure 4.** ^2H NMR spectrum of $[\text{Cr}_2(\text{edda-d}_4)_2(\mu\text{-pzdc})]^-$ in H_2O .**Figure 5.** Molecular structure of $\text{Na}[\text{Cr}_2(\text{edda})_2(\mu\text{-pzdc})]\cdot 5\text{H}_2\text{O}$ (**1**): The solid line shows the edda backbone for *sym*- and *unsym-cis* configuration around the Cr(1) (left) and Cr(2) (right) ions, respectively. The broken line refers to the $\text{H}(1)\cdots\text{O}(7)$ hydrogen bond.**Figure 6.** Molecular structure of $\text{Na}[\text{Cr}_2(\text{trdda})_2(\mu\text{-pzdc})]\cdot 3\text{H}_2\text{O}$ (**2**).

and the coordinated oxygen (O(7)) for complex **1**; $\text{N}(1)\cdots\text{O}(7) = 2.886$ Å and $\text{N}(1)\text{—H}\cdots\text{O}(7) = 166.67^\circ$. The torsion angle $\text{N}(1)\text{—Cr}(1)\cdots\text{Cr}(2)\text{—O}(7)$ is 40.75° . This large deformation may be caused by formation of the hydrogen bond between two planes. On the other hand, the small torsion angle of $\text{N}(\text{L}1)\text{—Cr}(1)\cdots\text{Cr}(2)\text{—N}(\text{L}2)$ (5.84°) indicates that the pzdc ligand is so rigid as to maintain the planar structure by coordination. The hydrogen bond together with the steric requirement between the chelate rings results in high stereoselectivity for only one

- (14) (a) Harlow, R. L.; Simonsen, S. H. *Acta Crystallogr.* **1974**, *B30*, 2505. (b) Kamiyuki, T.; Okawa, H.; Matsumoto, N.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1990**, 195. (c) Prins, R.; Birker, P. J. M. W. L.; Haasnoot, J. G.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.* **1985**, *24*, 4128. (d) Koomen-van Oudenniel, W. M. E.; de Graaff, R. A. G.; Haasnoot, J. G.; Prins, R.; Reedijk, J. *Inorg. Chem.* **1989**, *28*, 1128. (e) Nishida, Y.; Kida, S. *Inorg. Chem.* **1988**, *27*, 447.
- (15) For example: *Nomenclature of Inorganic Chemistry, Recommendations 1990*; Blackwell Scientific Publications: Oxford, England, p 182 (1990).

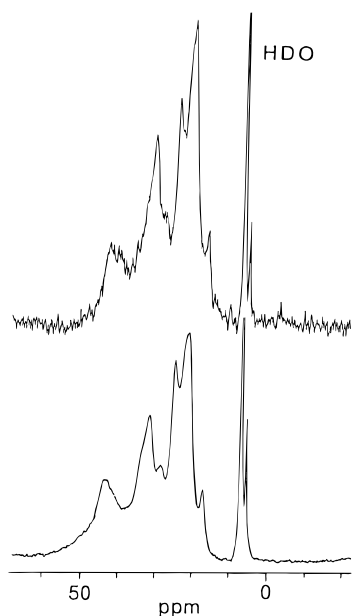


Figure 7. ^2H NMR spectra of $[\text{Cr}(\text{eddp-d}_4)(\text{pzdc})]^{2-}$ in H_2O : **3** (lower); **4** (upper).

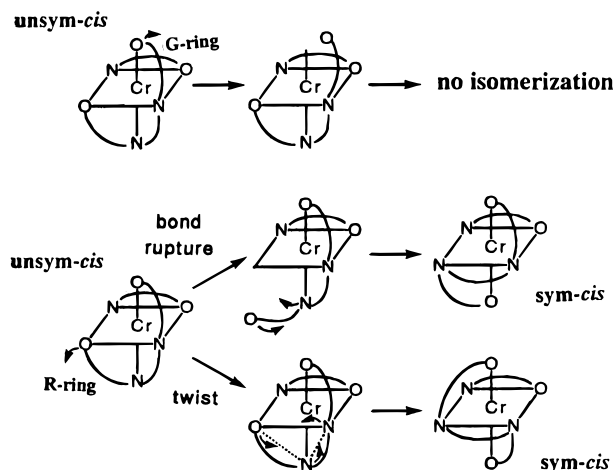
combination (C) among 12 possible isomers, exhibiting stereogenic coordination.¹⁶

Complex **2** has a {unsym-*cis*(mer)}–{unsym-*cis*(mer)} configuration with a 2-fold symmetry axis bisecting the pzdc molecular plane as shown in Figure 6, corresponding to isomer **G** in Figure 3. The absolute configuration of each Cr(III) ion is (*R,S*) and vice versa. The diamine ring takes a favored chair conformation in this complex. The bond distances and angles for the trdda ligand are almost the same as those of unsym-*cis*- $\text{Na}[\text{Cr}(\text{trdda})(\text{ox})]\cdot 3.5\text{H}_2\text{O}$ ¹⁷ and unsym-*cis*- $\text{Na}[\text{Cr}(\text{trdda})(\text{mal})]\cdot \text{H}_2\text{O}$ ¹⁸ as in Table 3. The $\text{Cr}\cdots\text{Cr}$ distance is 4.560(4) Å, being a little longer than that for the edda complex. The deformation in the complex **2** is smaller as a whole than in the complex **1**. The torsion angles $\text{O}(3)\text{---}\text{Cr}\cdots\text{Cr}^*\text{---}\text{O}(3)^*$ and $\text{N}(\text{L}1)\text{---}\text{Cr}\cdots\text{Cr}^*\text{---}\text{N}(\text{L}1)^*$ are 26.74 and 1.89°, respectively. The $\text{O}(3)\cdots\text{O}(3)^*$ distance in the complex **2** is 2.953 Å, which is close to the sum of the van der Waals radius of oxygen (1.4–1.52 Å). This van der Waals contact or steric congestion between the $\text{O}(3)\cdots\text{O}(3)^*$ atoms may result in a little inclination of the N_1O_3 coordination planes.

Among twelve possible geometrical isomers in Figure 3, the **C** and **G** seem to be favorable to form in view of the proximity between two N–H bonds or chelate rings of the ligands coordinated to each Cr(III) ion. In fact, these configurations were observed in the crystals obtained. From the examination of the structure of the complexes **1** and **2**, however, it is apparent that there are notable noncovalent intramolecular interactions between two Cr(III)–edda or –trdda units even in the **C** and **G** configurations. Accordingly, the subtle structural change or chelate ring size enlargement may lead to differing the stability in the isomers of this type of dinuclear complexes. These cases are encountered for the eddp complex as discussed below.

Characterization of Complexes 3 and 4. The column chromatographic behavior and elemental analyses show that the complexes **3** and **4** are mononuclear complexes, $[\text{Cr}(\text{eddp})(\text{pzdc})]^{2-}$. As shown in Figure 7, ^2H NMR spectra of

Scheme 1



two isomers of $[\text{Cr}(\text{eddp-d}_4)(\text{pzdc})]^{2-}$ are almost identical with each other. The observation of more than four signals suggests that these eddp complexes are two geometrical isomers of unsym-*cis* form probably corresponding to mer- and fac- $[\text{Cr}(\text{eddp})(\text{pzdc})]^{2-}$ and also that there may exist conformational isomers due to inversion in the ethylenediamine ring or the coordinated asymmetric nitrogen of the secondary amine as found for the unsym-*cis*- $[\text{Co}(\text{eddp})(\text{en})]^+$.¹⁹ Since the unsym-*cis* configuration of the eddp complex is more favorable than the sym-*cis* one,^{6,9} the preferential formation of the (unsym-*cis*)–(unsym-*cis*) dinuclear complex with pzdc failed to give the dinuclear complex, but yielded the mononuclear complex so far. Difficulty of dinuclear complex formation may result from severe noncovalent contact due to the closer proximity of the $\text{N}\cdots\text{O}$ or $\text{O}\cdots\text{O}$ atoms in the **C** or **G** isomers, since the six-membered propionato chelates in the eddp give larger N–Cr–O bite angles than the five-membered acetato ones in the edda or trdda ligand.

Inertness of Complex 1 in Solution. The unsym-*cis* Cr(III)–edda complexes are in general thermodynamically unstable in aqueous solution and so labile to isomerize to the sym-*cis* isomers relatively fast.^{3,4} Nevertheless, the unsym-*cis* configuration in the present dinuclear complex is stable and robust, since no UV–vis absorption and ^2H NMR spectral change was observed after allowing the aqueous solution to stand for 2 days at 40 °C. This stabilization or inertness of the unsym-*cis* moiety may result from the intramolecular hydrogen bond at the second coordination sphere. It is noted that the hydrogen bond fastens only the strain-free out-of-plane acetate arm (R-ring), but not the strained in-plane one (G-ring)²⁰ in the unsym-*cis* edda configuration, as shown in Figure 5. This fact gives a clue for the elucidation of the isomerization mechanism. If the Cr(III)–O(G-ring) bond ruptures in the unsym-*cis* isomer, isomerization occurs only when the O(G-ring) shifts to the position occupied by the coordinated oxygen of pzdc. In this case, the configurational change from unsym-*cis* to sym-*cis* may result in decomposition to mononuclear $[\text{Cr}(\text{edda})(\text{pzdc})]^{2-}$ and $[\text{Cr}(\text{edda})(\text{H}_2\text{O})_2]^+$ complexes or the formation of a sterically unstable (sym-*cis*)–(sym-*cis*) isomer with close contact between N–H's. Either case is not the finding. On the other hand, bond rupture between the Cr(III) and the O(R-ring) may cause

(16) Francyk, T. S.; Czerwinski, K. R.; Raymond, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 8138.

(17) Unpublished data: triclinic $P\bar{1}$, $a = 13.241(6)$ Å, $b = 16.010(6)$ Å, $c = 7.897(2)$ Å, $\alpha = 99.18(3)^\circ$, $\beta = 91.05(3)^\circ$, $\gamma = 78.78(3)^\circ$, $Z = 4$.

(18) Radanović, D. J.; Trifunović, S. R.; Grujić, S. A.; Maricondi, C.; Parvez, M.; Douglas, B. E. *Inorg. Chim. Acta* **1989**, *157*, 33.

(19) (a) Sakagami, N.; Yasui, T.; Kawaguchi, H.; Ama, T.; Kaizaki, S. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 680. (b) Kawaguchi, H.; Maruyama, N.; Ama, T.; Yasui, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 175.

(20) Radanović, D. J. *Coord. Chem. Rev.* **1984**, *54*, 159 and references therein.

isomerization easily by exchanging the positions between the *sec*-N atom and the O(R-ring) atom in two ways as shown in Scheme 1: metal–O(R-ring) bond rupture or the twist of three ligating atoms around the octahedral triangular faces. In either case, the fixation of the O(R-ring) atom with the hydrogen bond suppresses the isomerization of the unsym-*cis* configuration in complex **1**. This suggests that the geometrical isomerization for the edda Cr(III) complex is accounted for by the recently proposed bond rupture mechanism at the R-ring site for the edda–Co(III) complexes.²¹ Such a prohibition of the isomerization reaction due to the second sphere hydrogen bond

(21) Kawaguchi, H.; Uchiyama, N.; Ama, T.; Yasui, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3535.

formation with only one specific ligator is the first example to our knowledge.

Conclusion. The above experimental facts for the edda type complexes indicate that noncovalent interactions between the N–H's and/or chelate rings and O···O van der Waals contact governs the molecular recognition at each moiety and leads to stereoselective formation or stereognostic coordination in the dinuclear complex.

Supporting Information Available: Tables of all atomic coordinates, anisotropic thermal parameters, and all bond distances and angles (13 pages). Ordering information is given on any current masthead page.

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