

# Syntheses and Structures of Bridge and Chelate Isomers of Tetraplatinum(II) Cluster Complex with Diethyldithiophosphate Ion ( $\text{Et}_2\text{dtp}$ ) at In-Plane Sites, $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$ , and Their Mutual Isomerization via Cluster Core Rotation

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**Abstract:** A reaction of  $[\text{Pt}_4(\text{CH}_3\text{COO})_8]$  (**1**) with an excess of diethyldithiophosphate ( $\text{Et}_2\text{dtp}$ ) in  $\text{CH}_3\text{CN}$  affords a tetrasubstituted derivative,  $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$ , which is a mixture of two isomers. X-ray analyses of the isolated two isomers revealed that  $\text{Et}_2\text{dtp}$  ligands in both isomers are coordinated in the plane of the  $\text{Pt}_4$  cluster core, and that coordination mode of  $\text{Et}_2\text{dtp}$  is the chelate type in one isomer (**2**) whereas it is the bridge type in the other (**3**).  $^1\text{H}$  NMR studies showed that both **2** and **3** isomerize slowly in solution to give the same equilibrium mixture. The rate constants for the isomerization in  $\text{CDCl}_3$  at  $40^\circ\text{C}$  were  $k_1 = 1.2 \times 10^{-4} \text{ s}^{-1}$  (for the reaction from **2** to **3**) and  $k_2 = 1.5 \times 10^{-4} \text{ s}^{-1}$  (for the reaction from **3** to **2**), respectively. Both **2** and **3** undergo the isomerization also in acetonitrile with similar reaction rate, but the mechanism is different from that in chloroform. Activation entropy for the reaction starting from **2** to **3** was  $-9 \pm 9 \text{ J mol}^{-1} \text{ K}^{-1}$  in chloroform and  $-47 \pm 11 \text{ J mol}^{-1} \text{ K}^{-1}$  in acetonitrile. The small  $|\Delta S^\ddagger|$  value for the reaction in chloroform suggests that the isomerization proceeds without bond cleavage through an intermediate where three sulfur atoms from two  $\text{Et}_2\text{dtp}$ 's are coordinated to each platinum. That is, the isomerization in chloroform is caused by rotation of the  $\text{Pt}_4$  cluster core within an array of eight S atoms arranged circularly in a single plane. On the other hand, the isomerization in acetonitrile proceeds via a Pt–S bond cleaved intermediate possibly by the solvent assisted mechanism. All the kinetic parameters for the reactions in  $\text{CDCl}_3$  and  $\text{CD}_3\text{CN}$  are reported.

## Introduction

Octaacetatetetraplatinum(II)  $[\text{Pt}_4(\text{CH}_3\text{COO})_8]$  (**1**) is a well-known cluster complex of divalent platinum with Pt–Pt bonds and has unique structure<sup>1</sup> and reactivity.<sup>2–4</sup> The acetate ligands in **1** which are in the plane of the square-planar cluster core are labile, whereas the out-of-plane ligands are inert to substitution.<sup>2</sup> Tetrasubstituted derivatives with bidentate ligands (L) at in-plane sites,  $[\text{Pt}_4(\mu\text{-CH}_3\text{COO})_4(\text{L})_4]^{n+}$ , are classified into two types by the coordination mode of L. One is the bridge type as in **1** and the other is the chelate type (Chart 1).

Bidentate ligands such as carboxylate,<sup>1,2</sup> acetamidate,<sup>5</sup> and acetylacetonate-*O,C*<sup>6</sup> make the bridge type complexes, whereas ethylenediamine,<sup>7</sup> picolinate,<sup>7</sup> or amino acidates<sup>8</sup> afford the

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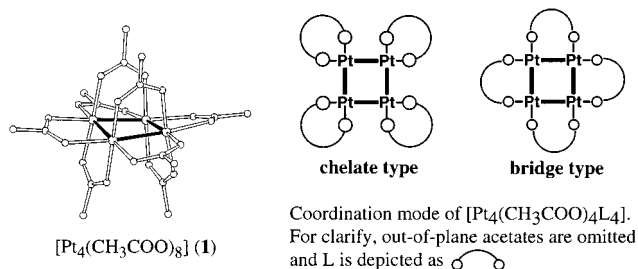
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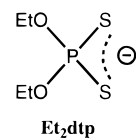
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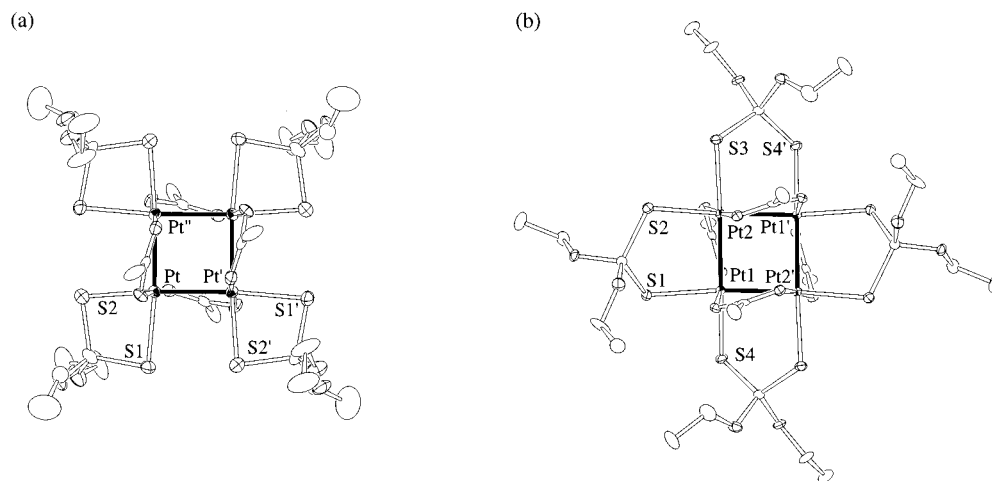
Chart 1



chelate type structure. Which type of the structure is formed depends likely on the bite distance of L. A ligand with a shorter bite distance tends to give the bridge type cluster and those with longer bite distances the chelate type. In this study, we used diethyldithiophosphate ion ( $\text{Et}_2\text{dtp}$ ) as L, which has an



intermediate bite distance. We report here that both the bridge and chelate isomers of  $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$  are isolated, that each isomer undergoes isomerization in solution to give an equilibrium mixture of two isomers, and that the isomerization in chloroform proceeds by the unique “cluster core rotation”



**Figure 1.** ORTEP drawings of two isomers: (a) *chelate*-[Pt<sub>4</sub>(CH<sub>3</sub>COO)<sub>4</sub>(Et<sub>2</sub>dtp)<sub>4</sub>] (**2**) in 2·CCl<sub>4</sub>·<sup>4</sup>/<sub>3</sub>CHCl<sub>3</sub> and (b) *bridge*-[Pt<sub>4</sub>(CH<sub>3</sub>COO)<sub>4</sub>(Et<sub>2</sub>dtp)<sub>4</sub>] (**3**). Atoms are drawn at the 30% probability level.

**Table 1.** Crystallographic Data and X-ray Experimental Conditions for 2·CCl<sub>4</sub>·<sup>4</sup>/<sub>3</sub>CHCl<sub>3</sub> and **3**

compound	2·CCl <sub>4</sub> · <sup>4</sup> / <sub>3</sub> CHCl <sub>3</sub>	<b>3</b>
empirical formula	Pt <sub>4</sub> C <sub>26.33</sub> H <sub>53.33</sub> O <sub>28</sub> S <sub>8</sub> P <sub>4</sub> Cl <sub>8</sub>	Pt <sub>4</sub> C <sub>24</sub> H <sub>52</sub> O <sub>16</sub> S <sub>8</sub> P <sub>4</sub>
formula weight	2262.34	1757.40
crystal system	cubic	orthorhombic
space group	<i>I</i> 43 <i>d</i> (No. 220)	<i>Pbcn</i> (No. 60)
<i>a</i> , Å	26.388(4)	12.794(8)
<i>b</i> , Å		24.990(3)
<i>c</i> , Å		14.927(3)
<i>V</i> , Å <sup>3</sup>	18374(1)	4772(2)
<i>Z</i> value	12	4
<i>D</i> <sub>calc</sub> , g/cm <sup>3</sup>	2.453	2.446
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	9.87	12.18
temp, K	183	183
trans. factors	0.9010–0.9781	0.6787–0.9987
no. of residuals: <i>R</i> ; <i>R</i> <sub>w</sub>	0.046; 0.044	0.034; 0.037
GOF indicator	1.27	1.48

mechanism, whereas that in acetonitrile proceeds by the solvent assisted mechanism.

## Results and Discussion

**Syntheses and Structures.** [Pt<sub>4</sub>(CH<sub>3</sub>COO)<sub>4</sub>(Et<sub>2</sub>dtp)<sub>4</sub>] was easily obtained from a reaction of **1** with an excess of Et<sub>2</sub>dtpH in CH<sub>3</sub>CN. The product of the synthetic reaction was a mixture of two isomers. It was impossible to separate the mixture into pure compounds by silica gel column chromatography, because each component of the mixture isomerizes to give an equilibrium mixture (vide infra). *chelate*-[Pt<sub>4</sub>(CH<sub>3</sub>COO)<sub>4</sub>(Et<sub>2</sub>dtp)<sub>4</sub>] (**2**) and *bridge*-[Pt<sub>4</sub>(CH<sub>3</sub>COO)<sub>4</sub>(Et<sub>2</sub>dtp)<sub>4</sub>] (**3**) were separated into pure forms with use of the difference in solubilities in chloroform and tetrachloromethane.

Single-crystal X-ray analyses of the isolated two products (Table 1) showed that the less soluble isomer in CCl<sub>4</sub> was the chelate type, *chelate*-[Pt<sub>4</sub>(CH<sub>3</sub>COO)<sub>4</sub>(Et<sub>2</sub>dtp)<sub>4</sub>] (**2**), and the more soluble isomer was the bridge type, *bridge*-[Pt<sub>4</sub>(CH<sub>3</sub>COO)<sub>4</sub>(Et<sub>2</sub>dtp)<sub>4</sub>] (**3**) (Figure 1). The cluster core structures in **2** and **3** are essentially the same as that in **1**, but slight changes are seen (Table 2). The Pt–Pt distances of 2.573(1) Å in **2** and 2.583(1) and 2.584(1) Å in **3** are somewhat longer than that in **1** (2.492(1)–2.501(1) Å).<sup>1</sup> This may be due to the trans influence of the sulfur donor. The squares of the cluster core in **2** and **3** are slightly distorted from the square-plane toward tetrahedron: deviation from the least-squares plane defined by four platinum atoms is as much as 0.211(1) Å in **2** and 0.280(1) Å in **3**, while that in **1** is less than 0.116(1) Å. The Pt–S distances of

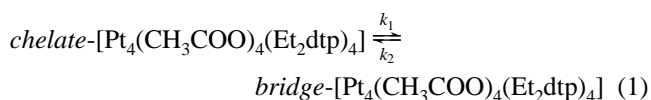
**Table 2.** Selected Bond Distances and Angles for 2·CCl<sub>4</sub>·<sup>4</sup>/<sub>3</sub>CHCl<sub>3</sub> and **3**<sup>a</sup>

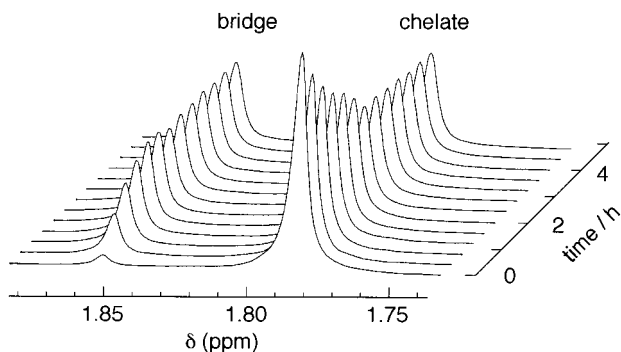
	2·CCl <sub>4</sub> · <sup>4</sup> / <sub>3</sub> CHCl <sub>3</sub>	<b>3</b>	
		bond distance (Å)	
Pt–Pt'	2.573(1)	Pt(1)–Pt(2)	2.583(1)
		Pt(1)–Pt(2')	2.5836(7)
Pt–S(1)	2.494(7)	Pt(1)–S(1)	2.461(3)
Pt–S(2)	2.482(7)	Pt(1)–S(4)	2.492(3)
		Pt(2)–S(2)	2.500(3)
		Pt(2)–S(3)	2.485(3)
S(1)···S(2)	3.20(1)	S(1)···S(2)	3.375(4)
S(1)···S(2')	3.18(1)	S(2)···S(3)	3.187(4)
		S(3)···S(4')	3.372(4)
		S(1)···S(4)	3.293(4)
		bond angle (deg)	
Pt'–Pt–Pt''	88.46(1)	Pt(2)–Pt(1)–Pt(2)	88.79(4)
		Pt(1)–Pt(2)–Pt(1)	85.82(3)
S(1)–Pt–S(2)	80.0(2)	S(1)–Pt(1)–S(4)	83.36(9)
		S(2)–Pt(2)–S(3)	79.47(9)
Pt'–Pt–S(1)	95.5(2)	Pt(2)–Pt(1)–S(1)	95.17(7)
Pt''–Pt–S(2)	96.4(2)	Pt(2)–Pt(1)–S(4)	93.79(7)
		Pt(1)–Pt(2)–S(2)	98.79(6)
		Pt(1)–Pt(2)–S(3)	96.12(7)

<sup>a</sup> Key to symmetry operation for 2·CCl<sub>4</sub>·<sup>4</sup>/<sub>3</sub>CHCl<sub>3</sub>: (') = <sup>5</sup>/<sub>4</sub> – *z*, –<sup>1</sup>/<sub>4</sub> – *y*, <sup>5</sup>/<sub>4</sub> – *x*; (") = <sup>1</sup>/<sub>4</sub> – *z*, –<sup>1</sup>/<sub>4</sub> – *y*, –<sup>1</sup>/<sub>4</sub> + *x*; and for **3**: (') = –*x*, *y*, <sup>1</sup>/<sub>2</sub> – *z*.

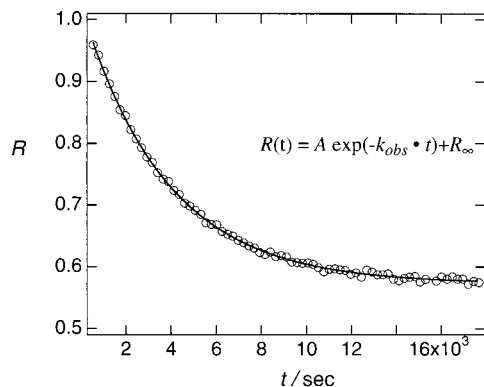
2.494(7) and 2.482(7) Å in **2** and 2.461(3)–2.500(3) Å in **3** are longer than that of mononuclear platinum(II) complex of dithiophosphate, [Pt(Pr<sub>2</sub>dtp)<sub>2</sub>] (2.33–2.34 Å).<sup>9</sup> This may be a result of the trans influence of the Pt–Pt bond as is observed in other tetraplatinum complexes.<sup>1,2,7</sup> It is noteworthy that intra- and interligand S···S distances are similar to each other within each isomer and also between the two isomers (3.20(1) and 3.18(1) Å for **2**, and 3.375(4), 3.372(4) Å and 3.187(4), 3.293(4) Å for **3**, respectively). The resemblance of the S···S contacts appears to be related to the ease with which the isomerization takes place (vide infra).

**Isomerization of **2** and **3** to an Equilibrium Mixture.** Both **2** and **3** isomerize slowly in chloroform to give the same equilibrium mixture.





**Figure 2.** Time course of  $^1\text{H}$  NMR spectra around the acetate methyl region of **2** in  $\text{CDCl}_3$  at  $40^\circ\text{C}$ .



**Figure 3.** Change in a molar fraction of **2**,  $R = \{[2]/([2] + [3])\}$ , during the reaction as a function of time in  $\text{CDCl}_3$  at  $40^\circ\text{C}$ .

**Table 3.** Kinetic Parameters for Chelate/Bridge Isomerization of Eq 1<sup>a</sup>

solvent	$k/\text{s}^{-1}$ (at $40^\circ\text{C}$ )	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1}\text{K}^{-1}$
$\text{CDCl}_3$	$k_1$	$1.2 \times 10^{-4}$	$98 \pm 3$
	$k_2$	$1.5 \times 10^{-4}$	$89 \pm 3$
$\text{CD}_3\text{CN}$	$k_1$	$1.4 \times 10^{-4}$	$85 \pm 4$
	$k_2$	$3.4 \times 10^{-4}$	$74 \pm 2$

<sup>a</sup> Thermodynamic parameters for the reaction of eq 1:  $\Delta H(2 \rightarrow 3) = 9 \pm 1 \text{ kJ mol}^{-1}$  and  $\Delta S(2 \rightarrow 3) = 25 \pm 4 \text{ J mol}^{-1}\text{K}^{-1}$  in  $\text{CDCl}_3$ ;  $\Delta H(2 \rightarrow 3) = 11 \pm 3 \text{ kJ mol}^{-1}$  and  $\Delta S(2 \rightarrow 3) = 28 \pm 8 \text{ J mol}^{-1}\text{K}^{-1}$  in  $\text{CD}_3\text{CN}$ .

Figure 2 shows the time course of the  $^1\text{H}$  NMR spectrum around the acetate methyl region of **2** in  $\text{CDCl}_3$  at  $40^\circ\text{C}$ . The intensity of the out-of-plane acetate (1.78 ppm) decreases with time, and concomitantly the signal of that in **3** (1.85 ppm) appears and increases. Change in the molar fraction of **2**,  $R = \{[2]/([2] + [3])\}$ , during the reaction is shown as a function of time in Figure 3. The  $R$  value decreases exponentially and reached an equilibrium within a few hours under the experimental conditions. A least-squares fitting nicely agrees with the data giving the apparent first-order rate constant  $k_{\text{obs}} = 2.7 \times 10^{-4} \text{ s}^{-1}$  and  $R$  at equilibrium,  $R_\infty = 0.56$ . From these values, the equilibrium constant  $K = (1 - R_\infty)/R_\infty = 0.79$  was obtained. Since  $k_{\text{obs}} = k_1 + k_2$  and  $K = k_1/k_2$ , the rate constants  $k_1 = 1.2 \times 10^{-4} \text{ s}^{-1}$  and  $k_2 = 1.5 \times 10^{-4} \text{ s}^{-1}$  were obtained. The opposite reaction starting from **3** in  $\text{CDCl}_3$  gave the same  $K$ ,  $k_1$ , and  $k_2$  within experimental errors. The same experiments were carried out at five temperatures from  $30$  to  $50^\circ\text{C}$ , which gave activation parameters for  $k_1$  and  $k_2$  (Table 3).

The isomerization of eq 1 proceeded also in acetonitrile with similar reaction rates. Kinetic studies were carried out in a similar way by means of  $^1\text{H}$  NMR in  $\text{CD}_3\text{CN}$ . The apparent first-order rate constant was nearly twice as large as that in chloroform and the equilibrium constant was slightly smaller

than that in chloroform. These gave the rate constants  $k_1 = 1.4 \times 10^{-4} \text{ s}^{-1}$  and  $k_2 = 3.4 \times 10^{-4} \text{ s}^{-1}$  at  $40^\circ\text{C}$ . Activation parameters in acetonitrile were also obtained from temperature-dependence study (Table 3).

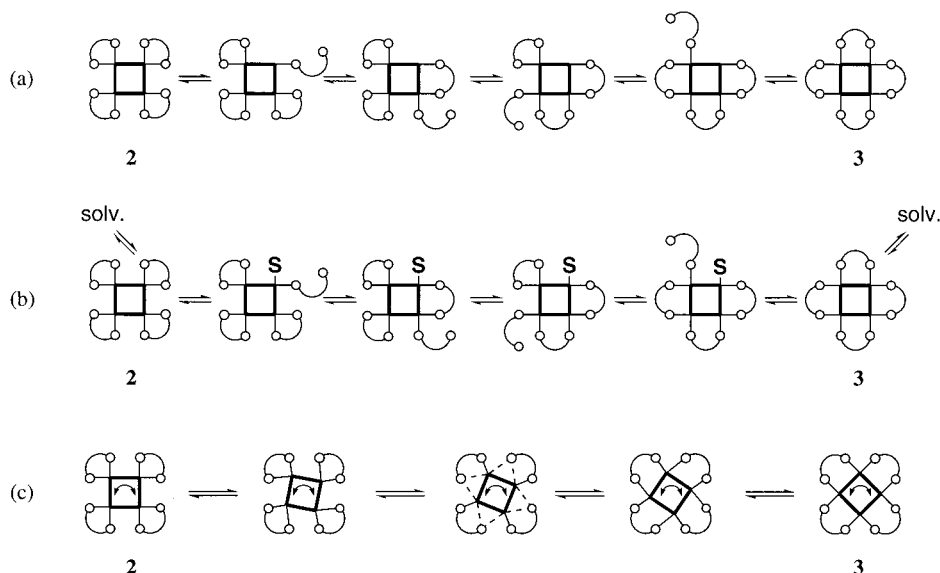
**Mechanism of the Isomerization Reaction.** For the chelate/bridge interconversion, three mechanisms shown in Figure 4 would be possible. Mechanism a is successive ligand migration through intermediates containing the unidentate  $\text{Et}_2\text{dtp}$  ligand, and the solvent molecule is not involved in the reaction. Mechanism b is of the solvent-assisted type, in which successive ligand migration is accompanied by coordination of the solvent molecule to the  $\text{Pt}_4$  core. In concerted mechanism c, the reaction proceeds through an intermediate in which three sulfur atoms from two  $\text{Et}_2\text{dtp}$  ligands are coordinated simultaneously to each platinum. By which mechanism the chelate/bridge isomerization of  $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$  proceeds is distinguishable by the sign and magnitude of an activation entropy of the reaction  $\Delta S^\ddagger$ . It should be positive for mechanism a, whereas negative for mechanism b, taking into account entropy changes for the formation of unidentate  $\text{Et}_2\text{dtp}$  species and coordination of the solvent molecule. For mechanism c,  $|\Delta S^\ddagger|$  is expected to be much smaller than those for mechanisms a and b, since the process in this mechanism is mainly the rotation of the  $\text{Pt}_4$  cluster core.

In actual fact, a striking difference in  $\Delta S^\ddagger_1$  was found between the reactions in chloroform and acetonitrile (Table 3). It was  $-9 \pm 9 \text{ J mol}^{-1}\text{K}^{-1}$  in  $\text{CDCl}_3$  and  $-47 \pm 11 \text{ J mol}^{-1}\text{K}^{-1}$  in  $\text{CD}_3\text{CN}$ . This suggests strongly that the mechanism of the isomerization is different in these solvents. The very small  $|\Delta S^\ddagger_1|$  in  $\text{CDCl}_3$  is consistent with mechanism c, where the isomerization proceeds without Pt–S bond cleavage. Note that  $|\Delta S^\ddagger_2|$ , which is not so small as  $\Delta S^\ddagger_1$ , contains a contribution from the entropy change of the reaction:  $\Delta S^\ddagger_2 = \Delta S^\ddagger_1 - \Delta S(2 \rightarrow 3)$ . On the other hand, the relatively large negative value of  $\Delta S^\ddagger_1$  for the reaction in  $\text{CD}_3\text{CN}$  shows that the isomerization proceeds by the solvent-assisted mechanism b.

To confirm further the reaction mechanism in  $\text{CDCl}_3$ , kinetic measurements for the isomerization from **2** to **3** were carried out at  $35^\circ\text{C}$  in  $\text{CDCl}_3$  solution containing a small amount of water added on purpose. The concentration of water was varied from 0 to 80 mM. Irrespective of the concentration of water, values of  $k_{\text{obs}}$  and  $R_\infty$  were constant within experimental errors, respectively (see Supporting Information). This fact suggests that the mechanism is not of the type promoted by contaminated water. The  $\text{Pt}_4$  cluster core is surrounded by eight S atoms circularly in a single plane, and the  $\text{S}_8$  ring is close to a regular octagon as shown by X-ray structures of **2** and **3** (vide ante). Simultaneous coordination of three S atoms from two  $\text{Et}_2\text{dtp}$ 's to each Pt, giving three approximately equivalent Pt–S bonds, is possible only when eight S atoms form a regular octagon. Such circumstances are consistent with mechanism c. The highly symmetric arrangement of S atoms facilitates the cluster core rotation that leads to the transformation of the bridge mode of  $\text{Et}_2\text{dtp}$  into the chelate mode, or vice versa. The rotational motion of the cluster core may be taken as “molecular bearing”.

We have isolated and structurally characterized both *chelate*- and *bridge*- $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$  ( $\text{Et}_2\text{dtp}$  = diethyldithiocarbamate ion),<sup>10</sup> in which the  $\text{Pt}_4$  cluster core is surrounded by eight S atoms similarly to **2** and **3**. Both *chelate*- and *bridge*- $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$ , however, do not undergo isomerization at all in chloroform. An arrangement of eight S atoms

(10) Yamaguchi, T.; Saito, H.; Ito, T. *The 1995 International Chemical Congress of Pacific Basin Societies*; Honolulu, December 1995; Abst. INOR 0094. Details will be reported elsewhere.



**Figure 4.** Three mechanisms for the bridge/chelate isomerization of  $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$ . The square shown with thick lines denotes the  $\text{Pt}_4$  cluster core, and out-of-plane acetates are omitted for clarity.  $\circ$   $\circ$  represents  $\text{Et}_2\text{dtp}$  ligand.

around the  $\text{Pt}_4$  core in these compounds deviates largely from the regular octagon, with intra- and interligand  $\text{S}\cdots\text{S}$  distances being respectively 2.904(4) and 3.424(4) Å in the chelate form and 3.01(1) and 3.26(1) Å in the bridge form. Irregular  $\text{S}_8$  arrangement in  $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$  may be responsible for the inactive isomerization.

## Experimental Section

**Apparatus.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{195}\text{Pt}$  NMR spectra were recorded on a JEOL GSX-270 FT-NMR spectrometer at 270, 67.9, and 58.0 MHz, respectively. The chemical shifts of  $^{195}\text{Pt}$  NMR were referenced to a  $\text{D}_2\text{O}$  solution of  $\text{K}_2\text{PtCl}_4$  using the high-frequency positive-shift sign convention.

**Kinetic Measurements.** Typically 10 mg of **2** (or **3**) was dissolved in 0.85 mL of deuterated solvent (ca 6.7 mM). As soon as a sample solution reaches the desired temperature in the spectrometer,  $^1\text{H}$  NMR spectra of the solution were recorded at 1–7 min intervals. Concentration of water in  $\text{CDCl}_3$  was determined by relative integrated intensities of  $^1\text{H}$  NMR signals due to water and  $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$ .

**Synthesis of chelate- $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$  (**2**).** To an acetonitrile solution of  $[\text{Pt}_4(\text{CH}_3\text{COO})_8]$  (**1**) (61 mg) was added 0.16 mL of diethyldithiophosphate. After 30 min, the color of the solution turned dark brown and the solution was evaporated to dryness. The residue was dissolved in tetrachloromethane/dichloromethane (1:1) and charged on a silica gel column (Wakogel CF-40). The main dark brown fraction eluted by dichloromethane/acetonitrile (9:1) was evaporated to dryness. This residue was a mixture of the chelate (**2**) and the bridge isomer (**3**). It was impossible to separate the mixture into pure compounds by silica gel column chromatography because of the isomerization (see text).

Pure chelate- $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$  (**2**) was isolated in the following way. The isomer mixture was dissolved in chloroform and to this solution was added 1/3 vol of tetrachloromethane. Chloroform in the solution was slowly evaporated in a refrigerator for a few days to give black crystals of chelate- $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]\cdot\text{CCL}_4\cdot\frac{4}{3}\text{CHCl}_3$  ( $2\cdot\text{CCL}_4\cdot\frac{4}{3}\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$  1.38 (t, 12H,  $\text{Et}_2\text{dtp-CH}_3$ ), 1.78 (s, 12H,  $\text{OAc-CH}_3$ ), 4.20 (m, 8H,  $\text{Et}_2\text{dtp-CH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$  15.92 ( $\text{Et}_2\text{dtp-CH}_3$ ), 22.26 ( $\text{OAc-CH}_3$ ), 64.27 ( $\text{Et}_2\text{dtp-CH}_2$ );  $^{195}\text{Pt}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$  693.

**Synthesis of bridge- $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$  (**3**).** The above isomer mixture was suspended in tetrachloromethane, insoluble materials were filtered off, and the filtrate was evaporated at low temperature. The residue was dissolved in a small amount of tetrachloromethane and the solution was layered with hexane and kept in a refrigerator for a few days. Black prismatic crystals of bridge- $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$

(**3**) were formed and collected by filtration.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$  1.38 (t, 12H,  $\text{Et}_2\text{dtp-CH}_3$ ), 1.85 (s, 12H,  $\text{OAc-CH}_3$ ), 4.20 (m, 8H,  $\text{Et}_2\text{dtp-CH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$  15.92 ( $\text{Et}_2\text{dtp-CH}_3$ ), 21.68 ( $\text{OAc-CH}_3$ ), 63.44 ( $\text{Et}_2\text{dtp-CH}_2$ );  $^{195}\text{Pt}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$  329.

**X-ray Data Collection and Structure Determination.** A suitable crystal coated with epoxy glue was attached to a glass fiber and mounted on a Rigaku AFC 7S four-circle diffractometer. The unit cell parameters were obtained by a least-squares refinement of the angular settings of 25 high-angle ( $22.5^\circ < 2\theta < 30.0^\circ$ ) reflections. Crystallographic and structural determination data are listed in Tables 1 and S1. Intensity data in the range  $3 < 2\theta < 55^\circ$  were collected by using a  $2\theta-\omega$  scan and at a scanning rate of  $4.0 \text{ deg min}^{-1}$ . The intensities of three standard reflections did not vary significantly throughout the data collection. Lorentz, polarization, and absorption correction ( $\psi$ -scan) were applied to the intensity data.

All calculations were performed using the teXsan<sup>11</sup> crystallographic software package. Atomic positional and anisotropic thermal parameters and interatomic distances and bond angles are given in Tables S2–S9.

**chelate- $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]\cdot\text{CCL}_4\cdot\frac{4}{3}\text{CHCl}_3$  ( $2\cdot\text{CCL}_4\cdot\frac{4}{3}\text{CHCl}_3$ ).** A black crystal ( $0.30 \times 0.25 \times 0.25 \text{ mm}^3$ ) was used for data collection. A total of 1776 independent reflections were measured at 183 K. The structure was solved by the automatic Patterson analysis method (DIRDIF92 PATTY<sup>12</sup>) and successive difference Fourier synthesis and refined by the full-matrix least-squares method. Anisotropic temperature factors were applied to all non-hydrogen atoms. Three chlorine atoms of solvate chloroform were disordered around the crystallographic 3-fold axis. The final refinement gave  $R = 0.046$  and  $R_w = 0.044$  for 1148 independent reflections having  $|I_o| > 3\sigma(I_o)$  and 158 independent parameters.

**bridge- $[\text{Pt}_4(\text{CH}_3\text{COO})_4(\text{Et}_2\text{dtp})_4]$  (**3**).** A black crystal ( $0.23 \times 0.20 \times 0.15 \text{ mm}^3$ ) was used for data collection. A total of 5507 independent reflections were measured at 183 K. The structure was solved by the automatic Patterson method (DIRDIF92 PATTY<sup>12</sup>) and successive difference Fourier synthesis and refined by the full-matrix least-squares method. Anisotropic temperature factors were applied to all non-hydrogen atoms. The final refinement gave  $R = 0.034$  and  $R_w = 0.037$  for 4052 independent reflections having  $|I_o| > 3\sigma(I_o)$  and 254 independent parameters.

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**Supporting Information Available:** Tables of crystallographic data, experimental conditions, atomic positional and thermal parameters, interatomic distances and bond angles,

Eyring plot, and effect of water upon the kinetic data in chloroform (PDF). An X-ray crystallographic file (CIF). These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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