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^{195}Pt NMR of Tetranuclear Platinum(II) Cluster Complexes That Have Chemically Nonequivalent Nuclei: [$Pt_4(CH_3COO)_7(CH_3CONH)$] and [$Pt_4(CH_3COO)_5(CH_3CONH)_3$]

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Introduction

^{195}Pt NMR is a powerful tool for the study of platinum cluster complexes with Pt–Pt bond(s).[1] ^{195}Pt NMR spectra for such compounds, however, are in general complicated because of the presence of isotopomers (natural abundance of ^{195}Pt = 33.8%) and large Pt–Pt coupling constants. Furthermore, when a coupling constant is large relative to the chemical shift difference, a second-order pattern is observed. Because of the presence of isotopomers, ^{195}Pt NMR spectra for such species are the result of the summation of the resonances for the isotopomers. Therefore, useful information such as spectral assignments, connectivity of the nuclei, or coupling constants between interacting nuclei can be derived, giving a successful analysis. In this paper, we wish to report such an example, the ^{195}Pt NMR spectra of [$Pt_4(CH_3COO)_{8-n}(CH_3CONH)_n$] (*n* = 1 (**2**), 3 (**3**)), along with those of [$Pt_4(CH_3COO)_8$] (**1**)[2] and [$Pt_4(CH_3COO)_4(CH_3CONH)_4$] (**4**). The structures of compounds **1–4** are shown schematically in Figure 1.[3–5] The four platinum nuclei in **2** and **3** are chemically nonequivalent, while those in **1** and **4** are equivalent. Note that, when we use the term "isotopomer" in this paper, platinum isotopes other than ^{195}Pt are regarded as single species since they have no nuclear spin.

Results and Discussion

Figures 2a and 3a show ^{195}Pt NMR spectra of [$Pt_4(CH_3COO)_7(CH_3CONH)$] (**2**) and [$Pt_4(CH_3COO)_5(CH_3CONH)_3$] (**3**), respectively, in CD_3CN. Corresponding to the chemical nonequivalence of the platinum nuclei, compounds **2** and **3** show very complicated spectra. On the other hand, compounds **1** and **4** exhibit only singlet peaks at −579 and −677 ppm, respectively. There are 16 possible isotopomers for the tetranuclear cluster complex with nonequivalent nuclei, which are classified into six types, a–f, as shown in Figure 4 along with their natural abundances. Isotopomer a has no ^{195}Pt nucleus and shows no ^{195}Pt NMR resonance. Isotopomers of types e and f have three and four mutually coupled ^{195}Pt nuclei, respectively, and they should show very complicated spectra. Their signal intensities, however, must be very weak because of the combination of the low population of the isotopomers and the spread of the total intensity. In fact, many very weak peaks possibly ascribed to these species have been actually observed (Figures 2a and 3a). We analyzed the spectra by taking into account resonances due to isotopomers of types b–d, signal intensities of which would be relatively strong. Each of four isotopomers of type b shows a singlet peak. In the following discussion we call these four singlets main peaks. In the type c isotopomers, there are two directly bonded ^{195}Pt nuclei and the coupling constants between them ($^1J_{Pt-Pt}$) should be large relative to a chemical shift difference. Therefore four isotopomers of type c should show four AB type signals. In the case of type d isotopomers, two ^{195}Pt nuclei are located at diagonally opposite sides in the square planar cluster core and the coupling constants $^2J_{Pt-Pt}$ should be relatively small. It is expected, therefore, that each ^{195}Pt nucleus within type d isotopomers will show a doublet as a satellite of its main peak.

Assuming the above discussion, it follows that ^{195}Pt NMR spectra for compounds **2** and **3** should consist of four main singlets accompanied by doublet satellites and four AB patterns, in addition to many very weak peaks. In actual fact, such spectral patterns can be seen in Figures 2a and 3a. First, we will discuss the spectrum of **2**. It should be noted that the singlet with the highest intensity at −579 ppm (marked with *) is due to [$Pt_4(CH_3COO)_8$] (**1**)[5] (see Experimental Section). The four main singlet peaks are easily identified from their high integrated intensities at −719 (Pt_a), −673 (Pt_b), −523 (Pt_c), and −456 (Pt_d) ppm. And the satellite peaks due to type d isotopomers are partly observed ($^2J_{ad}$ = 180 and $^2J_{bc}$ = 110 Hz).[6] The four AB type signals were assigned as shown in Figure 2a from the relationship between chemical shifts and coupling constants.[7] The four coupling constants obtained from the four AB patterns (J_{ab} = 5920, J_{ac} = 5450, J_{bd} = 7130, and J_{cd} = 7700 Hz) provide information regarding the connectivity of the four nuclei, since the compound is cyclic:

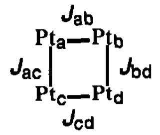

Figure 2b shows a simulated spectrum for compound **2**, which was calculated[8] by use of the observed chemical shifts and coupling constants for the isotopomers of types b–f. The calculated

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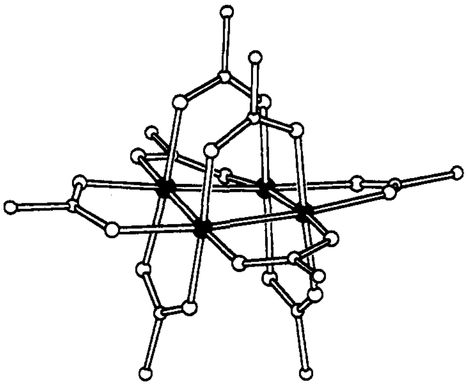
[1] (a) Pregosi, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247–291. (b) Mason, J. Ed. *Multinuclear NMR*; Plenum Press: New York, 1987.

[2] (a) Carrondo, M. A. A. F. d. C. T.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1976**, 410–411. (b) *Acta Crystallogr., Sect. B* **1978**, *B34*, 1857–1862. (c) *Ibid.* **1978**, *B34*, 3576–3578.

[3] The structural assignments for **2** and **3** in Figure 1, that is, the facts that the acetamide ligands in **2** and **3** are in the plane of the cluster core and that the three acetamide ligands in **3** are arranged as shown in Figure 1, are based on their ^{1}H NMR (Experimental Section), ^{195}Pt NMR in the text, and the following evidence. [$Pt_4(CH_3COO)_8$] (**1**) has the schematic structure[2]



It has been shown that the four acetate ligands in **1** and the four acetamide ligands in **4**, which are in the plane of the square-planar platinum cluster core, are labile, whereas the out-of-plane acetate ligands are inert to substitution.[5] The present compound **3** was derived from **4** by in-plane ligand substitution as described in the Experimental Section. It has been also shown that the strong catalytic activity of **1** toward the hydrolysis of acetonitrile is associated with the lability of the in-plane coordination sites. And X-ray analysis of [$Pt_4(CH_3COO)_6(CH_3CONH)_2$], which was obtained from silica gel chromatography of the reaction mixture for the synthesis of **2** (Experimental Section), shows that the acetamide ligands are in the plane of the cluster core with (N,O) bridging modes (see ref 4 and: Yamaguchi, T.; Sasaki, Y.; Ito, T. *Abstracts of Papers*, 56th National Meeting of the Chemical Society of Japan, Tokyo, April 1988; No. 3VA31).

[4] Yamaguchi, T. Ph.D. Dissertation, Tohoku University, Sendai, Japan, 1990.

[5] Yamaguchi, T.; Sasaki, Y.; Nagasawa, A.; Ito, T.; Koga, N.; Morokuma, K. *Inorg. Chem.* **1989**, *28*, 4311–4312.

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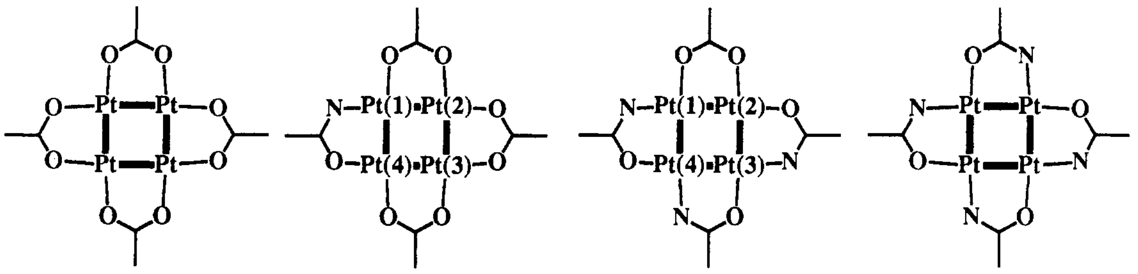

1 (n = 0) **2** (n = 1) **3** (n = 3) **4** (n = 4)

Figure 1. Structures of $[Pt_4(CH_3COO)_{8-n}(CH_3CONH)_n]$ (**1** (n = 0), **2** (n = 1), **3** (n = 3), **4** (n = 4)). Only the cluster cores and the ligands in the cluster planes are shown along with the numbering. See ref 3 for the overall structure of **1**.

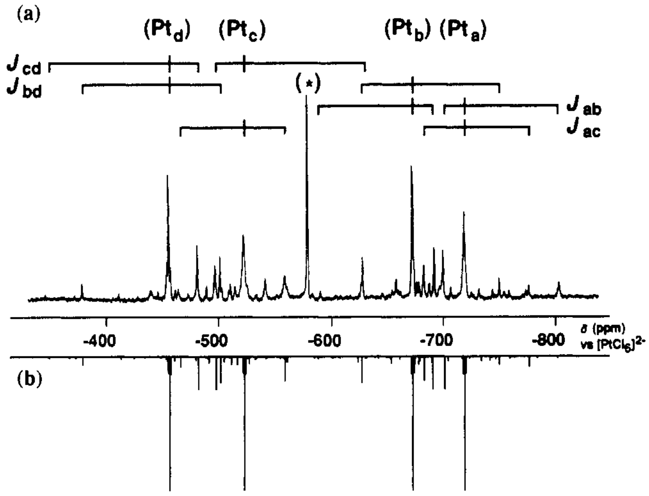

Figure 2. (a) ^{195}Pt NMR spectrum of $[Pt_4(CH_3COO)_7(CH_3CONH)]$ (**2**) in CD_3CN. The asterisked peak at −579 ppm is due to $[Pt_4(CH_3COO)_8]$ (**1**) (see text). (b) Calculated spectrum.

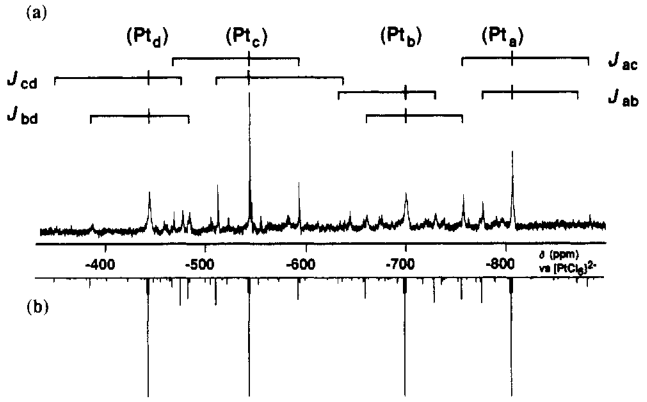

Figure 3. (a) ^{195}Pt NMR spectrum of $[Pt_4(CH_3COO)_5(CH_3CONH)_3]$ (**3**) in CD_3CN. (b) Calculated spectrum.

spectrum reproduces four main singlets, four AB type signals, and some weak signals. The fairly good agreement between observed and simulated spectra indicates the validity of the analysis. Observed weak lines which are not accounted for by the simulation should be due to impurities, possibly disubstituted derivatives.

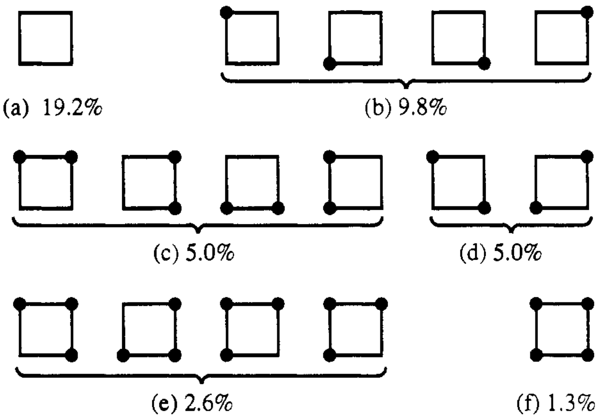

Figure 4. Sixteen possible isotopomers and their classification into six types (a–f) for a tetranuclear cluster complex with chemically nonequivalent ^{195}Pt nuclei. A square denotes a tetranuclear cluster core, and a filled circle shows the position of ^{195}Pt nucleus. The percentages are the natural abundances of the isotopomers.

The analysis so far described, however, cannot identify which peak corresponds to which platinum nucleus of **2** in Figure 1. When the signal shapes for the four main singlets are compared, only the signal at −523 ppm is broad relative to the other three. The broadening appears to arise from the coordination of the nitrogen of acetamide, since ^{14}N is a quadrapolar nucleus. On this basis, the main singlet peak at −523 ppm was assigned to Pt(1) of **2** in Figure 1. We need further information on whether the connecting mode is clockwise or anticlockwise in order to assign the remaining three signals. It is difficult to form a definite conclusion. However, we propose tentative assignments, again on the basis of the signal shapes of the remaining three singlets. The donation of nitrogen should affect the line width of not only the directly bonded nucleus but also the adjacent ^{195}Pt nuclei through the Pt–Pt bonds. The degree of this effect should be larger for the trans platinum compared to the cis platinum.[9] As a result, the line width of the signal due to the nucleus trans to the Pt–N bond should be broader. The spectrum of **2** in Figure 2a shows that the singlet at −719 ppm has the second broadest line width among the four main singlets, and thereby it is assigned to Pt(2) of **2**. Assignments of other signals are straightforward, and the results are summarized in Figure 5.

The ^{195}Pt NMR spectrum of $[Pt_4(CH_3COO)_5(CH_3CONH)_3]$ (**3**) was successfully analyzed in the same way, and the assignments are given in Figure 5. In the spectrum of this compound (Figure 3a), the sharpest singlet at −544 ppm is assigned to Pt(2) of **3** in Figure 1, which has no nitrogen donor. The second sharpest singlet due to Pt(3) is at −806 ppm. The simulated spectrum (Figure 3b) supports the analysis and the assignments. Observed weak lines which are not accounted for by the simulation would

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(6) The satellite doublet was clearly observed only at the main peak due to Pt$_d$ (−456 ppm) with ^2J = 180 Hz, and those for the other three main peaks were not seen in the spectrum in Figure 2a because of the broadness of the main peaks. However, when a spectrum was obtained by Fourier transformation without applying the window function, the sattelite of Pt$_b$ was observed as a clearly resolved doublet with ^2J = 110 Hz.

(7) The relationship among the main peak separatin, coupling constant, and inner peak separation of the AB pattern is easily derived. (For example, see: Bovey, A. B. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1969; Chapter 4.)

(8) The simulation was carried out by use of LAOCN5 (Vassidei, L.; Sciacovelli, Q. *QCPE* No. 458).

(9) The line broadening is due to the Pt–N coupling, and the larger the coupling constant the broader the peak. The two-bond coupling constant $^2J_{N\text{-trans-Pt}}$ would be larger than $^2J_{N\text{-cis-Pt}}$.

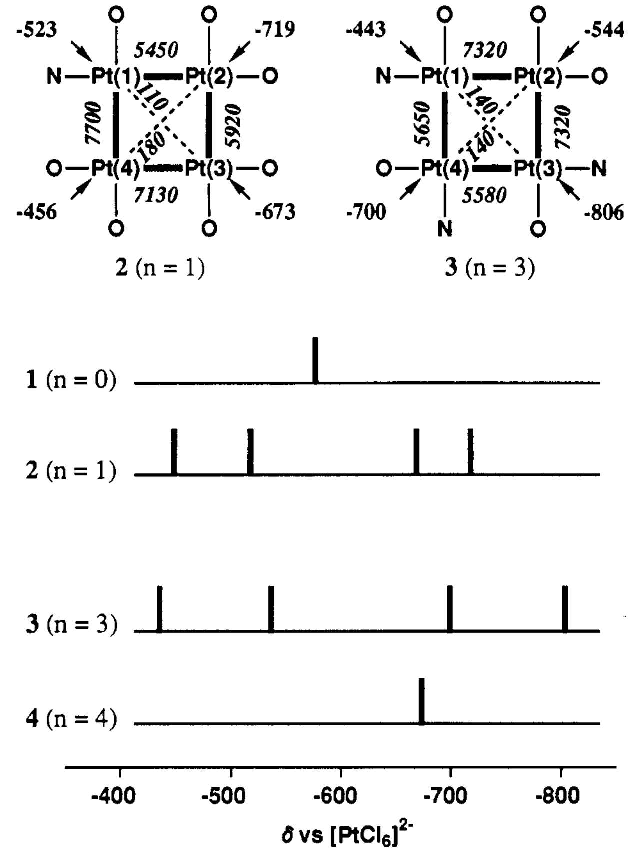

Figure 5. ^{195}Pt chemical shifts for $[Pt_4(CH_3COO)_{8-n}(CH_3CONH)_n]$ (**1** (n = 0), **2** (n = 1), **3** (n = 3), **4** (n = 4)) and coupling constants for **2** and **3** (in *italics*).

be due to impurities, possibly isomers of **3** and/or disubstituted derivatives.

To our knowledge, this is the first paper reporting the Pt–Pt coupling constants for tetranuclear platinum cluster complexes. The large coupling constants show the presence of direct Pt–Pt bonds. The values of the chemical shifts for **2** and **3** are spread over a rather wide range, as compared with the chemical shifts seen for compounds **1** and **4** (Figure 5). It seems, however, that there is a trend that the average chemical shifts for **1**–**4** decrease as the number of n in $[Pt_4(CH_3COO)_{8-n}(CH_3CONH)_n]$ increases. The data suggest that the ligating atom affects the chemical shift of not only the directly bonded platinum nucleus but also the adjacent platinum through the Pt–Pt bond, as has been reported for the ^{195}Pt NMR spectra of platinum(III) dimers with a Pt–Pt bond.[10]

Experimental Section

Materials. $[Pt_4(CH_3COO)_8]$ (**1**) was prepared by a literature method.[5]

$[Pt_4(CH_3COO)_4(CH_3COO)_3(CH_3CONH)]$ (2). After a CH_3CN/H_2O (100 mL:15 mL) solution of **1** (100 mg) was refluxed at 60 °C for 3 h, the solution was evaporated to dryness. The residue was a mixture of yellow complex and acetamide, which is the catalytically produced hydrolysis product of acetonitrile.[4] The byproduct of acetamide was removed by sublimation, the residue dissolved in a small amount of CH_2Cl_2/CH_3CN (2:1 (v/v)) was passed through a gel-filtration column (Sephadex LH-20), and the yellow eluate was evaporated to dryness, giving a mixture of a partially substituted complex $[Pt_4(CH_3COO)_{8-n}(CH_3CONH)_n]$ ($n < 4$). The mixture was separated by silica gel column chromatography (eluent: CH_3CN/CH_2Cl_2/THF; 50:50:1 (v/v)). The first yellow band contained unreacted **1**. The eluate from the second band was collected and evaporated to dryness. Because of the tailing of the first band, the boundary of the first and second bands was not clear. Therefore, the isolated solid contained a small amount of **1** in addition to the desired product $[Pt_4(CH_3COO)_7(CH_3CONH)]$ (**2**). Further purification was not carried out, and the mixture was used for the measurement of the ^{195}Pt NMR of **2**, the reasons being that a relatively large amount of **2** is necessary to obtain a good spectrum and that the contaminant **1** shows only a sharp ^{195}Pt NMR singlet. Therefore the contamination did not interfere with the analysis of the spectrum of **2**. ^{1}H NMR (CD_3CN): 2.34 (3H), 2.31 (3H), 2.30 (3H), 2.29 (3H) ppm (in-plane CH_3); 1.99 (3H), 1.96 (3H), 1.94 (3H), 1.92 (3H) ppm (out-of-plane CH_3).

$Pt_4(CH_3COO)_4(CH_3CONH)_4$ (4). A 200-mg sample of $[Pt_4(CH_3COO)_8]$ (**1**) and 500 mg of acetamide were added to 100 mL of dichloromethane. Sodium hydroxide (10 g) was added, and the resulting suspension was stirred for 10 h (acetamide and sodium hydroxide were not completely dissolved). The color of the solution became yellow. The mixture was filtered, and the filtrate was evaporated to give a yellow oil. To this oil was added 10 mL of chloroform. After a few hours, yellow crystals of the desired product precipitated. ^{1}H NMR (CD_3CN): 5.92 (s, 1H), 2.34 (s, 3H), 1.92 ppm (s, 3H). ^{13}C NMR (CD_3CN): 192.9, 181.6, 22.7, 22.2 ppm. Anal. Calcd for $Pt_4C_{16}H_{28}O_{12}N_4$: C, 15.38; H, 2.24; N, 4.49. Found: C, 14.67; H, 2.50; N, 4.18.

$[Pt_4(CH_3COO)_5(CH_3CONH)_3]$ (3). This was prepared in solution from $[Pt_4(CH_3COO)_4(CH_3CONH)_4]$ (**4**) by use of acetate substitution and was not isolated. Addition of acetic acid to a deuterated acetonitrile solution of **4** immediately gave an equilibrated mixture of $[Pt_4(CH_3COO)_{4+n}(CH_3CONH)_{4-n})$ ($n < 4$), as evidenced by ^{1}H NMR, n being dependent on the relative amount of acetic acid added. By monitoring the ^{1}H NMR, we determined the ratio of complex **4** to acetic acid which maximized the amount of $[Pt_4(CH_3COO)_5(CH_3CONH)_3]$ (**3**) formed under the solution conditions of the ^{195}Pt NMR measurements. The ^{1}H NMR of complex **4** shows two singlets due to the methyl protons at 1.85 and 2.34 ppm in CD_3CN whereas that of **3** shows eight methyl singlets with equal intensities at 1.84 (3H+3H), 1.88 (3H), 1.89 (3H), 2.24 (3H), 2.26 (3H), and 2.28 ppm (3H+3H). When 2 μL of acetic acid was added to a CD_3CN solution (4 mL) of **2** (40 mg), the mixture was found to contain the desired complex **3** in more than 90% abundance in addition to a very small amount of **4**. This solution was subjected to ^{195}Pt NMR measurements. The contaminant **4** caused no interference with the analysis of the spectrum of **3**.

Measurements. ^{195}Pt NMR spectra were recorded on a JEOL GSX-270 spectrometer equipped with a multinuclear accessory, operating at 58.0 MHz. The spectral measurements were carried out under proton-decoupled conditions. The spectra were acquired in a 120-kHz window with a pulse width of 9.6 μs (representing a flip angle $\alpha = 45°$), a pulse repetition time of 0.23 s, and a delay time (between the end of the pulse and the acquisition) of 100 μs. A typical number of scans was ca. 130 000 (ca.8 h). The chemical shifts were referenced to $[PtCl_6]^{2-}$ (external standard −1630 ppm for K_2PtCl_4) using the high-frequency positive-shift sign convention.

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(10) Appleton, T. G.; Hall, J. R.; Neale, D. W. *Inorg. Chim. Acta* **1985**, *104*, 19–31.