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Tetranuclear Platinum(II) Cluster Complexes Having Nonbridging Chelate Ligands in the Plane of the Square-Planar Cluster Core: $[Pt_4(CH_3COO)_4(en)_4]Cl_4 \cdot 4H_2O$ and $[Pt_4(CH_3COO)_4(pic)_4] \cdot CH_3OH \cdot 4H_2O$ (en = Ethylenediamine; picH = Picolinic Acid)

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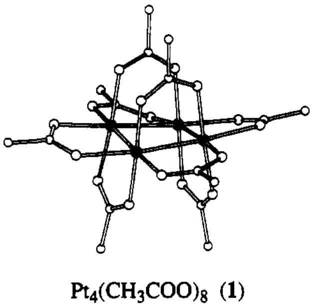
Octakis(acetato)tetraplatinum(II), $[Pt_4(CH_3COO)_8]$ (**1**), is a well-known divalent platinum cluster complex of unique structure[1] and reactivity.[2-4] It has a square-planar cluster core comprised of four Pt(II) ions.[5] The coordination geometry around each platinum(II) ion is a distorted octahedron if the Pt–Pt bonds are included. Previously, we reported that 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. Thus, we prepared derivatives of the type $[Pt^{II}_4(\mu\text{-}CH_3COO)_4(\mu\text{-}RCOO)_4]$.[2] Acetylacetone (acacH) also replaces easily the four in-plane acetate ligands in **1** to give tetrakis(acetylacetonato) complex $[Pt^{II}_4(\mu\text{-}CH_3COO)_4(\mu\text{-}acac\text{-}O,C^3)_4]$.[3] In all the thus far known compounds derived from **1**, eight bidentate ligands doubly bridge four edges of the square-planar cluster core. Despite the direct Pt–Pt single bonds, it has been believed that the doubly bridging ligands stabilize the cluster core in a rather unusual octahedral geometry around platinum(II) ion. We now report two new tetranuclear Pt(II) cluster complexes having *nonbridging chelate ligands* at the in-plane coordination sites (see Chart I, showing only the cluster core and the coordination mode of the in-plane ligands).



$Pt_4(CH_3COO)_8$ (**1**)

Complex **1** was allowed to react with an excess of ethylenediamine (en) and picolinic acid (picH) to yield the tetrasubstituted red crystalline solids $[Pt^{II}_4(\mu\text{-}CH_3COO)_4(en)_4]Cl_4 \cdot 4H_2O$ ($\mathbf{2}Cl_4 \cdot 4H_2O$)[6] and $[Pt^{II}_4(\mu\text{-}CH_3COO)_4(pic)_4] \cdot CH_3OH \cdot 4H_2O$ ($\mathbf{3} \cdot CH_3OH \cdot 4H_2O$),[7] respectively.[8] Complexes **2** and **3** are ionic and neutral, respectively, but the formal oxidation state of each platinum remains +2 in both complexes.

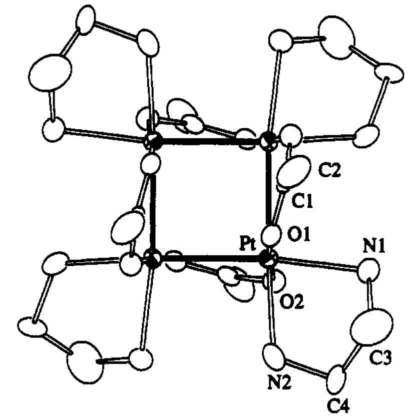
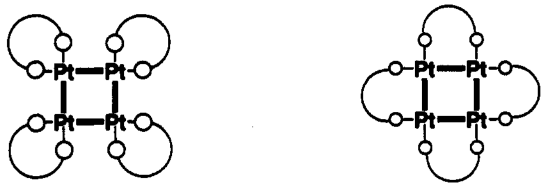


Figure 1. ORTEP drawing of $[Pt_4(\mu\text{-}CH_3COO)_4(en)_4]^{4+}$ (**2**) in $2Cl_4 \cdot 4H_2O$. Relevant bond lengths (Å) and angles (deg): Pt–Pt′ = 2.5574(7), Pt–O(1) = 2.01(1), Pt–O(2) = 2.02(1), Pt–N(1) = 2.18(1), Pt–N(2) = 2.21(1); Pt–Pt′–Pt″ = 88.567(9), N(1)–Pt–N(2) = 79.51.

Chart I



chelate coordination **bridge coordination**

The ORTEP drawings of **2**[9] and **3**[10] show that the square-planar cluster core structure has remained essentially unchanged (Figures 1 and 2). The bridging structure of the four out-of-plane acetate ligands in the parent octaacetato complex **1** has also basically remained unaltered in **2** and **3**. The four in-plane acetate ligands in **1**, however, have been substituted in the present reactions by ethylenediamine in complex **2** and by picolinate ions in **3**. Very interestingly, ethylenediamine and picolinate ligands are in the plane of the cluster core but they take the *chelate* coordination mode. To our knowledge, the present compounds are the first examples in which the square cluster core of platinum-

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

(2) Yamaguchi, T.; Sasaki, Y.; Nagasawa, A.; Ito, T.; Koga, N.; Morokuma, K. *Inorg. Chem.* **1989,** *28*, 4311–4312.

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(4) Yamaguchi, T.; Nishimura, N.; Ito, T. *J. Am. Chem. Soc.* **1993,** *115*, 1612–1613.

(5) Square-planer Pd_4 cores are reported in some palladium cluster complexes: (a) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047–1054. (b) Moiseev, I. I.; Stromnova, T. A.; Vargaftig, M. N.; Mazo, G. J.; Kuz'mina, L. G.; Struchkov, T. *J. Chem. Soc., Chem. Commun.* **1978**, 27–28. (c) Kuz'mina, L. G.; Struchkov, T. *Koord. Khim.* **1979**, *5*, 1558–1562. (d) Stromnova, T. A.; Busygina, I. N.; Katser, S. B.; Antsyshkina, A. S.; Porai-Koshits, M. A.; Moiseev I. I. *J. Chem. Soc., Chem. Commun.* **1988**, 114–115.

(6) Preparation of complex **2**: Ethylenediamine (2 mL) was added to a dichloromethane solution (20 mL) of **1** (100 mg) at room temperature. Orange precipitates separated out immediately and were filtered off. The solid was dissolved in water (1 mL), and to this solution was added a small amount of saturated NaCl aqueous solution. The solution was allowed to stand for several days at room temperature to yield red crystals, which were filtered off and air-dried. Yield: 77 mg. NMR data in CD_3OD: ^1H, 1.98 (s, 3H, CH_3), 2.81 ppm (mult, 4H, CH_2–N); ^{13}C, 22.32 (CH_3), 46.56 (CH_2–N), 197.34 ppm (COO); ^{195}Pt, 802 ppm (vs K_2PtCl_4 in D_2O).

(7) Preparation of complex **3**: Picolinic acid (400 mg) and complex **1** (100 mg) were dissolved in acetonitrile (30 mL), and the mixture was stirred at room temperature for 15 min. The solution was then evaporated to dryness. A methanol solution of the residue was passed through a gel fitration column (Sephadex LH-20; eluant methanol) to remove excess picolinic acid. The orange eluate was collected and evaporated to dryness, and the crude product was recrystallized from methanol. Yield: 105 mg. FABMS: *m/e* 1505 (calcd MW for **3** = 1504.9). NMR data in $CDCl_3$: ^1H, 1.68 (s, 12H, CH_3), 7.91 (t, 4H, ring *H*), 8.13 (t, 4H, ring *H*), 8.34 (d, 4H, ring *H*), 9.90 ppm (d, 4H, ring *H*); ^{13}C, 21.9 (CH_3), 128.1, 128.4, 140.6, 151.8, 153.0 (ring *C*), 173.6, 195.2 ppm (COO); ^{195}Pt, 1170 ppm (vs K_2PtCl_4 in D_2O).

(8) Both the compounds gave satisfactory C, H, and N analytical data.

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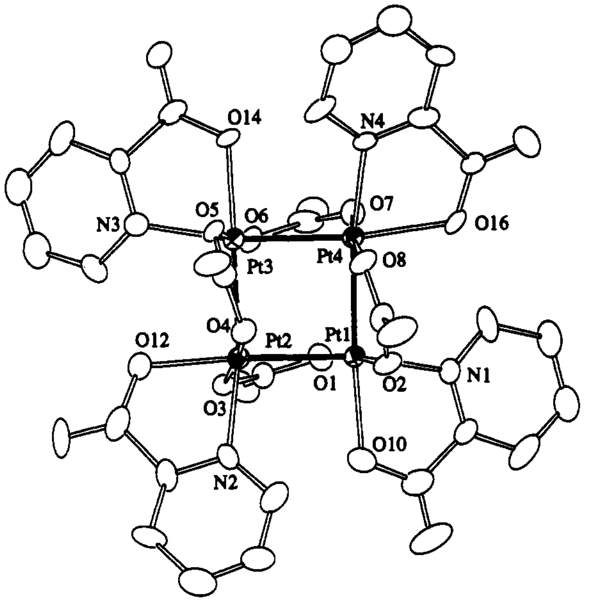

Figure 2. ORTEP drawing of $[Pt_4(\mu\text{-}CH_3COO)_4(pic)_4]$ (3) in $3CH_3OH{\cdot}4H_2O$. Relevant bond lengths (Å) and angles (deg): Pt(1)–Pt(2) = 2.5552(8), Pt(2)–Pt(3) = 2.5459(8), Pt(3)–Pt(4) = 2.5471(9), Pt(4)–Pt(1) = 2.5487(8), Pt(1)–O(1) = 2.03(1), Pt(1)–O(2) = 1.99(1), Pt(2)–O(3) = 2.01(1), Pt(2)–O(4) = 2.00(1), Pt(3)–O(5) = 2.00(1), Pt(3)–O(6) = 2.01(1), Pt(4)–O(7) = 2.01(1), Pt(4)–O(8) = 2.01(1), Pt(1)–O(10) = 2.17(1), Pt(2)–O(12) = 2.11(1), Pt(3)–O(14) = 2.15(1), Pt(4)–O(16) = 2.17(1), Pt(1)–N(1) = 2.21(1), Pt(2)–N(2) = 2.18(1), Pt(3)–N(3) = 2.17(1), Pt(4)–N(4) = 2.16(1); Pt(4)–Pt(1)–Pt(2) = 86.65(3), Pt(1)–Pt(2)–Pt(3) = 88.35(2), Pt(2)–Pt(3)–Pt(4) = 86.88(3), Pt(3)–Pt(4)–Pt(1) = 88.47(3), N(1)–Pt(1)–O(10) = 75.7(4), N(2)–Pt(2)–O(12) = 77.0(5), N(3)–Pt(3)–O(14) = 77.5(4), N(4)–Pt(4)–O(16) = 76.1(5).

(II) is maintained with the four single bridges. The loss of the in-plane bridge coordination brings about a change in the skeletal structure of the cluster core. First, the Pt–Pt bonds lengthen. They are 2.5574(7) Å in **2** and 2.5459(8)–2.5552(8) Å in **3**, whereas that in **1** is 2.50 Å.[1,11] Second, the squares of the cluster cores in **2** and **3** are distorted toward a tetrahedron as compared with that in **1**. That is, the cores in **2** and **3** are folded along a line connecting two diagonally opposite apexes of the square. Dihedral angles between the folded planes are 19.01° in **2** and 33.26° (between the planes of [Pt(1), Pt(2), Pt(3)] and [Pt(1), Pt(3), Pt(4)] in **3**). The four platinum atoms in **1** are almost within 0.116 Å of a least-squares plane,[1c,11] whereas the maximum deviation from a least-squares plane among the four Pt atoms is as much as 0.203 Å in **2** and 0.262 Å in **3**. The maximum torsional angle along the Pt–Pt bonds is 18.01° in **2** and 23.24° [Pt(1)–Pt(4)–Pt(3)–Pt(2)] in **3** (10.71°[1c] for **1**). The Pt–Pt bond lengths in **2** and **3** show the presence of direct Pt–Pt bonding. Accordingly, the coordination geometry around each platinum(II) ion is taken as a distorted octahedron in both structures.[12]

A special comment which deserves emphasis is that the ethylenediamine complex **2** is a cationic complex. All the tetranuclear Pt(II) cluster complexes so far known including **3** are neutral. Because of its ionic character, compound **2** is soluble in H_2O.

The picolinate ion has potentially two bidentate sites, two oxygens of the carboxylate group and the pyridine nitrogen and carboxylate oxygen, which form a five-membered chelate ring. The picolinate ion in **3** adopts the latter coordination mode but not the former, which would give rise to the bridge coordination. There is no experimental evidence for a carboxylate-bridged isomer. The reason for this is not clear, but nitrogen would be a stronger donor than oxygen for Pt in tetranuclear cluster complexes.

^1H NMR spectra of **2** and **3** show that the solid-state structures are maintained in solution.[6,7]

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Supplementary Material Available: Tables of crystallographic data and experimental conditions, atomic positional and thermal parameters, interatomic distances and bond angles, and torsion angles for **2** and **3** and an ORTEP diagram with labeling scheme for **3** (15 pages). Ordering information is given on any current masthead page.

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(9) X-ray analysis of **2**. Crystal data: $[Pt_4(\mu\text{-}CH_3COO)_4(en)_4]Cl_4{\cdot}4H_2O$ = $Pt_4O_{12}N_8C_{16}H_{52}Cl_4$, tetragonal, space group $I\bar{4}$ (No. 82), a = 13.052(1) Å, c = 11.196(1) Å, V = 1907.3(2) Å^3, Z = 2. With the use of 1350 unique reflections ($I > 3\sigma(I)$) collected at room temperature with Mo Kα (λ = 0.710 69 Å) radiation up to 2θ = 60.0° on a Rigaku AFC7S diffractometer, the structure was solved by the Patterson method (DIRDIF92 PATTY) and refined by full-matrix least squares with anisotropic temperature factors for non-hydrogen atoms to a final R value of 3.6%.

(10) X-ray analysis of **3**. A specimen recrystallized from CH_3OH was used. Crystal data: $[Pt_4(\mu\text{-}CH_3COO)_4(pic)_4]{\cdot}CH_3OH{\cdot}4H_2O$ = $Pt_4O_{21}N_4C_{33}H_{40}$, orthorhombic, space group *Pbca* (No. 61), a = 21.655(2) Å, b = 27.576(4) Å, c = 14.455(2) Å, V = 8631(1) Å^3, Z = 8. With the use of 5106 unique reflections ($I > 3\sigma(I)$) collected at room temperature with Mo Kα (λ = 0.710 69 Å) radiation up to 2θ = 55.0° on a Rigaku AFC7S diffractometer, the structure was solved by the Patterson method (SAPI) and refined by full-matrix least squares with anisotropic temperature factors for non-hydrogen atoms to a final R value of 4.4%.

(11) There are two modifications in the crystal structure of **1**.[1a,b] The molecular structures of **1** in both the modifications are almost the same.

(12) Another common structural feature among **1**,[1] **2**, and **3** is that the in-plane coordination bond lengths are slightly longer than the out-of-plane ones in general (see captions of Figures 1 and 2).