Observation of the New κ^2C,O:κ^2C′,O′ Coordination Mode of 1,1,2,2-Tetraacetylethanato Ligand in a Dinuclear 1,1,1,5,5,5-Hexafluoroacetylacetonato Palladium(II) Complex

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We have isolated a new dinuclear palladium(II) complex containing 1,1,2,2-tetraacetylethanato (taet) and 1,1,1,5,5,5-hexafluoroacetylacetonato (hfac) ligands, [(hfac)Pd(*C*,*O*-taet)-Pd(hfac)] (**2b**), whose crystallographic study has revealed that taet is coordinated to each palladium center as a κ^2C,O ligand to form a five-membered chelate ring. Complex **2b** provides the first example of the κ^2C,O:κ^2C′,O′ coordination mode of β-diketonato ligand, which slowly tautomerizes to [(hfac)Pd-(*O*,*O*-taet)Pd(hfac)] (**2a**).

So far, various coordination modes of β-diketonato (abbreviated as dike) ligands in binary metal complexes, [M(dike)$_n$] (where the oxidation state of the metal ion is +2 or +3 and n = 2 or 3, respectively), have been reported as O and/or C donor sets (Figure 1).[1–8] Among them, complexes with a soft metal ion such as platinum(II) or palladium(II) can sometimes form C-bonded complexes.

In the extended work dealing with these β-diketonato ligands, a branched 1,1,2,2-tetraketonato (teke) ligand (bis(β-diketonato), a tetradentate bridging ligand) has been reported to form the mixed-ligand dinuclear complexes with a bidentate ligand (L), [(L)M(teke)M(L)]X$_n$, where M = Cu(II), Ni(II), or Pd(II), and L = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, 2,2′-bipyridine, or 1,10-phenanthroline.[9] In these complexes, the bridging teke ligand coordinates to the metal center through the O,O-donor set.[10,11] For the synthesis of this type of complexes, 1,1,2,2-tetraacetylethanate (taet; H_2taet shown in Figure 2) has been used most extensively.

In this study, we have succeeded in isolating a new type of mixed-ligand dinuclear palladium(II) complex containing taet and 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac) ligands, whose crystal structure revealed that each palladium(II) metal center has a four-coordinate square-planar coordination and contains a metal–carbon bond (Pd–C).

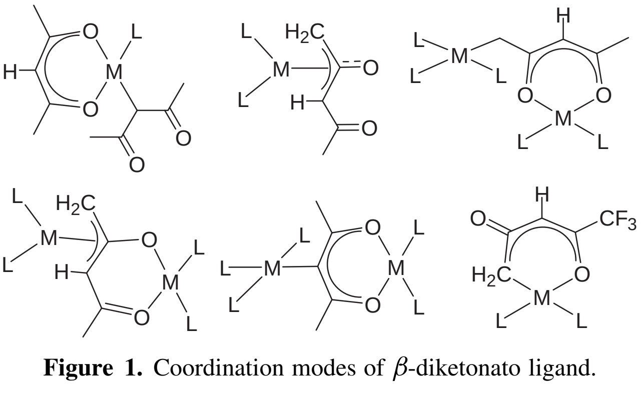


Figure 1. Coordination modes of β-diketonato ligand.

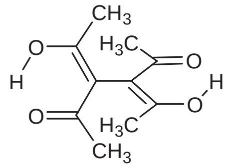
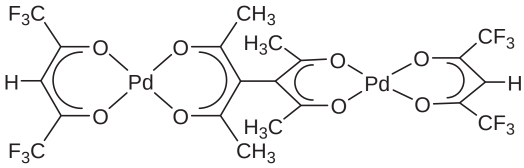


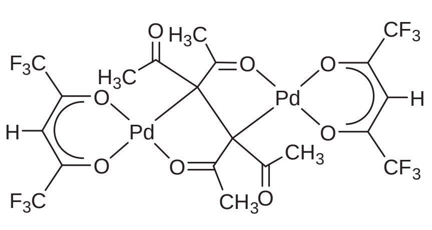
Figure 2. Structure of 1,1,2,2-tetraacetylethane (H_2taet).

H_2taet was prepared from the coupling reaction of Na(acac) (Hacac = acetylacetone) and I_2 in dioxane.[12] When H_2taet was added to a CH_2Cl_2 solution of methoxo-bridged dinuclear complex [(hfac)Pd(OMe)$_2$Pd(hfac)] (**1**)[13] in the ratio of 1:1 at room temperature, a mixture of the *O*,*O*-taet dinuclear complex, [Pd$_2$(*O*,*O*-taet)(hfac)$_2$] (**2a**, Figure 3, Type A),[14] and the *C*,*O*-taet one, [Pd$_2$(*C*,*O*-taet)(hfac)$_2$] (**2b**, Figure 3, Type B), was obtained. These two isomers were further separated by silica-gel column chromatography (Wako-gel C300, ϕ3 cm column, solvent: CH_2Cl_2), and red crystals of **2b** were isolated as a minor product (yield: less than 1%), while orange crystals of **2a** were obtained as the major product (yield: 80%).

Complex **2b** exhibits ^{1}H NMR signals at 2.46 and 2.51 ppm due to the CH_3 protons of the *C*,*O*-taet ligand and at 6.32 ppm due to the –CH= protons of the hfac ligands, while the *O*,*O*-taet isomer **2a** shows ^{1}H NMR signals at 2.01 and 6.26 ppm assignable to the CH_3 protons of *O*,*O*-taet and –CH= of hfac, respectively. In the ^{13}C NMR spectrum the central carbon atoms of the *C*,*O*-taet ligand in **2b** resonate at 74.8 ppm, which suggests that these carbons are sp^3 hybridized and bonded to the palladium atoms. This makes a striking contrast to that of **2a** which shows



Type A; *O*,*O*-taet coordination mode



Type B; *C*,*O*-taet coordination mode

Figure 3. Structures of the dinuclear palladium(II) complexes with tetraacetylethanate.

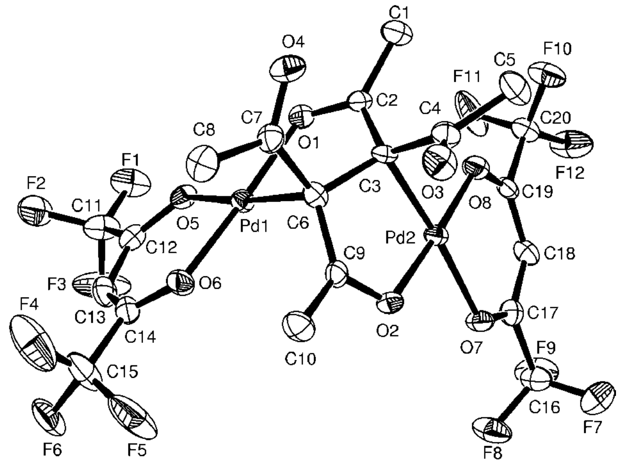


Figure 4. An ORTEP drawing of [Pd_2(*C*,*O*-taet)$(hfac)_2$] with the thermal ellipsoids at 50% probability level. Selected bond distances and angles: Pd(1)–O(1), 2.004(2); Pd(1)–O(5), 2.077(2); Pd(1)–O(6), 1.994(2); Pd(1)–C(6), 2.061(3); Pd(2)–O(2), 1.993(2); Pd(2)–O(7), 2.057(3); Pd(2)–O(8), 2.004(2); Pd(2)–C(3), 2.055(4); O(1)–C(2), 1.264(4); O(2)–C(9), 1.267(5); C(2)–C(3), 1.473(5); C(3)–C(6), 1.544(5); C(6)–C(9), 1.461(5) Å; O(1)–Pd(1)–O(5), 91.1(1); O(1)–Pd(1)–O(6), 174.1(1); O(1)–Pd(1)–C(6), 82.0(1); O(5)–Pd(1)–O(6), 92.7(1); O(5)–Pd(1)–C(6), 173.1(1); O(6)–Pd(1)–C(6), 94.2(1); O(2)–Pd(2)–O(7), 91.1(1); O(2)–Pd(2)–O(8), 176.5(1); O(2)–Pd(2)–C(3), 81.6(1); O(7)–Pd(2)–O(8), 92.3(1); O(7)–Pd(2)–C(3), 172.7(1); O(8)–Pd(2)–C(3), 95.0(1)°.

the corresponding carbon resonance at 111.4 ppm due to its sp^2 hybridization. The $^{13}C\{^1H\}$ NMR signals of the CF_3CO (116.1, 116.5; 173.4, 176.5 ppm) and CH_3CO carbons (28.8, 29.7; 194.4, 229.1 ppm) in **2b** appear as two distinct sets of peaks, also indicating the formation of the C,O-isomer.[15]

Figure 4 shows the molecular structure of **2b**, which has been determined by an X-ray analysis.[16] It is unambiguously confirmed that the taet ligand behaves as a κ^2C,O:κ^2C′,O′ bridging ligand to link two palladium atoms which adopt square-planar coordination structures. The Pd–C(taet) and Pd–O(taet) bond distances are 2.06 and 2.00 Å (mean), respectively. The Pd–O(hfac) bond distances are nonequivalent owing to the trans influence of taet, i.e., the bond lengths of the Pd–O(hfac) placed at the trans position of C-coordination (2.07 Å (mean)) are slightly longer than those at the trans position of O-coordination (2.00 Å (mean)). The dihedral angle between the coordination planes of the palladium atoms (Pd(1)–O(1)–O(5)–O(6)–C(6), Pd(2)–O(2)–O(7)–O(8)–C(3)) is 82.38(8)°. It is interesting to note that the central C–C bond length of taet in this C,O-isomer (C(3)–C(6): 1.544(5) Å) is longer than that of the O,O-isomer **2a** reported previously (1.510(4) Å).[14] In the former case both carbon atoms connected to the palladium(II) centers in the taet ligand are sp^3 hybridized, while in the latter the sp^2 hybridized carbons contact with each other.

It is also noteworthy that the tautomerization takes place from **2b** to **2a**: the κ^2*C*,*O*:κ^2*C*′,*O*′-taet slowly isomerizes to the common κ^2*O*,*O*′:κ^2*O*″,*O*‴-taet in solution. When a $CDCl_3$ solution of **2b** was left at room temperature for one week, the ^1H NMR spectra showed that more than 50% of **2b** was transformed into **2a**. This suggests that **2a** is actually the thermodynamically favored product, but **2b** has enough kinetic stability to be isolated at room temperature.

In conclusion, we have isolated a new dinuclear palladium(II) complex containing a bis(diketonato) ligand which is coordinated to each palladium center in a κ^2C,O:κ^2C′,O′ fashion. This is the first example of such a coordination mode of tetraketonato ligand.

References and Notes

1 S. Baba, T. Ogura, S. Kawaguchi, *Bull. Chem. Soc. Jpn.* **1974**, *47*, 665.
2 Y. Otani, Y. Nakamura, S. Kawaguchi, S. Okeya, T. Hinomoto, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1467.
3 Z. Kanda, Y. Nakamura, S. Kawaguchi, *Inorg. Chem.* **1978**, *17*, 910.
4 S. Okeya, S. Kawaguchi, *Inorg. Chem.* **1977**, *16*, 1730.
5 S. Okeya, H. Sazaki, M. Ogita, T. Takemoto, Y. Onuki, Y. Nakamura, B. K. Mohapatra, S. Kawaguchi, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1978.
6 S. Okeya, Y. Nakamura, S. Kawaguchi, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3396.
7 S. Matsumoto, S. Kawaguchi, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1577.
8 S. Okeya, S. Ooi, K. Matsumoto, Y. Nakamura, S. Kawaguchi, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1085.
9 Several $[(L)_2M(teke)M(L)_2]^{n+}$-type dinuclear complexes (L = bidentate ligand) have also been synthesized. a) Y. Fukuda, A. Seino, K. Mafune, H. Nakagawa, W. Linert, *J. Coord. Chem.* **1994**, *33*, 123. b) N. A. Lewis, W. Pan, *Inorg. Chem.* **1995**, *34*, 2244. c) Y. Zhang, S. Wang, G. D. Enright, S. R. Breeze, *J. Am. Chem. Soc.* **1998**, *120*, 9398. d) T. Koiwa, Y. Masuda, J. Shono, Y. Kawamoto, Y. Hoshino, T. Hashimoto, K. Natarajan, K. Shimizu, *Inorg. Chem.* **2004**, *43*, 6215.
10 H. Kambayashi, Y. Masuda, Y. Fukuda, *Chem. Lett.* **1991**, 303.
11 H. Kambayashi, J. Yuzurihara, Y. Masuda, H. Nakagawa, W. Linert, Y. Fukuda, *Z. Naturforsch.* **1995**, *50b*, 536.
12 R. G. Charles, *Org. Synth.* **1963**, Coll. Vol. *IV*, 869.
13 A. R. Siedle, L. H. Pignolet, *Inorg. Chem.* **1982**, *21*, 3090.
14 Y. Kobayashi, N. Nagao, S. Okeya, Y. Fukuda, *Chem. Lett.* **1996**, 663.
15 Spectral data for **2b**: $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 28.8, 29.7, 74.8, 92.6, 116.1 (q, $^1J_{CF} = 282$ Hz), 116.5 (q, $^1J_{CF} = 284$ Hz), 173.4 (q, $^2J_{CF} = 35$ Hz), 176.5 (q, $^2J_{CF} = 35$ Hz), 194.4, 229.1; IR (KBr, cm^{-1}): 1667, 1652, 1634, 1616, 1542, 1530, 1461, 1261, 1209, 1154, 791.
16 Crystallographic data for **2b** ($C_{20}H_{14}O_8F_{12}Pd_2$): fw 823.11, monoclinic, space group $P2_1/n$, $a = 10.88(2)$, $b = 11.03(2)$, $c = 21.97(7)$ Å, $\beta = 101.98(5)°$, $V = 2579.1(12)$ Å^3, $Z = 4$, $T = -150$ °C, $D_{calcd} = 2.120\ g\,cm^{-3}$, R_1 [$I > 2\sigma(I)$] (wR_2 [all data]) = 0.066 (0.072) for 394 variables, 6124 unique reflections ($R_{int} = 0.039$), GOF = 1.000. Crystallographic data reported in this manuscript have been deposited with CCDC (document number: CCDC-289612). Copies of the data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html.

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