Syntheses and Structure of New Dinuclear Palladium(II) Complexes with 1,1,2,2-Tetraacetylethanate and *β*-Diketonate

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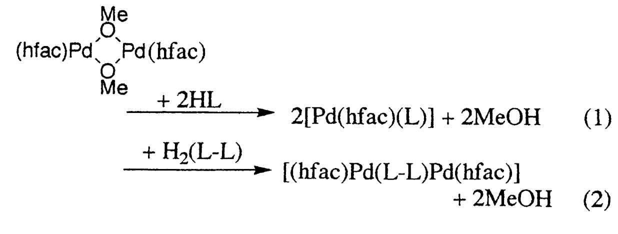
(Received April 17, 1996)

$[Pd_2(hfac)_2(\mu\text{-}MeO)_2]$ (**1**) (hfac$^-$ = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) reacts with 1,1,2,2-tetraacetylethanediide (H_2taet) to give a dinuclear mixed ligand complex $[Pd_2(taet)(hfac)_2]$ (**2**) having bridging taet^{2-} ligand. The terminal hfac$^-$ ligands in the dinuclear complex $[Pd_2(taet)(hfac)_2]$ (**2**) are replaced easily by acac$^-$ to obtain $[Pd_2(taet)(acac)_2]$ (**3**) (acac$^-$ = 2,4-pentanedionate). The structures of the two complexes obtained were determined by X-ray analysis.

A 1,1,2,2-tetraacetylethanediide dianion (taet^{2-}) is a potentially bridging ligand to form a dinuclear complex with metal ions. We have reported the preparation and structural varieties of Ni(II) and Cu(II) dinuclear mixed ligand complexes containing taet^{2-} and N,N,N',N'-tetramethylethylenediamine (tmen); general formula $[(tmen)M(taet)M(tmen)]X_2\cdot nH_2O$.[1-3] In the system of labile metal ions such as Ni(II) or Cu(II), the important factor to facilitate the formation of mixed ligand complexes is suitable combination of a bulky ligand (tmen) and a slim ligand (taet^{2-}), i.e. steric hindrance factor. It is difficult to obtain the mixed ligand complexes with the combination of both slim ligands without the steric hindrance factor. In the case of inert Pd(II)-system, however, it has been reported that stable mixed ligand Pd(II) complexes with combinations of slim β-diketonates, [Pd(hfac)(acac)] were synthesized.[4] For Pd(II)-system, therefore, not only steric factor but also reaction pathway (kinetic factor) is important for the formation of mixed ligands complexes, and a suitable choice in a starting material is important.

In this study, the dinuclear complex $[Pd_2(hfac)_2(\mu\text{-}MeO)_2]$ (**1**), which have been synthesized and structurally characterized by Siedle and Pignolet,[5] was chosen for the starting material of new mixed ligand dinuclear complexes. The dinuclear complex **1** has two different types of reaction sites, i.e. the μ-MeO groups which can be at first exchanged by an entering bidantate ligand (HL or H_2(L-L)) and hfac$^-$ ligands which are hard to exchange rather than the μ-MeO groups;



$$(hfac)Pd(\mu\text{-}OMe)_2Pd(hfac) \xrightarrow{+\,2HL} 2[Pd(hfac)(L)] + 2MeOH \quad (1)$$

$$\xrightarrow{+\,H_2(L\text{-}L)} [(hfac)Pd(L\text{-}L)Pd(hfac)] + 2MeOH \quad (2)$$

It is expected, therefore, that many kinds of mixed ligand dinuclear complexes may be synthesized by using of **1** as a starting material. No detail study, however, has been reported on the utilization of the dinuclear complex **1** for the synthesis of Pd(II) complexes. We report here the syntheses and structures of two Pd(II)-dinuclear complexes, $[Pd_2(taet)(hfac)_2]$ (**2**) and $[Pd_2(taet)(acac)_2]$ (**3**) which contain a bridging tetraketonate ligand. The complex, **2**, is the useful precursor for another dinuclear complex **3** as follows.

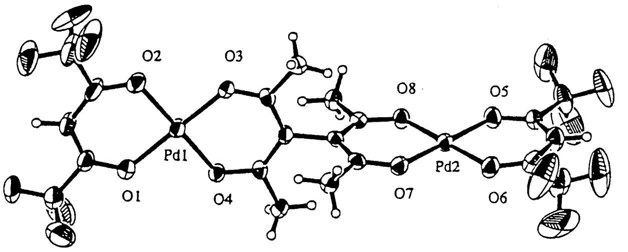


Figure 1. ORTEP drawing of $[Pd_2(taet)(hfac)_2]$ (**2**). Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (°) for a unit of Pd(1)-Pd(2) are as follows:[10] Pd(1)-O(1), 1.996(6); Pd(1)-O(2), 1.997(6); Pd(1)-O(3), 1.941(6); Pd(1)-O(4), 1.939(6); Pd(2)-O(5), 2.000(6); Pd(2)-O(6), 2.010(6); Pd(2)-O(7), 1.942(6); Pd(2)-O(8), 1.962(6); O(1)-Pd(1)-O(2), 92.7(3); O(3)-Pd(1)-O(4), 93.4(2); O(5)-Pd(2)-O(6), 93.7(3); O(7)-Pd(2)-O(8), 94.3(3).

$$[(hfac)Pd(taet)Pd(hfac)] + 2Hacac + 2NEt_3 \longrightarrow [(acac)Pd(taet)Pd(acac)] + 2HNEt_3hfac \quad (3)$$

Complex **1** was prepared by the modified method reported in literature.[5] A solution of $[Pd(hfac)_2]$ [4] and equal molar amount of proton-sponge (N,N,N',N'-tetramethyl-1,8,-naphthalenediamine, $C_{10}H_6[N(CH_3)_2]_2$) in MeOH was allowed to stand for several hours at room temperature. Complex **1** precipitated as rust-colored precipitate (yield 50%). Complex **1** and H_2taet were dissolved in CH_2Cl_2 with 1:1 molar ratio, and the mixture was stirred for 3 days at ambient temperature in the dark. The crude product was purified by silica-gel (Wako-gel C300) column chromatography using CH_2Cl_2 as an eluent. Two major bands eluted: The first fraction gave orange crystals of dinuclear complex $[Pd_2(taet)(hfac)_2]$ (**2**) in a 50% yield.[6] The second fraction gave a mononuclear complex [Pd(Htaet)(hfac)] (**2b**) in a 20% yield.[7] Crystals of **2** suitable for X-ray structure analysis were obtained by recrystallization from 1,2-dichloroethane/*n*-hexane.

Complex **2** and Hacac were dissolved in CH_2Cl_2 with molar ratio 1:2. A sample of Et_3N was added to the mixture in small excess. The mixture was stirred for 30 min. at ambient temperature. The resulting mixture was evaporated to dryness and the residue was washed with water to remove Et_3NH(hfac).

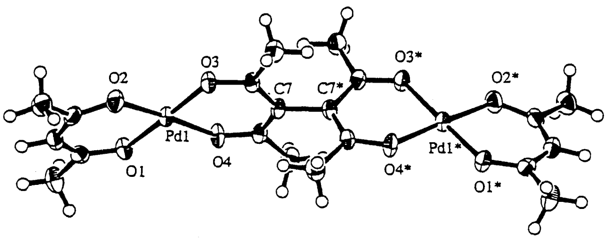


Figure 2. ORTEP drawing of [Pd_2(taet)$(acac)_2$] (**3**). Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (°) are as follows: Pd(1)-O(1), 1.983(3); Pd(1)-O(2), 1.984(3); Pd(1)-O(3), 1.984(3); Pd(1)-O(4), 1.981(3); O(1)-Pd(1)-O(2), 95.0(1); O(3)-Pd(1)-O(4), 92.7(1).

The crude product was recrystallized from CH_2Cl_2/Et_2O. The orange crystals of [Pd_2(taet)$(acac)_2$] (**3**) were yielded (80%).[8]

The crystal structure of **2** shows that the asymmetric unit consists of two crystallographically independent molecules.[9] Both molecules adopt the same dinuclear geometry with the bridging $taet^{2-}$ ligand and terminal bidentate oxygen-bounded $hfac^-$ ligands, and have no significant differences in bond lengths and angles. The structure of the one of molecules consisting of Pd(1) and Pd(2) is shown in Figure 1 and another molecule consisting of Pd(3) and Pd(4) is omitted for simplicity .[10] The four palladium atoms, Pd(1), Pd(2), Pd(3), and Pd(4) are in an approximately square-planar four-coordinated geometry with two oxygen atoms of $taet^{2-}$ and two oxygen atoms of $hfac^-$, and are displaced by 0.015, 0.008, 0.013, and 0.031 Å, respectively, from the least-squares planes of four surrounding oxygen atoms (the mean deviation for the least-squares planes is 0.014, 0.012, 0.025, and 0.016 Å, respectively). The Pd-O distances to $taet^{2-}$ ligands range from 1.939(6) to 1.978(6) Å ((Pd-O)av = 1.950(6) Å). The Pd-O distances to $hfac^-$ ligands range from 1.991(7) to 2.010(6)Å ((Pd-O)av = 2.000(4) Å) and are longer than those to $taet^{2-}$ ligands. Therefore, The $hfac^-$ ligands have weaker coordination ability than $taet^{2-}$ ligand, which reflects much acceleration on the second reaction (see Eq. (3)). The Pd-O distances to $hfac^-$ may be compared with 1.993(7) Å in [$Pd_2(hfac)_2(\mu\text{-}MeO)_2$] [5] and 2.014(6) and 1.996(7) Å in (hfac)[Pd(hfac)(bpy)] [11]

Figure 2 shows the molecular structure of **3**.[12] The molecule retains dinuclear geometry with the bridging $taet^{2-}$ ligand and terminal two $acac^-$ ligands. The crystallographic 2-fold axis passes across the C-C bond (C(7)-C(7*)) of bridging moiety in the $taet^{2-}$ ligand and complex **3** has a C_2 symmetry. The palladium atom Pd(1) is in a four-coordinated geometry, which is slightly distorted square-planar to tetrahedral, with two oxygen atoms of $taet^{2-}$ and two oxygen atoms of $acac^-$. The dihedral angle between the plane defined by atoms O(1), Pd(1), O(2), and O(3), Pd(1), O(4) is 9.1 °. The four Pd-O distances to the $taet^{2-}$ and $acac^-$ ligands have the same values within the standard deviations (from 1.981(3) to 1.984(3) Å). This suggests that $taet^{2-}$ and $acac^-$ have the same coordination ability.

In comparison with structure of **2** and **3**, the Pd-O distances to $taet^{2-}$ ligand in **3**, $(Pd\text{-}O)_{av}$ = 1.983(3) Å, are longer than those in **2**, $(Pd\text{-}O)_{av}$ = 1.950(6) Å. This indicates that the coordination competition between $acac^-$ and $taet^{2-}$ ligand in **3** causes the longer Pd-O distances to $taet^{2-}$ ligand in **3** than those in **2**, i.e. in the latter complex the coordination power of the $hfac^-$ ligand is weaker than that of the $acac^-$ ligand. The influence of the coordination competition is also observed in the ^1H NMR spectra. The chemical shift of methyl group of $taet^{2-}$ in **3**, δ = 1.96, is at upfield compared with that in **2**, δ = 2.01, which means that the coordination between Pd and $taet^{2-}$ in the case of $hfac^-$ is stronger than that in the case of $acac^-$.

Finally, from synthetic point of view, it is noteworthy that the reaction of **1** with H_2taet could occur spontaneously without base (see Eq. (2)) and the products retained the $hfac^-$ ligands. The μ-MeO groups in **1** can extract the protons of H_2taet and provide vacant coordination sites for a $taet^{2-}$ or a $Htaet^-$ ligand to give **2** or **2b**. On the other hand, the $hfac^-$ ligands in **1** can not extract the proton of H_2taet and are not displaced by H_2taet ligands. The nature of $hfac^-$ ligands due to lower pKa value of Hhfac than that of Hacac also was found in the second reaction (see Eq. (3)), which occurred to produce **3** in good yield immediately in the presence of the base (Et_3N) but not without base. The $hfac^-$ ligands in **2** can not extract the proton of Hacac but can be replaced by $acac^-$ easily. This suggests that complex **2** is good precursor for some other taet bridged dinuclear mixed ligand complexes with any bidentate ligands, which can be coordinate without deprotonation, such as diamine or diimine. The attempts are now underway.

The present work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan, under Grant No. 07454173 and by the Izumi Science and Technology Foundation, for which we express our thanks.

References and Notes

1 Y. Fukuda and K. Mafune, *Chem. Lett.*, **1988**, 697.

2 H. Kambayashi, J. Yuzurihara, Y. Masuda, H. Nakagawa, W. Linert, and Y. Fukuda, Z. *Naturforsch.*, **506**, 536(1995).

3 W. Linert, B. Pouresmaeil, V. Gutmann, K. Mafune, Y. Fukuda, and K. Sone, *Monatsh. Chem.*, **121**, 765(1990).

4 S. Okeya, S. Ooi, K. Matsumoto, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 1085(1981).

5 A. R. Siedle and L. H. Pignolet, *Inorg. Chem.*, **21**, 3090(1982).

6 [Pd_2(taet)$(hfac)_2$] (**2**): Found: C, 29.05; H, 1.64%. Calcd for $C_{20}H_{14}F_{12}O_8Pd_2$: C, 29.18; H, 1.71%. FAB-MS *m/z* 824 $(M+H)^+$, 616 (M - hfac + $H)^+$, 509 (M - Pd(hfac) + $H)^+$; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.01(s, 12H, CH_3), 6.26(s, 2H, CH). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 24.3(CH_3), 91.9(s, CH of $hfac^-$), 110.6(C-C of $taet^{2-}$), 114.6(q, *J*(C-F) = 284, CF_3), 174.9(q, *J*(C-F) = 35, $CF_3C{=}O$), 186.7($CH_3C{=}O$).

7 [Pd(Htaet)(hfac)] (**2b**): Found: C, 34.28; H, 2.77%. Calcd for $C_{15}H_{14}F_6O_6Pd$: C, 35.28; H, 2.76%. FAB-MS *m/z* 510 $(M+H)^+$, 302 (M - $hfac)^+$. Although the complex **2b** is by product in this synthesis, the complex is potential precursor for synthesis of any multinuclear complex or any dinuclear complex having different metal ion.

8 [Pd_2(taet)$(acac)_2$] (**3**): Found: C, 39.74; H, 4.35%. Calcd for $C_{20}H_{26}O_8Pd_2$: C, 39.56; H, 4.32%. ^1H NMR ($CDCl_3$, Me_4Si) δ 1.96(s, 12H, CH_3 of $taet^{2-}$), 2.08 (s, 12H, CH_3 of $acac^-$), 5.44(s, 2H, CH). ^{13}C NMR ($CDCl_3$, Me_4Si), δ 24.3 (CH_3 of $taet^{2-}$), 25.0 (CH_3 of $acac^-$), 100.5 (CH of $acac^-$), 111.0 (C-C of $taet^{2-}$), 186.3 (C=O of $taet^{2-}$), 186.8 (C=O of $acac^-$).

9 Crystal structure data for [Pd_2(taet)$(hfac)_2$] (**2**): $C_{20}H_{14}F_{12}O_8Pd_2$ (*Fw* = 823.11), monoclinic, *P*2/c, *a* = 14.73(1) Å, *b* = 11.62(2) Å, *c* = 32.67(1) Å, β = 92.93(6) °, *V* = 5582(9) $Å^3$, *Z* = 8, *D*(calcd) = 1.96 g/cm^3, *R* = 0.047 (*Rw* = 0.045) on 5240 reflection ($I > 3\sigma(I)$).

10 The structure data of one more Pd(3)-Pd(4) dinuclear unit : Pd(3)-O(9), 2.001(6); Pd(3)-O(10), 2.011(6); Pd(3)-O(11), 1.943(6); Pd(3)-O(12), 1.978(6); Pd(4)-O(13), 1.991(7); Pd(4)-O(14), 1.997(7); Pd(4)-O(15), 1.938(6); Pd(4)-O(16), 1.962(6); O(9)-Pd(3)-O(10), 93.0(3); O(11)-Pd(3)-O(12), 93.3(2); O(13)-Pd(4)-O(14), 94.1(3); O(15)-Pd(4)-O(16), 93.6(2).

11 A. R. Siedle, R. A. Newmark, A. A. Kruger, and L. H. Pignolet, *Inorg. Chem.*, **20**, 3399(1981).

12 Crystal structure data for [Pd_2(taet)$(acac)_2$] (**3**): $C_{20}H_{26}O_8Pd_2$ (*Fw* = 607.22), monoclinic, *C*2/c, *a* = 21.211(2) Å, *b* = 7.876(2) Å, *c* = 13.657(1) Å, β = 107.240(8) °, *V* = 2178.9(6) $Å^3$, *Z* = 4, *D*(calcd) = 1.85 g/cm^3, *R* = 0.033 (*Rw* = 0.025) on 1760 reflection ($I > 3\sigma(I)$).