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Synthesis and Molecular Structure of the Tetranuclear Complex $[(PPh_3)Pt(\mu_2\text{-}OAc)_2(\mu_3\text{-}OAc)Ag]_2$

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The reaction of *trans*-$[(PPh_3)PtCl_2]_2$ with AgOAc in HOAc gives the new tetranuclear complex $[(PPh_3)Pt(\mu_2\text{-}OAc)_2(\mu_3\text{-}OAc)Ag]_2$, in which the Ag and Pt atoms are bonded by bridging bi- and tri-coordinated acetate ligands, according to single crystal X-ray data.

Among the platinum–silver compounds documented to date,[1–4] only a few have a direct, unbridged Pt–Ag bond.[1–3] In most examples of such compounds, the Pt and Ag atoms are bonded by bridging ligands such as purine base, halide ions or diphosphines.[4] We report here the synthesis and X-ray structure determination of a new cluster bis[μ_3-acetato-μ_2-diacetato(triphenylphosphine)]diplatinum(II)disilver(I) $[(PPh_3)Pt(OAc)_3Ag]_2$. We believe this to be the first cluster with Pt and Ag atoms bonded by bi- and tri-coordinated acetate ligands.

The reaction of *trans*-$[(PPh_3)PtCl_2]_2$[5] **1** (0.1 mmol) with AgOAc (0.8 mmol) in HOAc solution (10 ml) (1 h at 20–40 °C under Ar atmosphere) was found to lead to $[(PPh_3)Pt(OAc)_3$-

Ag]$_2$ **2**† as shown in eqn. (1).

$$\underset{\mathbf{1}}{trans\text{-}[(PPh_3)PtCl_2]_2} + 6AgOAc \xrightarrow{HOAc} \underset{\mathbf{2}}{[(PPh_3)Pt(OAc)_3Ag]_2} + 4AgCl \quad (1)$$

Complex **2** was isolated from the reaction mixture after removal of HOAc and recrystallization of the residue from a large amount of hot benzene.

By contrast with the *trans*-isomer of **1**, *cis*-**1** reacts with AgOAc in HOAc solution or in a chlorinated solvent (CH_2Cl_2, $CHCl_3$, $C_2H_2Cl_4$) at ambient temperature to give complex $[(PPh_3)PtClOAc]_2$ **3**‡ as the main product [eqn. (2)].

$$\underset{\mathbf{1}}{cis\text{-}[(PPh_3)PtCl_2]_2} + 2AgOAc \xrightarrow{H_2C_2Cl_4} \underset{\mathbf{3}}{[(PPh_3)PtCl(OAc)]_2} + 2AgCl \quad (2)$$

According to IR and ^{1}H NMR data complex **3** was found, similarly to $[(Me_2PhP)PtCl(OAc)]_2$,[6] to contain two bridging acetate groups and terminal chloride ions. In a mixture of a chlorinated solvent and acetic acid, under conditions when *cis–trans* isomerization of the initial compounds **1** is possible, a mixture of complexes **2** and **3** was obtained.

According to X-ray data,§ molecular complex **2** consists of two symmetrically bonded binuclear fragments with a Pt—Ag distance of 2.898(2) Å (Fig. 1). This comparatively short Pt—Ag distance {compared with Pt—Ag 2.915 Å in $[Pt_3Ag(\mu\text{-}CO)_3(PPh_3)_5]ClO_4\cdot 2H_2O$[2] and 2.919, 2.927 Å in $[Pt_3Ag(O_3SCF_3)(\mu\text{-}CO)_3(PCy_3)_2(dppm)]$[3] (Cy = cyclohexyl, dppm = $Ph_2PCH_2PPh_2$)} cannot exclude the possible existence of weak metal—metal interaction. Dimerization of the $[(Ph_3P)Pt(\mu_2\text{-}OAc)_2(\mu_3\text{-}OAc)Ag]$ fragments occurs due to bonding between the Pt and Ag atoms *via* the tricoordinated acetate bridge. Hence, the existence of Pt—Ag bonding is not certain in this instance. The mean Ag—Ag(a) distance of 3.797 Å excludes direct interaction between these metal atoms. The arrangement of O and P atoms in the coordination environment of the Pt^{II} atoms is close to that expected for ideal square-planar [Pt, P, O(1), O(3), O(5) atoms are coplanar within 0.09 Å]. The Ag atom is displaced above this plane by 2.88 Å. The Ag—Pt—O(1), O(3), O(5) angles are in the range 79.9–95.7°. The Pt—Ag vector is almost normal to the coordination plane of the Pt atom. The interplanar angle between this plane and the plane formed by the Ag, Ag(a), O(4), O(4a) atoms is 93.5°.

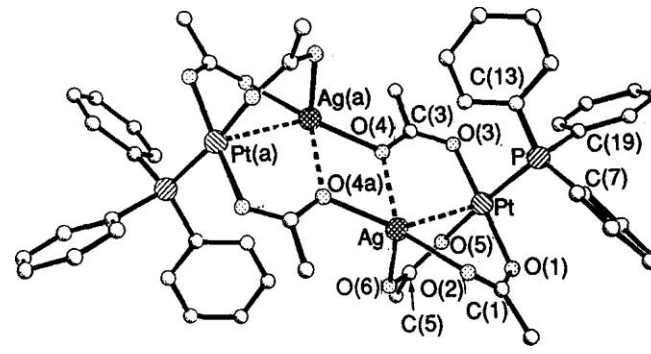

Fig. 1 The molecular structure of **2**. Important distances (Å) and bond angles (°): Pt···Ag 2.898(2), Ag···Ag(a) 3.797(3), Pt—P 2.216(4), Pt—O(1) 2.020(7), Pt—O(3) 2.030(8), Pt—O(5) 2.05(1), Ag—O(2) 2.356(8), Ag···O(4) 2.530(9), Ag—O(6) 2.37(1), Ag—O(4a) 2.33(1), P—C(7) 1.83(1), P—C(13) 1.85(1), P—C(19) 1.83(1); Ag···Pt—P 112.7(1), P—Pt—O(1) 92.2(3), P—Pt—O(3) 90.7(3), O(1)—Pt—O(3) 174.8(4), O(1)—Pt—O(5) 89.4(3), O(3)—Pt—O(5) 86.8(3), Ag···Pt—O(1) 87.2(3), Ag···Pt—O(3) 95.7(3) Ag···Pt—O(5) 79.9(3), O(4)···Ag—O(4a) 77.2(4)

The environment of the Ag atom consists of four oxygen atoms and one Pt atom. The silver atom is displaced by 0.533 Å above the plane O(2), O(4a), O(6) of the nearest oxygen atoms of the briding acetate ligands [distances Ag—O(2,4a,6) 2.33–2.37 Å]. The observed non-bonded distance between O(4) and the Ag atom is noticeably longer [2.530(9) Å] and may be ascribed to a weak interaction. Hence, we can consider the oxygen arrangement around the Ag atom as a distorted tetrahedral one.

On reaction with transition metal chloro compounds, complex **2** readily forms heteronuclear complexes retaining the initial coordination of the Pt atom. Thus, the reaction of complex **2** with $[\pi\text{-}C_3H_5PdCl]_2$ was found to give rise to the complex $\pi\text{-}C_3H_5Pd(OAc)_3Pt(PPh_3)$ **4**,[8] as shown in eqn. (3).

$$[\pi\text{-}C_3H_5PdCl]_2 + 2\underset{\mathbf{2}}{[(PPh_3)Pt(OAc)_3Ag]_2} \longrightarrow 2\underset{\mathbf{4}}{\pi\text{-}C_3H_5Pd(OAc)_3Pt(PPh_3)} + 2AgCl \quad (3)$$

Complex **5** $[(PPh_3)Pt(OAc)_2]_2$,[9] which cannot be obtained by the reaction of $Pt(OAc)_2$ and PPh_3,[10] was prepared by the reaction of $[(PPh_3)Pt(OAc)_3Ag]_2$ **2** with *cis*-$Re_2(OAc)_2Cl_4\cdot 2H_2O$ in dry C_6H_6 [eqn. (4)].

$$2 \xrightarrow{Re_2(OAc)_2Cl_4\cdot 2H_2O} \underset{\mathbf{5}}{[(PPh_3)Pt(OAc)_2]_2} \quad (4)$$

Thus, complex **2** may be used as a convenient starting compound for synthesis of various homo- and hetero-nuclear complexes.

† Complex **2** is soluble in $CHCl_3$, CH_2Cl_2, HOAc, *N*,*N*-dimethylformamide (DMF) and hot C_6H_6. It decomposes on exposure to light, slowly in the solid state and faster in solution, and is stable for a few months in darkness under Ar atmosphere. IR ν_{COO}/cm^{-1} 1585, 1540, 1440; ^{1}H NMR δ (CH_2Cl_2) 1.57 (s, 6H, μ_2-OAc), 2.06 (s, 3H, μ_3-OAc), 7.27 (m, 15H, Ph); ^{31}P NMR (rel. to H_3PO_4) δ 6.06 ($J_{Pt—P}$ 4652 Hz).

‡ The yield is 65–70% based on Pt. IR ν_{COO}/cm^{-1} 1580, 1440; ^{1}H NMR δ ($CDCl_3$) [2.06 (s), 1.54 (s), 1.51 (s)] (3H, μ_2-OAc, mixture of *cis*- and *trans*-isomers), 7.61 (m, 15H).

§ *Crystal data* for **2**: $Pt_2Ag_2P_3O_{18}C_{36}H_{42}$, M = 1484.7, triclinic, space group $P\bar{1}$, at 143 K, a = 11.049(2), b = 10.997(2), c = 11.158(2) Å, α = 97.54(3), β = 113.09(3), γ = 97.09(3)°, V = 1213.4(1.2) Å^3, Z = 1, ρ_c = 2.03(2) g cm^{-3}, μ(Mo-Kα) = 7.6 cm^{-1}, F(000) = 712. Using a Siemens P3/PC diffractometer [λ(Mo-Kα) = 0.7107 Å, graphite monochromator, 2θ < 52°, 143 K] 2674 unique reflections with $F > 4\sigma(F)$ were collected of the total of 2732 independent reflections. The structure was solved by direct methods and refined by the least-squares procedure in anisotropic approximation to R = 0.039, R_w = 0.042, GOF = 3.95. Weighting scheme $\omega^{-1} = \sigma^2(F)$. DIFABS[7] was used to correct absorption intensities. The H atoms, whose positions were calculated geometrically, were included in the calculations with fixed coordinates and isotopic thermal parameters U_{iso} = 0.08 Å^2. All calculations were carried out using SHELX PLUS programs. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1992, Issue No. 1.

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