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Unprecedented polymeric trifluoroacetate palladium–silver complexes: π-complex with η²- and η⁴-coordinated toluene, as well as a unique seventeen nuclear palladium–silver trifluoroacetate

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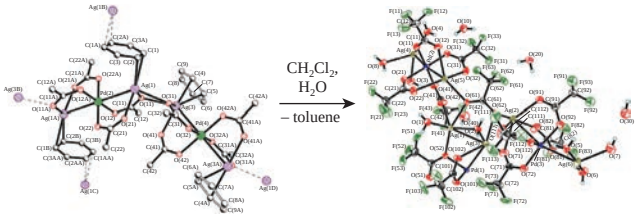
The first polynuclear heterodimetallic Pd^{II}–Ag^{I} trifluoroacetate π-complex with Ag^{I} η²- and η⁴-coordinated molecules of toluene, namely, $PdAg_2(\mu\text{-}TFA)_4(\eta^2\text{-}Tol)_2(\mu\text{-}\eta^4\text{-}Tol)]_n$ and $[Pd_2Ag_4(\mu\text{-}TFA)_8(\eta^2\text{-}Tol)_2(\mu\text{-}\eta^4\text{-}Tol)]_n$ (TFA = $OCOCF_3$, Tol = = toluene) as well as the unique seventeen nuclear Pd^{II}– Ag^{I} trifluoroacetate complex $Pd_5Ag_{12}(H_2O)_{16}(\mu\text{-}TFA)_8\cdot 7H_2O$ have been synthesized. Their solid-state structure was determined by X-ray method.



In recent years, carboxylate heterodimetallic complexes have attached considerable attention because of wide diversity of their structures and potent application.[1–8] The only one polymeric Pd–Ag heterometallic acetate complex $[PdAg_2(\mu\text{-}OAc)_3(HOAc)_2]_n$[6] was obtained. Thermal transformation of this complex produces palladium–silver alloy nanoparticles. To the best of our knowledge, no information of palladium-based heterometallic complexes with nuclearity more than four[6,9,10] and especially with π-coordinated ligands is still available in literature.

In this work we prepared the first heterometallic trifluoroacetate palladium–silver π-complexes $[PdAg_2(\mu\text{-}TFA)_4(\eta^2\text{-}Tol)_2(\mu\text{-}\eta^4\text{-}Tol)]_n$ **1** and $[Pd_2Ag_4(\mu\text{-}TFA)_8(\eta^2\text{-}Tol)_2(\mu\text{-}\eta^4\text{-}Tol)]_n$ **2** using similar synthetic approach, namely, the reaction of $PdCl_2$ with $Ag_2(\mu\text{-}TFA)_2$ in toluene except the test temperature† and their structure was determined.

The structure of complex **1** contains one crystallographically independent Pd atom and one independent Ag atom (Figure 1).‡ Pd atom lies on an inversion centre and adopts common square-planar coordination environment with the O–Pd–O angles lying within the long range of 88.90(7)–180.00(4)°, whereas in complex $Pd_3(\mu\text{-}OCOCX_3)_4(NO)_2(\eta^2\text{-}ArH)_2$ (X = F, Cl; ArH = toluene, benzene) the O–Pd–O angles lying within the short range of 88–92°.[12] The Pd–O distances in **1** are 1.999(2) and 2.006(2) Å. In the binary $Pd_3(\mu\text{-}OCOR)_6$ (R = CH_2Cl, CMe_3, C_6H_{11}), as an example, the Pd–O bond lengths are close

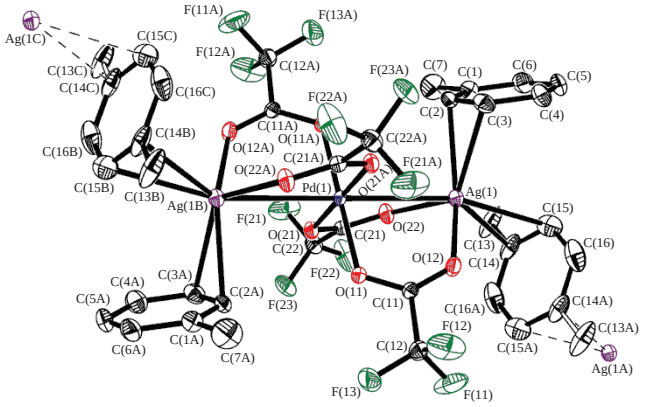


Figure 1 Section of chained structure **1**. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are not shown.

† *Complex $[PdAg_2(\mu\text{-}TFA)_4(\eta^2\text{-}Tol)_2(\mu\text{-}\eta^4\text{-}Tol)]_n$* **1**. A mixture of $PdCl_2$ (0.177 g, 1 mmol) and CF_3COOAg (0.44 g, 2 mmol) was dissolved in toluene (20 ml) and magnetically stirred in a shadowed flask at 17–18 °C for 24 h. The reaction solution was filtered and concentrated to 5 ml. After adding hexane (20 ml) on the wall of the reaction flask monocrystals suitable for X-ray investigation were found.

Synthesis of complex $[Pd_2Ag_4(\mu\text{-}TFA)_8(\eta^2\text{-}Tol)_2(\mu\text{-}\eta^4\text{-}Tol)]_n$ **2** was similar with the reaction temperature being 24–25 °C. Yield 0.32 g (67%). Found (%): Pd, 11.58; Ag, 22.39; C, 23.95; H, 1.65. Calc. for $Pd_2Ag_4C_{37}H_{24}F_{24}O_{16}$ (%): Pd, 11.66; Ag, 23.64; C, 24.35; H, 1.33. To prepare single-crystal sample of **2**, the mother solution was stored for 7 days at ambient temperature.

Synthesis of compound **2a** $[Pd_2Ag_4(\mu\text{-}TFA)_8(\eta^2\text{-}Benz)_2(\mu\text{-}\eta^4\text{-}Benz)]$ (Benz = benzene) was similar to that of **2** with using benzene instead of toluene. Yield 0.35 g (71%). Found (%): Pd, 11.58; Ag, 22.39; C, 22.00; H, 0.90. Calc. for $Pd_2Ag_4C_{34}H_{18}F_{24}O_{16}$ (%): Pd, 11.93; Ag, 24.20; C, 22.90; H, 1.02.

Monocrystals of complex $Pd_5Ag_{12}(H_2O)_{16}(\mu\text{-}TFA)_8\cdot 7H_2O$ **3** were formed on keeping solution of complex **2** in moist CH_2Cl_2 at 4 °C for 7 days.

‡ Experimental intensities were measured on a Bruker SMART APEX II diffractometer (graphite monochromated MoKα radiation, λ = 0.71073 Å) using ω-scan mode. The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[11]

Crystal data for **1**. Orange plate (0.40×0.35×0.08 mm), monoclinic, space group $P2_1/c$, at 150 K: a = 10.6990(5), b =19.9969(9) and c = = 8.5730(4) Å, β = 109.850(1)°, V = 1725.19(14) Å^3, Z = 2, d_{calc} = 2.023 g cm^{-3}. 18884 reflections were collected (2.27° < θ < 29.00°), absorption coefficient μ = 1.751 mm^{-1}. Data/restraints/parameters: 4578/0/243. 4578 independent reflections (R_{int} = 0.0240) and 4067 with $I > 2\sigma(I)$. The final refinement parameters were: R_1 = 0.0260, wR_2 = 0.0612 for reflections with $I > 2\sigma(I)$; R_1 = 0.0310, wR_2 = 0.0638 for all reflections; largest diff. peak/hole 0.708/–0.503 eÅ^{-3}. GOF = 1.039.

[1.987(6)–2.015(6) Å].[13] Coordination polyhedra of Ag atom may be regarded as distorted tetrahedra with π-bonded toluene occupying one position. The Ag(1)–O(12) and Ag(1)–O(22) bond lengths are equal to 2.323(2) and 2.389(2) Å, respectively. All trifluoroacetate ligands are bridging. They link the neighboring atoms of palladium and silver and form linear metal triad AgPdAg with bond angle of 179.999(1)° and Ag–Pd bond length of 3.020(2) Å. Each silver atom is bonded with both toluene molecules and the projections of Ag atoms on toluene ring planes are in close proximity to the centers of C(2)–C(3) and C(14)–C(15) bonds. Along with this, the η^2-coordinated ordered toluene molecule C(1)...C(7) is terminal, while the disordered on inversion center molecule C(13)…C(16) is η^4-coordinated to two Ag atoms, serves as bridging ligand bond neighboring triads and forms 1D-coordination polymer with the chains passing along *ac*-diagonals. The Ag–C distances vary within 2.461(2)–2.710(3) Å. Among them the distances between disordered molecules C(13)–C(16) are the longest.

Complex **2** was found to be Pd–Ag trifluoroacetatic π-complex with molecules of toluene with different ratio and position between metals and toluene molecules (Figure 2).‡ According to X-ray data, hexanuclear fragment consists of two triads. In triad I, $PdAg_2(\mu\text{-TFA})_4(\eta^2\text{-Tol})_2$, two toluene molecules η^2-coordinated to Ag are terminal. In triad II, $PdAg_2(\mu\text{-TFA})_4(\mu\text{-}\eta^4\text{-Tol})$, two crystallographically independent toluene molecules act as bridging

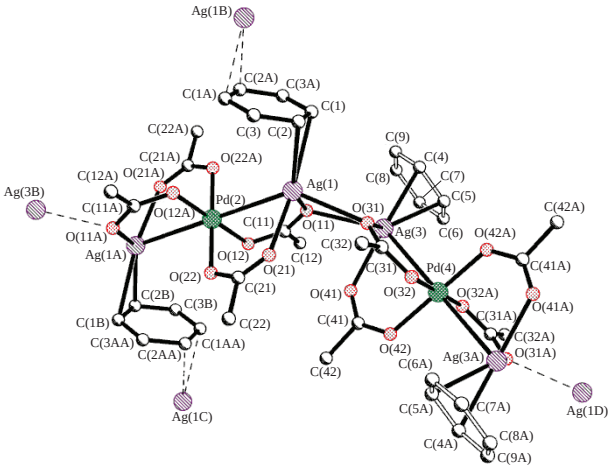


Figure 2 Section of 2D-structure **2**. Disordered trifluoromethyl substituents and methyl groups of toluene molecules as well as hydrogen atoms are not shown.

Crystal data for **2**. Orange needle (0.18×0.10×0.01 mm), triclinic, space group $P\bar{1}$, at 150 K: a = 8.5723(13), b = 11.2795(17) and c = = 15.005(2) Å, α = 75.790(2),° β = 77.300(2)°, γ = 68.180(2)°, V = = 1292.3(3) Å^3, Z = 1, d_{calc} = 2.345 g cm^{-3}. 13 163 reflections were collected (1.98° < θ < 27.99°), absorption coefficient μ = 2.318 mm^{-1}. Data/restraints/parameters: 6201/596/532. 6201 independent reflections (R_{int} = 0.0322) and 4953 with $I > 2\sigma(I)$. The final refinement parameters were: R_1 = 0.0525, wR_2 = 0.1401 for reflections with $I > 2\sigma(I)$; R_1 = 0.0663, wR_2 = 0.1520 for all reflections; largest diff. peak/hole 3.414/–1.894 eÅ^{-3}. GOF = 1.027.

Crystal data for **3**. Orange plate (0.30×0.25×0.10 mm), orthorhombic, space group *Pbcn*, at 183 K: a = 16.0631(18), b = 18.088(2) and c = = 41.329(5) Å, V = 12008(2) Å^3, Z = 4, d_{calc} = 2.615 g cm^{-3}. 105 757 reflections were collected (2.25° < θ < 28.00°), absorption coefficient μ = 2.832 mm^{-1}. Data/restraints/parameters: 14482/495/995. 14 482 independent reflections (R_{int} = 0.0496) and 11 997 with $I > 2\sigma(I)$. The final refinement parameters were: R_1 = 0.0368, wR_2 = 0.1208 for reflections with $I > 2\sigma(I)$; R_1 = 0.0483, wR_2 = 0.1330 for all reflections; largest diff. peak/hole 2.177/–1.144 eÅ^{-3}. GOF = 1.006.

CCDC 1437770–1437772 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

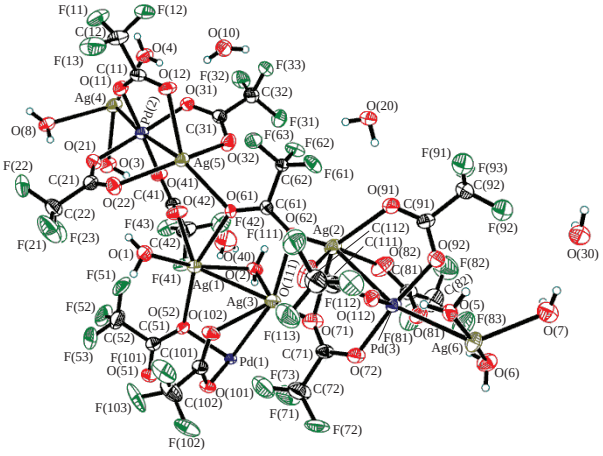


Figure 3 Asymmetric unit in the structure of **3**. Displacement ellipsoids are drawn at 50% probability level. Minor components of disordered CF_3 groups are not shown.

ligands and are η^4-coordinated to the pairs of centrosymmetrically related silver atoms. These adjacent triads I and II are bonded by O(11) and O(31) atoms of two independent trifluoroacetate ligands forming two bridges Ag(1)–O(11)–Ag(3) and Ag(1)–O(31)–Ag(3). Distances Ag–O lie within 2.360(5)–2.576(5) Å. In contrast to **1**, crystal packing in **2** is a 2D polymer with the layers perpendicular to crystallographic *b* axis. In the course of dissolution of **2** in moist CH_2Cl_2, loss of toluene molecules occurs with formation of the first seventeen nuclear heterometallic trifluoroacetate complex $Pd_5Ag_{12}(H_2O)_{16}(\mu\text{-TFA})_8\cdot 7H_2O$ **3** (Figure 3).‡ Its structure contains three crystallographically independent atoms of palladium, one of which is sited on inversion center. All of them adopt ordinary square-planar coordination formed only by trifluoroacetate ligands. The Pd–O distances lie within 1.992(4)–2.009(4) Å. Of interest, in the structure **3** all trifluoroacetate groups act as bridging ligands and link neighboring Pd···Ag or Ag···Ag atom pairs, but not Pd···Pd pairs. Note that in complex **3**, hexanuclear fragment consists of two triads Ag(4)–Pd(2)–Ag(5) (triad III) and Ag(2)–Pd(3)–Ag(6) (triad IV) with bond angles [170.850(19) and 160.877(19)°, respectively] more narrow than in **1** and **2**. In these triads Ag(5) and Ag(2) are bonded by only one trifluoroacetic bridging bond with distances Ag(5)–O(61) of 2.495(3) Å and Ag(2)–O(62) of 2.471(3) Å. This bond has been strengthened as a result of forming extra bonds O(61)–Ag(1) [2.544(3) Å] and O(62)–Ag(3) [2.566(3) Å]. All six silver atoms occupy general positions and exhibit coordination numbers equal to 6 [Ag(1), Ag(2), Ag(5), Ag(6)] or 5 [Ag(3), Ag(4)]. Their coordination environment represents either distorted octahedra or distorted trigonal bipyramid formed by bridging carboxylate ligands, bridging and terminal water molecules. The distances Ag–O($COCF_3$) vary within 2.398(4)–3.022(4) Å, while Ag–OH_2 bond lengths are 2.246(4)–2.812(4) Å. The crystal packing in **3** is 3D polymer with complicated system of hydrogen bonds [2.724(5)–2.970(5) Å].

In conclusion, the first heterometallic trifluoroacetate Pd–Ag π-complexes with η^2- and η^4-coordinated molecules of toluene were synthesized. Compounds **1** and **2** represent 1D and 2D coordination polymers, respectively. The unique seventeen nuclear Pd–Ag trifluoroacetate comprising complicated bridging system from trifluoroacetate ligands and H_2O molecules has formed 3D polymer. In all of the complexes, the Ag–Pd–Ag triads serve as a function of the structure-determining building block. The obtained complexes are of interest not only for fundamental coordination chemistry, but also as starting materials for the synthesis of Pd–Ag heterometallic nanomaterials with different Pd–Ag content.

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