

The first heterodimetallic palladium–rare-earth metal complexes $\text{Pd}_2^{\text{II}}\text{Sm}_2^{\text{III}}(\mu, \eta^2\text{-OOCMe})_2(\mu\text{-OOCMe})_8\text{L}_2$ ($\text{L} = \text{OH}_2, \text{THF}$): synthesis and crystal structure

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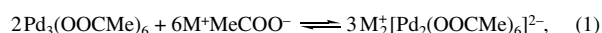
The title complexes were synthesised and structurally characterised by single-crystal X-ray diffraction analysis.

Palladium(II)–transition metal complexes are of both academic and practical interest, particularly, as precursors of palladium nanoalloys¹ and mixed-metal catalysts.² Reported data on the Pd^{II}-based heterometallic complexes are scanty. Most of them contain halide bridges and/or organic N- and P-donor ligands, which can pose difficulties in the preparation of metallic nanoparticles. In view of the synthesis of mixed-metal nanomaterials, the organosoluble Pd^{II}-based heterometallic complexes with easily removable carboxylate ligands (acetate, pivalate, *etc.*) show considerable promise. Of special interest are palladium(II)–rare-earth(III) carboxylate complexes, which were unknown previously.

The CSD contains only two records for Pd^{II}-based purely acetate complexes with post-transition metals, $\text{Pd}_2\text{Cd}_2(\mu\text{-OOCMe})_8(\text{HOOCMe})_2$ ³ and $\text{PdTi}(\mu\text{-OCOMe})_4(\text{OCOMe})$,⁴ but none of the complexes with transition or rare-earth metals.

Here, we propose a convenient protocol for the synthesis of unprecedented palladium(II)–rare-earth(III) acetate complexes exemplified by the preparation and characterization by elemental analysis, IR spectrum and single-crystal X-ray diffraction structural investigation of tetranuclear complexes $\text{Pd}_2\text{Sm}_2(\mu\text{-OOCMe})_8(\mu, \eta^2\text{-OOCMe})_2(\text{OH}_2)_2 \cdot 2\text{HOOCMe}$ **1** and $\text{Pd}_2\text{Sm}_2(\mu\text{-OOCMe})_8(\mu, \eta^2\text{-OOCMe})_2(\text{thf})_2 \cdot \text{THF}$ **2**.

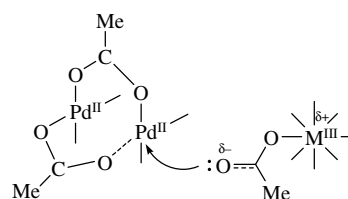
The palladium(II) acetate $\text{Pd}_3(\mu\text{-OOCMe})_6$ was used as a starting compound. The trinuclear cyclic structure of this complex is poorly reactive but is readily cleaved by nucleophilic agents such as alkaline, NR_4^+ , or $[(\text{Ph}_3\text{P})_2\text{N}]^+$ acetates.⁵ The coordination vacancies that arose in the Pd^{II} coordination sphere upon the acetate bridge cleavage are filled with the attacking acetate groups to produce the dinuclear $[\text{Pd}_2(\text{OCOMe})_6]^{2-}$ [equation (1)] and mononuclear $[\text{Pd}(\text{OCOMe})_4]^{2-}$ anionic complexes [equations (1), (2)]:



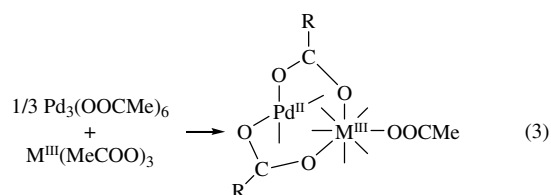
which exist in solution as close ion pairs with the corresponding cations ($\text{M}^+ = \text{Na}^+, \text{K}^+, \text{NR}_4^+, [(\text{Ph}_3\text{P})_2\text{N}]^+$).

By analogy with reactions (1) and (2), we expected the trivalent rare-earth metal acetates to serve as a source of terminal

acetate groups to perform a nucleophilic attack on the Pd^{II} acetate molecule:



Should this be the case, then not only the close ion pair but also a covalently linked mixed-metal complex can be formed [equation (3)].



Our experiments showed that $\text{Pd}_3(\text{OOCMe})_6$ readily reacts with the samarium(III) acetate $\text{Sm}(\text{OOCMe})_3 \cdot 4\text{H}_2\text{O}$ in an AcOH solution[†] to form crystalline tetranuclear mixed-metal complexes $\text{Pd}_2\text{Sm}_2(\mu\text{-OOCMe})_8(\mu, \eta^2\text{-OOCMe})_2(\text{OH}_2)_2 \cdot 2\text{HOOCMe}$ **1** and $\text{Pd}_2\text{Sm}_2(\mu\text{-OOCMe})_8(\mu, \eta^2\text{-OOCMe})_2(\text{thf})_2 \cdot \text{THF}$ **2** depending on the procedure of separation and crystallization.

The X-ray study[‡] revealed that complexes **1** (Figure 1) and **2** (Figure 2) contain the square-planar moiety $[\text{Pd}(\mu\text{-OOCMe})_4]$ as a structure-determining building block.

The palladium atom in each of the complexes is linked to the complementary metal atom through four carboxylate bridges. The molecules of both complexes are built of two Pd–Sm ‘chinese lantern’ dinuclear units $\text{PdSm}(\mu\text{-OOCMe})_4$ connected through two μ, η^2 -acetate bridges [for **1**: Sm...Sm, 4.124(1) Å; Sm–O, 2.363(7)–2.378(8) Å; Pd–O, 1.990(7)–1.995(7) Å; for **2**:

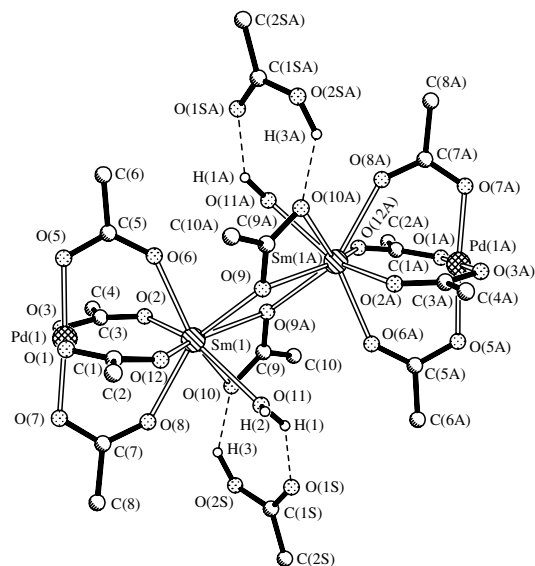


Figure 1 Molecular structure of complex 1.

† Palladium(II) acetate $\text{Pd}_2(\text{OOCMe})_4$ (prepared by the oxidation of Pd black with HNO_3 in acetic acid according to a procedure⁶) (224 mg, 1 mmol based on Pd) and $\text{Sm}(\text{OOCMe})_3 \cdot 4\text{H}_2\text{O}$ (analytical grade, Reakhim, Russia) (400 mg, 1 mmol) in glacial acetic acid (10 ml) was stirred under reflux for 1.5 h. The reaction solution was concentrated at 120 °C in an argon flow to a volume of 5 ml and then slowly cooled to room temperature. After 6 h, the precipitated yellow crystals of complex 1 were separated from the mother liquid and used for an X-ray study. Yield, 120 mg (20% based on Pd). Found (%): C, 27.08; H, 3.75. Calc. for $\text{C}_{28}\text{H}_{46}\text{O}_{22}\text{Pd}_2\text{Sm}_2$ (%): C, 26.94; H, 3.71. IR (KBr, ν/cm^{-1}): 3445 (vs, broad), 2925 (m), 2864 (w), 1684 (w), 1622 (s), 1558 (s), 1456 (s), 1414 (s), 1385 (m), 1344 (w), 1283 (w), 1049 (w), 1020 (w), 951 (w), 673 (m), 622 (w). The mother liquid after separation of crystals 1 was evaporated to dryness. The residue was several times dissolved in benzene (10 ml) followed by evaporation to dryness. The acetic acid-free solid residue was crystallised from THF to produce the yellow-orange crystals of complex 2 in a yield of 375 mg (60% based on Pd). The crystals of 2 readily lose the THF crystallization molecule upon drying. Found (%): C, 27.01; H, 3.72. Calc. for $\text{C}_{28}\text{H}_{46}\text{O}_{22}\text{Pd}_2\text{Sm}_2$ (%): C, 26.94; H, 3.71. IR (KBr, ν/cm^{-1}): 2984 (w), 2870 (w), 1558 (vs, broad), 1449 (vs), 1415 (vs), 1343 (m), 1051(w), 1022 (m), 939 (w), 877 (w), 670 (m), 645 (w), 620 (w), 469 (w).

‡ Crystal data for 1 and 2. Data collection was performed on an Enraf Nonius CAD 4 diffractometer (graphite monochromator, $\text{MoK}\alpha$ radiation, $\lambda = 0.71073$ Å, ω -scans).

For 1: $\text{C}_{28}\text{H}_{46}\text{O}_{22}\text{Pd}_2\text{Sm}_2$, $M = 1260.04$, space group $P2_1/n$, $a = 8.8190(18)$, $b = 19.903(4)$ and $c = 11.820(2)$ Å, $\beta = 90.72(3)^\circ$ at 293 K, $V = 2074.5(7)$ Å³, $Z = 4$ ($Z' = 8$), number of reflections collected 4414, independent reflections 1573 with $F^2 > 2\sigma(I)$, $d_{\text{calc}} = 2.017$ g cm⁻³, $\mu = 3.728$ cm⁻¹, $R_1 = 0.0351$, $wR_2 = 0.0753$.

For 2: $\text{C}_{32}\text{H}_{54}\text{O}_{23}\text{Pd}_2\text{Sm}_2$, $M = 1320.25$, space group $Pca2_1$, $a = 21.214(4)$, $b = 13.610(3)$ and $c = 35.394(7)$ Å, at 293 K, $V = 10219(4)$ Å³, $Z = 8$, number of reflections collected 8133, independent reflections 3338 with $F^2 > 2\sigma(I)$, $d_{\text{calc}} = 1.716$ g cm⁻³, $\mu = 3.027$ cm⁻¹, $R_1 = 0.0471$, $wR_2 = 0.1018$.

The structures were solved by the direct method and refined by the full-matrix least-squares technique against F^2 with the anisotropic displacement parameters for all non-hydrogen atoms except for the O and C atoms of disordered THF molecules in 2. The hydrogen atoms of the coordinated H_2O molecules and HOOCMe molecules of crystallization in complex 1 were revealed by the Fourier difference synthesis and were not refined. The other hydrogen atoms in the molecules of 1 and 2 were placed geometrically and included in the structure factors calculation in the riding motion approximation. All the data reduction and further calculations were performed using the SHELXTL-97 program package.⁷

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 289401 and 289402. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

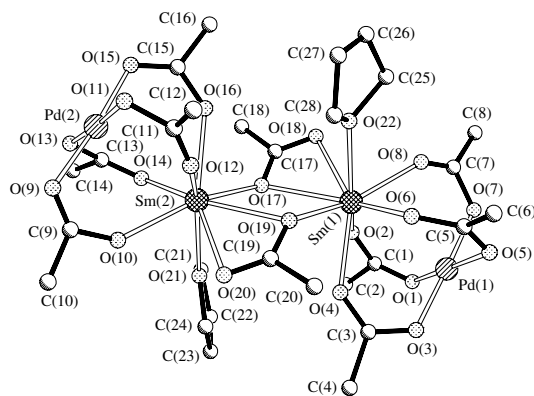


Figure 2 Molecular structure of complex 2. The THF molecule of crystallization is not shown.

$\text{Sm} \cdots \text{Sm}$, 4.132(3) Å; $\text{Sm}-\text{O}$, 2.33(4)–2.62(4) Å; $\text{Pd}-\text{O}$, 1.99(3)–2.06(4) Å].

In both of the 'chinese lantern' fragments the Pd–Sm metal distances [$\text{Pd}-\text{Sm}$, 3.2047(9) Å for 1, 3.218(4), 3.228(4) Å for 2] are much shorter than the sum of the van der Waals radii of the corresponding metals (*cf.* $\text{Pd}-\text{Sm}$, 4.38 Å), being close to the sum of the metal covalent radii (*cf.* $\text{Pd}-\text{Sm}$, 2.90 Å), implying a weak metal–metal interaction. The detailed nature of the metal–metal interactions in complexes 1 and 2 requires additional magnetic and quantum chemical studies, which are in progress now.

Note that complex 1 contains two MeCOOH molecules of crystallization, which are connected to the coordinated H_2O molecules and the $\mu, \eta^2\text{-OOCMe}$ ligands by short hydrogen bonds [$\text{H}(1) \cdots \text{O}(1s)$, 1.93 Å; $\text{O}(1s) \cdots \text{O}(11)$, 2.758 Å; $\text{O}(10) \cdots \text{H}(3)$, 1.81 Å; $\text{O}(10) \cdots \text{O}(2s)$, 2.676 Å].

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