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Synthesis, crystal structure and thermal redox transformations of palladium(II)–alkaline earth tetraacetate-bridged lantern complexes $Pd^{II}(\mu\text{-}OOCMe)_4M^{II}(HOOCMe)_4$ (M = Ca, Sr, Ba)

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The title complexes were synthesised, structurally characterised with single-crystal X-ray diffraction and thermally converted into Pd^0 and MCO_3 solids.

Earlier,[1,2] we synthesised and structurally characterised by X-ray diffraction a series of the heterobimetallic Pd^{II}-based tetraacetate-bridged complexes containing transition and post-transition metals $Pd^{II}(\mu\text{-}OOCMe)_4M^{II}L$ (M = Mn, Co, Ni or Zn; L = MeCN or OH_2). More recently, we found[3] that the complex $Pd^{II}(\mu\text{-}OOCMe)_4Zn^{II}(OH_2)$ with a post-transition metal, Zn, is readily reduced to afford a PdZn nanoalloy catalyst under surprisingly mild conditions (150 °C, 5–10% H_2/He). In this connection, it was of interest to study the chemical behaviour of the main group metal analogues, which cannot basically be reduced with H_2 under mild conditions. Reductive decomposition of such complexes is expected to form Pd metal particles combined with non-transition metal oxides or carbonates, which could be of interest for catalysis. Several Pd^{II} acetate complexes with alkaline-earth metals were briefly reported as early as 1968;[4] however, the structure, chemical behaviour and detailed synthesis of these compounds are still unknown.

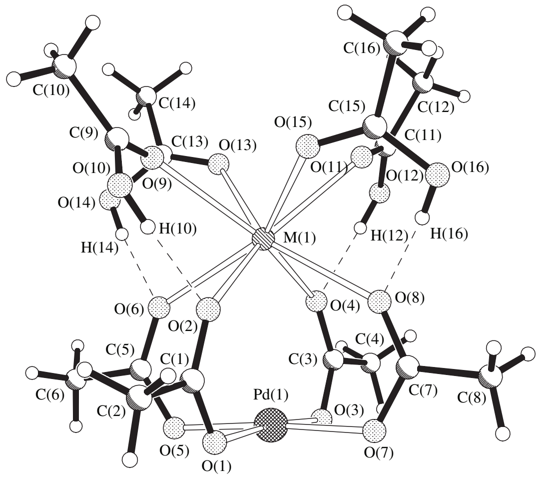

Figure 1 Molecular structure of the complex $Pd(\mu\text{-}OOCMe)_4M(HOOCMe)_4$ (**1**, M = Ca; **2**, M = Sr; **3**, M = Ba). Selected bond distances (Å) for **1**–**3**. **1**: Ca(1)···Pd(1) 3.291(4), Pd(1)–O(1) 1.997(4), Pd(1)–O(3) 1.991(4), Pd(1)–O(5) 2.000(3), Pd(1)–O(7) 2.001(3), Ca(1)–O(2) 2.465(4), Ca(1)–O(4) 2.458(4), Ca(1)–O(6) 2.462(4), Ca(1)–O(8) 2.465(4), Ca(1)–O(9) 2.516(4), Ca(1)–O(11) 2.462(4), Ca(1)–O(13) 2.517(4), Ca(1)–O(15) 2.494(4). **2**: Sr(1)···Pd(1) 3.3464(13), Pd(1)–O(1) 1.993(7), Pd(1)–O(3) 1.989(7), Pd(1)–O(5) 2.004(7), Pd(1)–O(7) 1.992(7), Sr(1)–O(2) 2.565(7), Sr(1)–O(4) 2.569(8), Sr(1)–O(6) 2.572(7), Sr(1)–O(8) 2.571(7), Sr(1)–O(9) 2.592(7), Sr(1)–O(11) 2.583(7), Sr(1)–O(13) 2.611(8), Sr(1)–O(15) 2.606(8). **3**: Ba(1)···Pd(1) 3.5701(12), Pd(1)–O(1) 1.987(5), Pd(1)–O(3) 1.998(5), Pd(1)–O(5) 2.002(5), Pd(1)–O(7) 2.001(5), Ba(1)–O(2) 2.774(6), Ba(1)–O(4) 2.789(6), Ba(1)–O(6) 2.770(6), Ba(1)–O(8) 2.749(5), Ba(1)–O(9) 2.774(6), Ba(1)–O(11) 2.775(7), Ba(1)–O(13) 2.794(3), Ba(1)–O(15) 2.831(6).

Herein, we report on the synthesis, structure characterisation and thermal redox transformations of the Pd^{II}-based acetate complexes containing Ca^{II}, Sr^{II} and Ba^{II} as complementary metals. We found that the synthetic procedure[2] proposed for the synthesis of the heterobimetallic Pd^{II}-based complexes with transition and post-transition metals can be extended to alkaline-earth acetates. Our experiments showed that Pd^{II} acetate reacts with the alkaline-earth acetates in hot acetic acid according to the stoichiometry [equation (1)] affording crystalline tetraacetate-bridged complexes **1**–**3** in 85–90% yields.[†]

$$Pd_3(\mu\text{-}OOCMe)_6 + 3M(OOCMe)_2 + 12MeCOOH \rightarrow 3PdM(OOCMe)_4(HOOCMe)_4 \qquad (1)$$

1 M = Ca
2 M = Sr
3 M = Ba

1–**3**

The X-ray diffraction study[‡] showed that complexes **1**–**3** have virtually identical lantern-like structures (Figure 1). The Pd and M atoms are linked by four μ-acetate groups [Pd–O

[†] *Syntheses*. **1**: A suspension of palladium(II) acetate $Pd_3(OOCMe)_6$ (449 mg, 2 mmol based on Pd) and $Ca(OOCMe)_2$ (316 mg, 2 mmol) in acetic acid (20 ml) was stirred at 90 °C for 40 min until complete dissolvation. The solution that formed was evaporated on a rotary evaporator to 10 ml and kept at room temperature to crystallization. The peach-coloured crystals of the title complex were filtered off and used for X-ray diffraction study. Evaporation of the mother liquid gave an additional portion of the complex. The dry residue was dissolved in hot benzene and precipitated with hexane. Total yield 1084 mg (87%). IR, ν/cm^{-1}: 3430 (w), 2629 (w), 2577 (w), 1707 (s), 1627 (s), 1545 (w), 1433 (s), 1376 (m), 1350 (w), 1296 (s), 1050 (m), 1017 (m), 956 (m), 697 (s), 622 (m), 540 (w), 461 (m). Found (%): C, 30.66; H, 4.51. Calc. for $PdCaC_{16}O_{16}H_{28}$ (%): C, 30.85; H, 4.53.

2 was prepared similarly from $Pd_3(OOCMe)_6$ (449 mg, 2 mmol based on Pd) and $Sr(OOCMe)_2\cdot 1/2H_2O$ (429 mg, 2 mmol). Yield 1140 mg (85%). IR, ν/cm^{-1}: 3435 (w), 2625 (w), 2574 (w), 1704 (s), 1636 (s), 1521 (w), 1414 (s), 1376 (m), 1349 (w), 1298 (s), 1049 (m), 1020 (m), 960 (m), 694 (s), 621 (m), 540 (w), 461 (m). Found (%): C, 28.49; H, 4.17. Calc. for $PdSrC_{16}O_{16}H_{28}$ (%): C, 28.66; H, 4.21.

3 was prepared similarly from $Pd_3(OOCMe)_6$ (449 mg, 2 mmol based on Pd) and $Ba(OOCMe)_2\cdot 2H_2O$ (583 mg, 2 mmol). Yield 1296 mg (90%). IR, ν/cm^{-1}: 3415 (w), 2616 (w), 2556 (w), 1700 (s), 1639 (s), 1526 (w), 1412 (s), 1375 (m), 1347 (w), 1301 (s), 1047 (m), 1012 (m), 895 (m), 695 (s), 621 (m), 461 (m). Found (%): C, 26.58; H, 3.89. Calc. for $PdBaC_{16}O_{16}H_{28}$ (%): C, 26.69; H, 3.92.

1.991(4)–2.001(3) Å for **1**, 1.989(7)–2.004(7) Å for **2** and 1.987(5)–2.002(5) Å for **3**], and the Pd···M distances are 3.291(4), 3.346(1) and 3.570(1) Å for **1**, **2** and **3**, respectively. The Pd atoms have a square-plane coordination (deviations of the Pd atom from the O_4 plane are 0.08, 0.11 and 0.12 Å in **1**, **2** and **3**, respectively). The coordination sphere of the alkaline-earth atoms is a slightly distorted square antiprism formed by four O atoms of the bridging acetate groups [Ca–O 2.458(4)–2.465(4) Å, Sr–O 2.565(7)–2.572(7) Å, Ba–O 2.749(5)–2.789(6) Å] and four O atoms of the coordinated acetic acid molecules [Ca–O 2.462(4)–2.517(4) Å, Sr–O 2.583(7)–2.611(8) Å, Ba–O 2.774(6)–2.831(6) Å]. The structure involves short intramolecular hydrogen bonds between the H atoms of the terminal MeCOOH molecules and the O atoms of the bridging $MeCOO^-$ anions, forming six-member metallocycles with close M–O distances. The parameters of the H-bonds are virtually independent of the alkaline earth metal (OH···O 2.594–2.611 Å, 2.598–2.619 Å, 2.592–2.615 Å for **1**, **2** and **3**, respectively). Meantime, the Pd···M and M–O distances in the molecules of **1**–**3** are different and increase in parallel to the M covalent radii in the series Ca–Sr–Ba.

The structures of similar tetraacetate-bridged complexes of alkaline-earth metals are not available. According to CSD (version 5.28, November 2006; update 1, January 2007), the single comparable compound is the trinuclear tetraacetate-bridged complex $Au_2(\mu\text{-}OOCMe)_8Sr$,[8] in which the bond distances between the Sr atom and bridging acetate ligands [Sr–O 2.577(5)–2.596(6) Å] are nearly the same as those in the molecule of **2**.

Table 1 XRD data for the solid residue after thermal decomposition of complex **1** at 500 °C.

Decomposition product		$CaCO_3$ [83-0578][a]		Pd [46-1043][a]	
d/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)
3.0200	100	3.0345	100		
2.4850	20	2.4943	15		
2.2500 (br.)	100	2.2841	15	2.2458	100
2.0950	20	2.0940	15		
1.9340 (br.)	30	1.9269	5	1.9451	60
1.8750	20	1.8747	20		
1.6000	10	1.6037	10		
1.5250	10	1.5249	5		
1.4750	5	1.4728	2		

[a] Indexed by the TREOR90 program.[9]

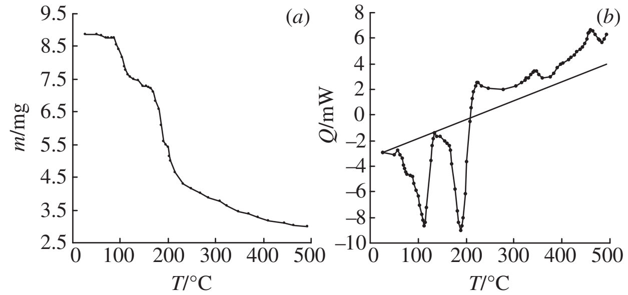

Figure 2 DTA-TG data for complex **1**: (*a*) weight loss curve; (*b*) heat flux curve.

According to DTA-TG data,[§] the thermal transformations of complex **1** on heating under Ar [Figure 2(*a*),(*b*)] occur as follows: (i) splitting of the intramolecular hydrogen bonds at 50–90 °C without weight change (shoulder in the first endotherm); (ii) two-step removal of the coordinated acetic acid molecules at 90–150 (weight loss of 17.9±1.0%, ~2MeCOOH molecules, the first endotherm) and 160–200 °C [weight loss of 20.1±1.0%, the rest MeCOOH molecules, the second endotherm, Figure 2(*b*)] with a total weight loss of 38.0±1.0% (calculated for 4MeCOOH molecules is 38.5%); (iii) gradual transformation of the coordinated acetate anions to carbonate anions with a weight loss of 28.2%.

The total weight loss upon heating of the complex to 500 °C (66.2±1.5%) corresponds to its transformation to Pd metal and $CaCO_3$ (calculated 66.8%):

$$PdCa(OOCMe)_4(HOOCMe)_4 \longrightarrow Pd^0 + CaCO_3 + 4MeCOOH + \text{organic products}^{\P} \qquad (2)$$

X-ray powder diffraction data[††] confirmed that the final products of decomposition of complex **1** at 500 °C are Pd metal and $CaCO_3$ (Table 1).

Note that the reflections from Pd metal are much broader than those from $CaCO_3$. From the half-widths of the diffraction lines, using the Scherrer equation $\beta = K\lambda/L\cos\theta$, the average size of Pd crystallites was estimated at 50–100 nm, while estimate for the carbonate crystallites is at least 10 μm. Hence, the solid materials produced by thermal decomposition of complex **1** seem Pd nanoparticles supported on alkaline-earth carbonates.

Complexes **1**–**3** readily react with H_2 both in solution and in a solid phase, resulting in the reduction of the constituent palladium(II) to Pd metal and H-loaded Pd metal phases, whereas the alkaline-earth part of the complexes remains as the M^{II} acetates even upon heating under H_2 at 250 °C.

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[‡] *Crystal data for* **1**–**3**. Data collection was performed on a Bruker P4 diffractometer at room temperature (graphite monochromator, MoKα radiation, $\lambda = 0.71073$ Å, ω-scans, $2\theta_{max} = 52°$).

For **1**: $C_{16}H_{28}CaO_{16}Pd$, $M = 622.86$, space group $P\bar{1}$, $a = 10.539(11)$, $b = 11.680(3)$ and $c = 11.785(3)$ Å, $\alpha = 89.15(3)°$, $\beta = 69.67(4)°$, $\gamma = 73.09(3)°$, $V = 1295.5(14)$ Å^3, $Z = 2$, number of reflections collected 5046, independent reflections 4343 with $F^2 > 2\sigma(I)$, $d_{calc} = 1.597$ g cm^{-3}, $\mu = 0.984$ cm^{-1}, $R_1 = 0.0577$, $wR_2 = 0.1548$.

For **2**: $C_{16}H_{28}SrO_{16}Pd$, $M = 670.40$, space group $P\bar{1}$, $a = 10.6431(15)$, $b = 11.732(2)$ and $c = 11.8476(18)$ Å, $\alpha = 89.064(8)°$, $\beta = 69.95(5)°$, $\gamma = 73.08(7)°$, $V = 1323.8(4)$ Å^3, $Z = 2$, number of reflections collected 5125, independent reflections 3130 with $F^2 > 2\sigma(I)$, $d_{calc} = 1.682$ g cm^{-3}, $\mu = 2.762$ cm^{-1}, $R_1 = 0.0704$, $wR_2 = 0.1270$.

For **3**: $C_{16}H_{28}BaO_{16}Pd$, $M = 720.12$, space group $P\bar{1}$, $a = 11.492(3)$, $b = 11.565(3)$ and $c = 11.602(2)$ Å, $\alpha = 89.992(11)°$, $\beta = 80.234(12)°$, $\gamma = 60.263(11)°$, $V = 1313.1(5)$ Å^3, $Z = 2$, number of reflections collected 4863, independent reflections 4006 with $F^2 > 2\sigma(I)$, $d_{calc} = 1.821$ g cm^{-3}, $\mu = 2.244$ cm^{-1}, $R_1 = 0.0647$, $wR_2 = 0.1767$.

The structures were solved by the direct method with the use of the SHELXTL PLUS (PC version) program package[5,6] and refined by the full-matrix least-squares technique against F^2 using the SHELXTL-97 program package.[7]

CCDC 640766–640768 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2007.

[§] The DTA-TG analysis was performed on DSC-20 and TG-50 units of a TA-3000 thermoanalyzer (Mettler) under argon with a rate of 5 K min^{-1}.

[¶] According to GC analysis, a mixture of CO, CH_4, C_2H_6 and traces of acetone and CO_2.

[††] The powder samples were studied by XRD with an FR-552 focusing Guinier camera (CuKα_1 radiation) using germanium as an internal standard. The X-ray diffraction patterns were measured on an IZA-2 comparator (LOMO, Russia) with an accuracy of 0.01 mm and indexed using the TREOR90 program.[9]

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