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Heterodimetallic Pd^{II} -based carboxylate-bridged complexes: Synthesis and structure of single-crystalline $Pd^{II}-M$ $(M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Nd^{III}, Eu^{III}, Ce^{IV})$ acetates

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Dedicated to Professor Brian James in recognition of his pioneering contribution to homogeneous catalysis and inorganic chemistry.

Abstract

A series of crystalline Pd^{II}-based heterodimetallic acetate-bridged complexes containing the transition (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}), post-transition (Zn^{II}) and rare-earth (Ce^{IV}, Nd^{III}, Eu^{III}) metals were synthesized starting from Pd₃(OOCMe)₆ and the complementary metal(II, III) acetates. The crystal and molecular structures of the binuclear Pd^{II}M^{II}(μ -OOCMe)₄L (M = Mn, Co, Ni, Zn; L = H₂O, MeCN), trinuclear Pd₂^{II}Cu^{II}(μ -OOCMe)₆ and tetranuclear Pd₂^{II}M₂^{III}(μ , η^2 -OOCMe)₂(μ -OOCMe)₆(THF)₂ (M = Nd, Eu) and Pd₂^{II}Ce₂^{IV}(μ , η^2 -OOCMe)₂(η -OOCMe)₂(μ -OOCMe)₈(H₂O)₂ complexes were established by X-ray diffraction. © 2006 Elsevier B.V. All rights reserved.

Keywords: Palladium(II); Heterodimetallic complexes; 3d-Metals; 4f-Metals; Synthesis; Crystal structures

1. Introduction

Palladium-based heterometallic complexes are of both academic and practical interest, particularly as promising precursors of mixed-metal catalysts [1]. Typical examples are bimetallic Pd–Co catalysts for alkene hydroformylation [2,3] and fuel cells [4,5] and Pd–Cu catalysts for selective olefin oxidation [6–12]. Meanwhile, only few structurally characterized Pd^{II}-transition metal complexes have been documented, for example [13–16], mostly containing 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 Pd-transition metal cluster

catalysts, organosoluble Pd^{II}-based heterometallic complexes with easily removable carboxylate ligands (acetate, pivalate, etc.) show considerable promise.

Several Pd^{II} -based heterodimetallic purely acetate complexes, $PdCo(OAc)_4 \cdot 2HOAc \cdot 2H_2O$, $PdNi(OAc)_4 \cdot HOA-c \cdot H_2O$, $PdCu(OAc)_4$, $PdCd(OAc)_4 \cdot H_2O \cdot HOAc$, etc., were synthesized as early as 1968 [17]; however, the molecular structures of these compounds are still unknown. We found in the CSD only two records for the X-ray structures of carboxylate Pd^{II} -based heterometallic complexes with post-transition metals, $PdTl(\mu-OOCMe)_4(OOCMe)$ [18] and $Pd_2Cd_2(\mu-OOCMe)_8 \cdot (HOOCMe)_2$ [19] but none of the Pd^{II} -based acetate complexes with transition and rear-earth metals.

Palladium(II) acetate $Pd_3(\mu$ -OOCMe)₆ is a convenient starting compound for the synthesis of such complexes. The trinuclear cyclic structure of this complex is stable

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and poorly reactive but is readily cleaved by nucleophilic agents such as alkaline, NR_4^+ or $[(Ph_3P)_2N]^+$ acetates [20–23]. The coordination vacancies that arose in the Pd^{II} square-plane upon the acetate bridge splitting are filled with additional acetate ligands, producing the binuclear $[Pd_2(OCOMe)_6]^{2-}$ and mononuclear $[Pd(OCOMe)_4]^{2-}$ anionic complexes:

$$\begin{split} & 2Pd_{3}(OOCMe)_{6} + 6M^{+}MeCOO^{-} \rightleftharpoons 3M_{2}^{+}[Pd_{2}(OOCMe)_{6}]^{2-}, \\ & M_{2}^{+}[Pd_{2}(OOCMe)_{6}]^{2-} + 2M^{+}MeCOO^{-} \rightleftharpoons 2M_{2}^{+}[Pd(OOCMe)_{4}]^{2-}, \\ & M^{+} = Na^{+}, K^{+}, NR_{4}^{+}, [(Ph_{3}P)_{2}N]^{+} \end{split}$$

which exist in solution as close ion pairs with the corresponding cations.

Based on analogy with these reactions, the mononuclear di- and trivalent transition and rare-earth metal acetates were expected to serve as a source of acetate group performing a nucleophilic attack on the $Pd_3(\mu$ -OOCMe)₆ molecule:



Should this be the case, not only the close ion pair but also a covalently linked mixed-metal complex can be formed:



Based on this approach, we proposed a convenient protocol for the synthesis of organosoluble, crystalline Pd^{II}based heterodimetallic acetate complexes containing no hard to remove ligands. According to this protocol, we prepared eight single-crystalline complexes involving 3d- and 4f-complementary metals: binuclear Pd^{II}M^{II}(μ -OOCMe)₄L (M = Mn, Co, Ni, Zn; L = H₂O, MeCN), trinuclear Pd₂^{II}Cu^{II}(μ -OOCMe)₆ and tetranuclear Pd₂^{II}Nd₂^{III}-(μ , η^2 -OOCMe)₂(μ -OOCMe)₈(THF)₂, Pd₂^{II}Eu₂^{III}(μ , η^2 -OOCMe)₂(η^1 -OOCMe)₂(μ -OOCMe)₈(H₂O)₂. The crystal and molecular structures of the complexes were established by single-crystal X-ray diffraction.

2. Experimental

2.1. Reagents and physical measurements

Solvents (glacial acetic acid, acetonitrile, tetrahydrofurane, benzene, *n*-hexane and *n*-pentane (all reagent grade, Reakhim, Russia)) were purified by standard procedures [24].

Palladium(II) acetate $Pd_3(OOCMe)_6$ was prepared by the oxidation of Pd black (prepared by reduction of $PdCl_2$ (reagent grade, Reakhim, Russia), with NaBH₄) with concentrated HNO₃ in glacial acetic acid by a known procedure [25]. The raw reaction product was purified from the admixture of Pd^{II} nitrito complexes by refluxing in glacial AcOH with a fresh portion of Pd black until NO₂ evolution ceased followed by recrystallization from hot AcOH.

The salts $Mn(OOCMe)_2 \cdot 4H_2O$, $Co(OOCMe)_2 \cdot 4H_2O$, $Ni(OOCMe)_2 \cdot 4H_2O$, $Cu(OOCMe)_2 \cdot H_2O$ and $Zn(OOCMe)_2 \cdot 2H_2O$ (all reagent grade, Acros, Belgium), $Ce(OOCMe)_3 \cdot 4H_2O$, $Nd(OOCMe)_3 \cdot 1.5H_2O$ and $Eu(OOCMe)_3 \cdot 4H_2O$ (all high purity grade, Reakhim, Russia) were used as received.

The elemental C, H, N analyses were performed on an automated C, H, N-analyzer (Carlo Erba Strumentazione, Italy). Single-crystal X-ray diffraction experiments were carried out on Bruker SMART 1000 CCD and Enraf Nonius CAD 4 diffractometers. The IR spectra were recorded on a Nicolet Nexus spectrometer (KBr pellets). The UV– Vis spectra were measured on a Varian Cary 100 spectrophotometer.

2.2. Syntheses

Typically, a slurry of palladium acetate Pd₃(OOCMe)₆ (448 mg, 2 mmol based on Pd) and the Mn^{II},Co^{II}, Ni^{II}, Zn^{II} , Ce^{III} , Nd^{III} , Eu^{III} (2 mmol) or Cu^{II} acetate (1 mmol) in glacial acetic acid (20 ml) was stirred under reflux until the salts completely dissolved (~ 1.5 h). The reaction solution was cooled to room temperature, filtered and evaporated to dryness on a rotary evaporator (temperature of water bath at most 60 °C). Benzene (15 ml) was added to the residue, evaporated to dryness on a rotary evaporator, and the procedure was repeated several times to remove acetic acid, affording in most cases a noncrystalline or microcrystalline mixed-metal complex. To prepare singlecrystalline samples, the dry residue was treated with different solvents depending on the nature of the complementary metal. As a rule, the single-crystalline complexes contained the incorporated solvent molecules.

2.3. $PdCo(\mu - OOCMe)_4(NCMe) \times 3MeCN$ (1a) and $PdCo(\mu - OOCMe)_4(NCMe) \times 0.5MeCN$ (1b)

The pinkish-beige dry residue prepared according to the general procedure from $Pd_3(OOCMe)_6$ (448 mg, 2 mmol based on $Pd(OOCMe)_2$ unit) and $Co(OOCMe)_2 \cdot 4H_2O$ (497 mg, 2 mmol) was dissolved in acetonitrile (20 ml),

concentrated to 5 ml on a rotary evaporator, and stored for crystallization at room temperature. Dark cherry-colored crystals of complex **1a** were precipitated in 2–4 h in a vield of 520 mg. After the removal of the crystals, the mother liquor was refrigerated for 24 h to produce 230 mg of smaller crystals of complex 1b. Slow evaporation in air at room temperature of the rest mother liquor afforded an additional portion of crystals 1b. Total yield of complexes 1a + 1b was 750 mg (~85% based on Pd). Complexes 1a and 1b readily lose the MeCN crystallization molecules in air at room temperature. Anal. Calc. for C₁₀H₁₅O₈NPdCo (without the MeCN crystallization molecule): C, 27.14; N, 3.16; H, 3.42. Found: C, 27.34; N, 3.23; H 3.49%. IR spectrum (KBr, cm⁻¹): 2945m, 2882w, 2822w, 1610s ($v_{as(CO)}$), 1409s (v_{s(CO)}), 1385w, 1345w, 1051w, 1029w, 698m, 624w. UV–Vis spectrum (acetic acid): 335 nm ($\varepsilon = 1.6 \times$ $10^3 \,\mathrm{l\,mol^{-1}\,cm^{-1}}), 260 \ (\varepsilon = 3.0 \times 10^3 \,\mathrm{l\,mol^{-1}\,cm^{-1}}).$

2.4. $PdNi(\mu$ -OOCMe)₄ (NCMe) × 3MeCN (2)

This complex was prepared according to the same protocol as complex **1a** (see above) starting from Pd₃(OCOMe)₆ (448 mg, 2 mmol) and Ni(OOCMe)₂ · 4H₂O (495 mg, 2 mmol). The yield of the yellow-green crystals of complex **2** was 820 mg (93% based on Pd). The crystals readily lose the MeCN crystallization molecules in air. *Anal.* Calc. for C₁₀H₁₅O₈NPdNi: C, 27.15; N, 3.17; H, 3.42. Found: C, 27.26; N, 3.21; H, 3.50%. IR spectrum (KBr, cm⁻¹): 2944m, 2882w, 2317w, 2291w, 2256w, 1611s ($v_{as(CO)}$), 1387s, br. ($v_{s(CO)}$), 1342m, 1049w, 1025w, 700m, 628w. UV–Vis spectrum (acetic acid): 325 nm ($\varepsilon = 1.9 \times 10^3$ 1 mol⁻¹ cm⁻¹), 250 ($\varepsilon = 3.0 \times 10^3$ 1 mol⁻¹ cm⁻¹).

2.5. $PdMn(\mu - OOCMe)_4(OH_2) \times THF(3)$

The orange dry solid prepared according to the general procedure from Pd₃(OOCMe)₆ (448 mg, 2 mmol) and $Mn(OOCMe)_2 \cdot 4H_2O$ (490 mg, 2 mmol) was dissolved in warm THF (5 ml) and stored at room temperature for 24 h. Orange crystals of the title complex (530 mg) were separated by decantation, washed with cold THF and dried at room temperature in an argon flow. An additional portion of smaller crystals was obtained from the mother liquor by precipitation with pentane. Total yield of complex 3 was 875 mg (90% based on Pd). Anal. Calc. for C₁₂H₂₂O₁₀PdMn: C, 29.57; H, 4.55. Found: C, 28.96; H, 4.59%. IR spectrum (KBr, cm⁻¹): 3416m, 2987w, 2878w, 1605vs (v_{as(CO)}), 1563vs (v_{as(CO)}), 1422s, br. (v_{s(CO)}), 1339m, 1154w, 1024w, 695m, 658w, 624w. UV-Vis spectrum (acetic acid): 340 nm ($\varepsilon = 1.0 \times 10^3 1 \text{ mol}^{-1} \text{ cm}^{-1}$), 250 ($\varepsilon = 2.0 \times 10^3 \, \mathrm{l \, mol^{-1} \, cm^{-1}}$).

2.6. $PdZn(\mu$ -OOCMe)₄(OH₂) × THF (4)

The dry residue obtained according to the general procedure from $Pd_3(OOCMe)_6$ (448 mg, 2 mmol) and Zn(OOC- $Me)_2 \cdot 2H_2O$ (440 mg, 2 mmol) was crystallized from THF similarly to the synthesis of complex **3** (see above) to produce 745 mg (75% based on Pd) of the pink crystals of complex **4**. *Anal*. Calc. for $C_{12}H_{22}O_{10}PdZn$: C, 28.94; H, 4.45. Found: C, 28.85; H, 4.50%. IR spectrum (KBr, cm⁻¹): 2924m, 2853w, 1595vs, br ($v_{as(CO)}$), 1397vs ($v_{s(CO)}$), 1339m, 1049m, 1024m, 933w, 676m, 621w.

2.7. $Pd_2Nd_2(\mu$ -OOCMe)₈ $(\mu,\eta^2$ -OOCMe)₂ $(THF)_2 \times 2THF$ (5)

The complex was prepared according to the general procedure starting from Pd₃(OOCMe)₆ (448 mg, 2 mmol) and Nd(OOCMe)₃ · 1.5H₂O (690 mg, 2 mmol) and crystallization from THF in a yield of 0.68 g. An additional portion of smaller crystals was obtained from the mother liquor by precipitation with pentane. Total yield of yellow-orange crystalline complex **5** was 940 mg (76% based on Pd). The crystals readily lose two THF crystallization molecules upon drying. *Anal.* Calc. for C₂₈H₄₆O₂₂Pd₂Nd₂: C, 27.21; H, 3.75. Found: C, 27.41; H, 3.68%. IR spectrum (KBr, cm⁻¹): 2977w, 2875w, 1622s ($v_{as(CO)}$), 1577 vs ($v_{as(CO)}$), 1412vs ($v_{s(CO)}$), 1344m, 1067w, 1050w, 1026m, 943 w, 875w, 690m, 674m, 621w, 529w, 460w.

2.8. $Pd_2Eu_2(\mu \text{-}OOCMe)_8(\mu,\eta^2\text{-}OOCMe)_2(THF)_2 \times THF$ (6)

The complex was synthesized according to the same protocol starting from $Pd_3(OOCMe)_6$ (448 mg, 2 mmol) and $Eu(OOCMe)_3 \cdot 4H_2O$ (800 mg, 2 mmol) followed by crystallization from THF in a yield of 0.55 g. An additional portion of smaller crystals was obtained from the mother liquor by precipitation with pentane. Total yield of yellow-orange crystalline complex **6** was 1.05 g (79% based on Pd). The crystals readily lose the THF crystallization molecule upon drying. *Anal.* Calc. for $C_{28}H_{46}O_{22}Pd_2Eu_2$: C, 26.87; H, 3.71. Found: C, 26.93; H, 3.85%. IR spectrum (KBr, cm⁻¹): 2926w, 2851w, 1634m ($v_{as(CO)}$), 1580vs ($v_{as(CO)}$), 1413vs ($v_{s(CO)}$), 1343w, 1029m, 943w, 877w, 689m, 676m, 620w, 470w, 357w.

2.9. $Pd_2^{\ II}Ce_2^{\ IV}(\mu, \eta^2 \text{-}OOCMe)_2(\eta^1 \text{-}OOCMe)_2(\mu \text{-}OOCMe)_8 \text{-} (H_2O)_2 \times 2H_2O \times 2MeCOOH \times C_6H_6 \ (7)$

The crystals of complex 7 were obtained directly from the reaction solution, omitting the evaporation and recrystallization stages. A slurry of $Pd_3(OOCMe)_6$ (200 mg, 0.89 mmol) and Ce(OOCMe)_3 · 4H₂O (350 mg, 0.89 mmol) in acetic acid (5 ml) was stirred at 90 °C until the initial complexes completely dissolved (1 h). Benzene (0.5 ml) was added to a warm yellow solution that formed and the solution was slowly cooled in a water bath to room temperature. The crystals of the title complex were separated by decantation and dried in air. The yield of yellow-orange crystalline complex 7 was 520 mg (79% based on Pd). *Anal.* Calc. for C₃₄H₅₈O₃₂Pd₂Ce₂: C, 27.74; H, 3.97. Found: C, 27.69; H, 3.95%. IR spectrum (KBr, cm⁻¹): 3424vs, 2926w, 2854w.

1718w, 1559vs, br ($v_{as(CO)}$), 1445vs, br ($v_{(CO)}$), 1343w, 1272m, 1052w, 1020m, 934w, 669s, 616m, 469w.

2.10. $Pd_2Cu(\mu - OOCMe)_6 \times 2C_6H_6$ (8)

Palladium acetate Pd₃(OOCMe)₆ (448 mg, 2 mmol based on Pd) and Cu(OOCMe)₂ \cdot H₂O (199 mg, 1 mmol) were stirred under reflux in glacial acetic acid (20 ml) until the initial salts completely dissolved (~ 1.5 h). The reaction solution was cooled to room temperature, filtered, concentrated on a rotary evaporator to 5 ml and stored for a night at room temperature. The fine-crystalline precipitate was filtered off (note: the precipitate should not be dry but slightly wet with acetic acid!) and immediately recrystallized from hot benzene to produce yellow-green crystals of the title complex. An additional amount of smaller crystals was obtained from the mother liquor by precipitation with hexane. Total yield of the crystalline complex 8 was 473 mg (75 % based on Pd). The complex is soluble in C₆H₆, AcOH, THF, and CH₃CN (in two latter solvents decomposes in several days). Anal. Calc. for C₁₂H₁₈O₁₂Pd₂Cu: C, 22.85; H, 2.88. Found: C, 23.03; H, 3.01%. (crystals readily lose crystallization benzene molecules upon drying). IR spectrum (KBr, cm⁻¹): 2988w, 2454w, 1607vs, br $(v_{as(CO)})$, 1429vs $(v_{s(CO)})$, 1348w, 1157w, 1029w, 948w, 695m, 625w, 580w. UV-Vis spectrum (acetic acid):¹ 380 nm ($\varepsilon = 0.68 \times 10^3 \, \mathrm{l \, mol^{-1} \, cm^{-1}}$), 260 $(\varepsilon = 1.5 \times 10^3 \,\mathrm{l \, mol^{-1} \, cm^{-1}}).$

2.11. Data collection

Details of the data collection and structure refinement for complexes 1-8 are presented in Table 1. Single-crystal X-ray diffraction experiments for complexes 1–6 and 8 were carried out on a Bruker SMART 1000 with CCD area detector (graphite monochromated Mo Ka radiation, $\lambda = 0.71073$ Å, ω -scans) and that for complex 7 was performed on an Enraf Nonius CAD 4 diffractometer (graphite monochromator, Mo K α radiation, $\lambda = 0.71073$ Å, ω scans). The semi-empirical method sADABS [26] was applied for the absorption correction for crystals 1–6 and 8. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms of the water molecules in complexes 3 and 4 were localized from Fourier syntheses; the other hydrogen atoms in all structures were placed geometrically and included in the structure factors calculation in the riding motion approximation. Analysis of the Fourier electron density synthesis in complexes 1a and 2 revealed that the metal atoms are disordered over two positions with equal occupancies. The distances between two positions in structures 1a and 2 are approximately 0.4 A. In complex 8 the Pd and Cu atoms are disordered over the coordination triangle and their positions coincide. The occupancies of the Pd and Cu atoms in the general and special positions are 0.7, 0.3 and 0.3, 0.2, correspondingly. The refinement procedure of the disordered heavy metal atoms includes the alternative refinement of occupancies with restraints on the equalized thermal motion parameters and consequent refinement of the thermal motion parameters with restrictions applied to occupancies. Such a refinement resulted in a considerable decrease in the residual electron density peaks and discrepancy factors. It should be noted that in all the above-mentioned disordered structures the refinement for lower symmetry space group did not eliminated the disorder and only lead to high correlations between the refined parameters. All the data reduction and further calculations were performed using SAINT [27] and SHELXTL-97 [28] program packages.

3. Results and discussion

3.1. Syntheses

Our experiments showed that $Pd_3(OOCMe)_6$ readily reacts in an AcOH solution with the mononuclear manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), neodimium(III), europium(III) and cerium(III) acetates to form the mixed-metal complexes. Glacial acetic acid was found to be the most convenient reaction medium. In other solvents, such as benzene or THF, no $Pd^{II}-M^{II,III}$ reaction was found to occur, whereas methanol and higher alcohols were improper because of their reducing ability towards palladium(II).

Typically, the complex formation occurs to completion for 1–2 h at 90–110 °C. In all cases, except for Cu(OOC-Me)₂ · H₂O, the reaction started from the Pd^{II}:M^{II,III} molar ratio 1:1 produced quite uniform samples of 1:1 heterometallic complexes. Unlike this, the product composition of the copper(II)–palladium(II) reaction depended on the initial Pd^{II}:Cu^{II} ratio, affording mixtures of differently colored small crystals in most cases. Synthetic runs with various Cu^{II}:Pd^{II} ratios showed that a chemically uniform sample can be obtained in a good yield at the initial Cu^{II}:Pd^{II} ratio equal to 1:2.

However, the prepared mixed-metal complex samples were as a rule amorphous or microcrystalline and unsuitable for X-ray diffraction investigation. Only complexes **7** and **8** were precipitated directly from the reaction solution as appropriate single crystals. For this reason, the mixed-metal acetate complexes were treated with THF or MeCN to furnish the complementary metal with a suitable additional ligand. All the synthesized Pd^{II}–M^{II,III} heterometal-lic complexes were obtained as well-shaped single crystals and their structures were established by X-ray diffraction.

3.2. Structure of complexes

The X-ray study revealed all the synthesized complexes to contain the square-planar moiety $[Pd(\mu-OOCMe)_4]$ as a structure-determining building block. The palladium

¹ Spectrum recorded for fresh-prepared solution.

Table 1							
Crystal	data	and	structure	refinement	for	complexes 1	-8

	1a	1b	2	3	4	5	6	7	8
Empirical formula	C ₁₆ H ₂₄ N ₄ O ₈ PdCo	C ₁₁ H _{16.5} N _{1.5} O ₈ PdCo	C ₁₆ H ₂₄ N ₄ O ₈ PdNi	C ₁₂ H ₂₂ O ₁₀ PdMn	C ₁₂ H ₂₂ O ₁₀ PdZn	C ₃₆ H ₆₂ O ₂₄ Pd ₂ Nd ₂	C36H62O24Pd2Eu2	C34H58Ce2O32Pd2	C24H30O12Pd2Cu
Fw	565.72	463.09	565.50	487.64	498.07	1380.14	1395.58	1471.84	786.82
Colour	dark-cherry	dark-cherry	yellow-green	orange	pink	yellow-orange	yellow-orange	yellow	yellow-green
Temperature (K)	200(2)	160(2)	200(2)	160(2)	160(2)	160(2)	160(2)	293(2)	160(2)
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic	triclinic	monoclinic	orthorombic	triclinic	orthorombic
Space group	Pnma	P2(1)/c	P2(1)/n	$P\bar{1}$	$P\overline{1}$	P2(1)/c	Pca2(1)	$P\bar{1}$	Pnma
Unit cell dimensions									
a (Å)	13.602(2)	13.8704(16)	10.735(2)	8.2095(16)	8.1673(14)	28.208(6)	21.114(4)	8.4420(17)	15.512(5)
$b(\mathbf{A})$	16.786(3)	14.0563(17)	10.281(2)	10.191(2)	10.1232(17)	13.376(3)	3.361(2)	11.800(2)	23.043(7)
$c(\dot{A})$	10.3033(17)	18.360(2)	10.979(3)	11.630(2)	11.5326(19)	21.246(5)	34.950(6)	14.133(3)	8.238 (2)
α (°)	90	90	90	82.53	81.490	90	90	76.68	90
β(°)	90	108.232	102.067(4)	72.97	72.985	110.531	90	75.69	90
γ (°)	90	90	90	75.05	73.898	90	90	88.36	90
$V(\dot{A}^3)$	2352.4(7)	3399.8(7)	1184.9(5)	897.2(3)	873.7(3)	7507(3)	9860(3)	1326.9(5)	2944.6(15)
Z(Z')	4 (0.5)	8 (2)	2 (0.5)	2 (1)	2 (1)	6 (1.5)	8 (4)	2(1)	4 (0.5)
D_{calc} (Mg/m ³)	1.597	1.809	1.585	1.805	1.893	1.832	1.880	1.842	1.775
Absorption coefficient (mm^{-1})	1.515	2.070	1.598	1.751	2.449	2.825	3.307	2.441	1.981 2
F(000)	1140	1840	572	490	500	4092	5504	726	1564
Crystal size (mm)	$0.36 \times 0.32 \times 0.39$	$0.34 \times 0.32 \times 0.24$	$0.29 \times 0.24 \times 0.23$	$0.34 \times 0.30 \times 0.28$	$0.25 \times 0.15 \times 0.10$	$0.32 \times 0.27 \times 0.24$	$0.34 \times 0.28 \times 0.22$	$0.26 \times 0.22 \times 0.20$	$0.14 \times 0.10 \times 0.08$
θ Range for data collection (°)	2.43-29.98	1.86–27.00	2.41-30.02	1.83-30.01	1.85–29.97	1.83-30.04	1.80-30.05	2.06-25.08.	2.63-25.99
Index ranges	$-19 \leq h \leq 19$,	$-16 \leq h \leq 17$,	$-15 \leq h \leq 15$,	$-11 \leq h \leq 10$,	$-11 \leq h \leq 11$,	$-39 \leq h \leq 20$,	$-27 \leq h \leq 29$,	$-1 \leq h \leq 10$,	$-19 \leq h \leq 19$,
C C	$-20 \leq k \leq 23$,	$-17 \leq k \leq 17$,	$-14 \leq k \leq 14$,	$-14 \leq k \leq 10$,	$-14 \leq k \leq 14$,	$-12 \leq k \leq 18$,	$-18 \leqslant k \leqslant 18$	$-14 \leq k \leq 14$	$-28 \leqslant k \leqslant 28$
	$-11 \leq l \leq 14$	$-17 \leq l \leq 23$	$-15 \leq l \leq 15$	$-16 \leq l \leq 15$	$-16 \leqslant l \leqslant 16$	$-29 \leqslant l \leqslant 29$	$-49 \leqslant l \leqslant 46$	$-16 \leq l \leq 16$	$-10 \leqslant l \leqslant 10$
Reflections collected	17087	21 307	12887	8717	10284	56781	104423	5419	24350
Independent reflections $[R_{int}]$	3451 [0.0380]	7139 [0.0317]	3355 [0.0503]	5148 [0.0197]	4995 [0.0244]	21401 [0.0686]	28 183 [0.0720]	4668 [0.0117]	2919 [0.2042]
Observed reflections	2155	5270	2285	4331	3797	10560	17253	4078	1345
Data/restraints/ parameters	3451/0/162	7139/0/406	3355/0/145	5148/0/217	4995/0/217	21 401/16/876	28 183/29/1152	4668/0/336	2919/0/172
Goodness-of-fit on F^2	0.951	1.084	0.996	1.011	1.021	1.081	1.094	1.063	0.884
Final R indices	$R_1 = 0.0535,$	$R_1 = 0.0569,$	$R_1 = 0.0610,$	$R_1 = 0.0448,$	$R_1 = 0.0450,$	$R_1 = 0.0646,$	$R_1 = 0.0579,$	$R_1 = 0.0335,$	$R_1 = 0.0551,$
$[I \ge 2\sigma(I)]^{\mathrm{a}}$	$wR_2 = 0.1336$	$wR_2 = 0.1370$	$wR_2 = 0.1708$	$wR_2 = 0.1136$	$wR_2 = 0.1101$	$wR_2 = 0.1330$	$wR_2 = 0.1156$	$wR_2 = 0.0870$	$wR_2 = 0.1133$
R^{a} indices (all data)	$R_1 = 0.0845,$	$R_1 = 0.0735,$	$R_1 = 0.0850,$	$R_1 = 0.0534,$	$R_1 = 0.0594,$	$R_1 = 0.1310,$	$R_1 = 0.1024,$	$R_1 = 0.0418,$	$R_1 = 0.1418,$
	$wR_2 = 0.1514$	$wR_2 = 0.1463$	$wR_2 = 0.1824$	$wR_2 = 0.1198$	$wR_2 = 0.1174$	$wR_2 = 0.1459$	$wR_2 = 0.1261$	$wR_2 = 0.0919$	$wR_2 = 0.1435$
Largest difference in peak and hole $(e A^{-3})^{b}$	2.028 and -0.678	2.727 and -1.336	1.658 and -0.642	2.245 and -0.950	2.745 and -0.761	2.818 and -1.135	3.028 and -1.056	1.932 and -2.057	1.080 and -0.665

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; \quad wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}.$ ^b In all structures the largest difference peak is observed in the vicinity of heavy atom.

atom in all the complexes is linked to the complementary metal atom through carboxylate bridges, forming the following geometrical figures:

(i) four-bridged asymmetrical "chinese lanthern" with an axial ligand attached to the complementary metal atom



(ii) two four-bridged "chinese lanthers" linked to each other by two acetate or two hydrogen-bonded acetate bridges attached to the M atoms



M = Nd, Eu, Ce: \cap = OOCMe; M = Mn, Zn: \cap = OC(Me)O-H…O

(iii) double-bridged triangle of two Pd atoms and one Cu atom almost identical to the Pd₃(OOCMe)₆ triangle.



The structural motif of the first two geometries is "faceto face" arrangement of the Pd^{II} and $M^{II,III}$ coordination planes, whereas in the third geometry the Pd^{II} and Cu^{II} coordination planes are turned 60° to each other.

Type 1: binuclear "chinese lanthern" complexes. PdCo(μ-OOCMe)₄(NCMe) × 3MeCN (1a) [29], PdCo(μ-OOCMe)₄(NCMe) × 0.5MeCN (1b), and PdNi(μ-OOCMe)₄(NCMe) × 3MeCN (2). The molecular structures of the Pd–Co and Pd–Ni acetates are quite similar (see Figs. 1–3). Meanwhile, the crystal structures of these complexes have some peculiarities. In the crystal of complex 1a, one of three MeCN crystallization molecules is positioned rather close to the

molecules is positioned rather close to the complex molecule, forming a fairly short $Pd \cdots N$ contact between the Pd atom and MeCN



Fig. 1. Molecular structure of the complex $PdCo(\mu-OOCMe)_4(NCMe) \times 3$ MeCN (1a) with thermal ellipsoids drawn at 50% probability level. The Pd and Co atoms are disordered over two positions with equal occupancies (two MeCN crystallization molecules are not shown).



Fig. 2. Molecular structure of the complex $PdCo(\mu-OOCMe)_4(NCMe) \times 0.5$ MeCN (1b) with thermal ellipsoids drawn at 50% probability level.



Fig. 3. Molecular structure of the complex $PdNi(\mu-OOCMe)_4(NCMe) \times 3$ MeCN (2) with thermal ellipsoids drawn at 50% probability level. The Pd and Ni atoms are disordered over two positions with equal occupancies (two MeCN crystallization molecules are not shown).

crystallization molecule (Pd(1)–N(1) 2.509 Å, Fig. 1). Crystal **1b** (Fig. 2) contains two slightly different molecules $PdCo(\mu$ -OOCMe)₄(NCMe), one of which (A) has no short contacts, while another molecule (B) is drawn together with the MeCN crystallization molecule. It can be seen from Tables 2 and 3 that the Pd···N contact in molecules **1a** and **1b**(B) somewhat changes their geometry compared to that of molecule **1b**(A), slightly shortening the Pd–Co distance (Pd(1)–Co(2) 2.515(3) Å in **1a**, Pd(2)–Co(2) 2.4591(10) Å in **1b**(B)) and elongating the Co–N

Table 2 Selected bond lengths (\AA) and angles $(^{\circ})$ for complex 1a

beleeted bond lengths (1) and angles () for complex 1						
Pd(1)–Co(2)	2.515(3)	Pd(2)–Co(1)	2.551(3)			
Pd(1)–O(1)	2.025(3)	Pd(2)–O(2)	2.013(3)			
Pd(1)-O(3)	2.041(3)	Pd(2)–O(4)	2.037(3)			
Co(2)–O(2)	2.070(4)	Co(1)–O(1)	2.091(4)			
Co(2)–O(4)	2.027(4)	Co(1)–O(3)	2.050(4)			
Co(2)–N(2)	2.279(6)	Co(1) - N(1)	2.073(5)			
Pd(1)N(1)	2.509(5)	Pd(2)N(2)	2.678(6)			
O(1)-Pd(1)-O(3)	90.69(9)	O(2)-Pd(2)-O(4)	90.67(9)			
$O(1A)^{a} - Pd(1) - O(1)$	89.78(15)	$O(2A)^{a}-Pd(2)-O(2)$	89.58(16)			
O(3)-Pd(1)-O(3A) ^a	88.74(14)	O(4)-Pd(2)-O(4A) ^a	88.72(16)			
O(1)-Pd(1)-Co(2)	91.18(11)	O(2) - Pd(2) - Co(1)	93.56(11)			
O(3)-Pd(1)-Co(2)	91.27(12)	O(4) - Pd(2) - Co(1)	90.97(11)			
N(2)-Co(2)-Pd(1)	176.7(3)	N(1)-Co(1)-Pd(2)	177.1(3)			

^a Symmetry transformations used to generate equivalent atoms: x, -y + 3/2, z.

Table 3 Selected geometrical parameters for two independent molecules (A and B) in crystal 1b

Molecule A		Molecule B	
Bond lengths (Å)			
Pd(1)-Co(1)	2.5304(8)	Pd(2)–Co(2)	2.4591(10)
Pd(1)–O(1)	2.000(4)	Pd(2)–O(9)	2.008(4)
Pd(1)-O(3)	2.006(4)	Pd(2)–O(11)	2.017(4)
Pd(1)–O(5)	1.994(4)	Pd(2)-O(13)	2.000(4)
Pd(1)–O(7)	1.996(4)	Pd(2)-O(15)	2.012(4)
Co(1)–O(2)	2.082(4)	Co(2)-O(10)	2.069(4)
Co(1)–O(4)	2.061(4)	Co(2)–O(12)	2.054(4)
Co(1)-O(6)	2.085(4)	Co(2)-O(14)	2.056(4)
Co(1)-O(8)	2.037(4)	Co(2)–O(16)	2.047(4)
Co(1)–N(1)	2.057(5)	Co(2)–N(2)	2.183(6)
		Pd(2)N(3)	2.687(6)
Bond angles (°)			
O(1)-Pd(1)-O(3)	88.97(16)	O(9)-Pd(2)-O(15)	90.29(16)
O(5)-Pd(1)-O(3)	90.33(16)	O(13)-Pd(2)-O(9)	88.46(17)
O(5)-Pd(1)-O(7)	89.43(17)	O(13)-Pd(2)-O(11)	91.64(17)
O(7)–Pd(1)–O(1)	91.29(17)	O(15)-Pd(2)-O(11)	89.59(15)
O(1)-Pd(1)-Co(1)	90.96(10)	O(9)-Pd(2)-Co(2)	89.26(12)
O(3)-Pd(1)-Co(1)	89.77(11)	O(11)-Pd(2)-Co(2)	89.79(11)
O(5)-Pd(1)-Co(1)	90.24(11)	O(13)-Pd(2)-Co(2)	90.40(12)
O(7)-Pd(1)-Co(1)	89.26(11)	O(15)-Pd(2)-Co(2)	88.62(11)
N(1)-Co(1)-Pd(1)	177.39(14)	N(2)-Co(2)-Pd(2)	174.67(14)

bond (Co(2)–N(2) 2.279(6) Å in **1a**, Co(2)–N(2) 2.183(6) Å in **1b**(B)) (cf. Pd(1)–Co(1) 2.5304(8) Å, Co(1)–N(1) 2.057(5) Å in **1b**(A)). Similar short contacts Pd–N are observed in the Pd–Ni crystal **2** Pd(1)–Ni(1) 2.526(6) Å (Fig. 3, Table 4).

The metal–metal distances in molecules 1a, 1b, and 2 are much shorter than the sum of van der Waals radii of the corresponding metals, being rather close to the sum of the metal covalent radii (cf. Pd–Co 2.44, Pd–Ni 2.43 Å). Meanwhile, the direct metal–metal bonding between Pd^{II} (4d⁸) and Co^{II} (3d⁵) or Ni^{II} (3d⁸) seems to be questionable. If the Pd^{II}–M^{II} bonding were taken into account, the coordination polyhedron of the 3d-

Table 4	
Selected bond lengths (Å) and angles (°) in complex ${\bf 2}$	

Pd(1)–Ni(1)	2.483(2)	Pd(1)–O(1)	2.027(4)
Pd(1) - O(2)	2.034(5)	Pd(1)–O(3)	2.036(4)
Pd(1) - O(4)	2.020(5)	$Ni(1)-O(1A)^{a}$	2.076(6)
$Ni(1)-O(2A)^{a}$	2.055(6)	$Ni(1)-O(3A)^{a}$	2.028(6)
$Ni(1) - O(4)^{a}$	2.040(6)	$Ni(1)-N(1A)^{a}$	2.160(6)
Pd(1)N(1)	2.526(6)		
O(1)–Pd(1)–O(2)	90.82(18)	O(2)-Pd(1)-O(3)	88.85(18)
O(4) - Pd(1) - O(1)	89.53(19)	O(4) - Pd(1) - O(3)	90.56(18)
$O(1A)^{a}$ -Ni(1)-Pd(1)	80.83(12)	$O(2A)^{a}$ -Ni(1)-Pd(1)	82.31(12)
$O(3A)^{a}-Ni(1)-Pd(1)$	82.34(13)	$O(4A)^{a}-Ni(1)-Pd(1)$	81.03(12)
Ni(1) - Pd(1) - N(1)	178.87(11)		

^a Symmetry transformations used to generate equivalent atoms: -x, -y, -z.

metal would be an octahedron. Alternatively, if the direct Pd–Co(Ni) bond were lacking, the MO_5 coordination polyhedron of the complementary metals would be a tetragonal pyramide. A similar problem arises when discussing the other Pd^{II}-based complexes under study. Studies of the magnetic properties and quantum chemistry of these complexes, which are in progress now, could clarify the problem.

Type 2: two "chinese lantherns" linked to each other. PdMn(μ -OOCMe)₄(OH₂) × THF (3) and PdZn(μ -OOCMe)₄(OH₂) × THF (4). The palladium – complementary metal units of these complexes are similar to those of complexes 1a,b and 2 with the exception that the additional ligand L = H₂O instead of L = MeCN is connected to the complementary metals (Figs. 4 and 5, Tables 5 and 6).²

> Meanwhile, the molecules **3** and **4** are packed in the crystals in another way: the Pd–Mn and Pd– Zn binuclear moieties are connected by two Hbonded bridges



(H(2w)–O(6A) 1.86 and 1.78 Å; O(6)···O(9) 2.691(6) and 2.692(6) Å in complexes **3** and **4**, respectively, see Fig. 6). Such a contact results in a noticeable elongation of one the M–O distance compared to the other ones (M–O(6) 2.200(3) and 2.135(3) Å for complexes **3** and **4**, respectively, see Tables 5 and 6). Hence, compounds **3** and **4** can be classified, at least in the crystal phase, as tetranuclear di-chinese lanthern complexes. In addition, the coordinated H₂O molecules are H-bonded to the THF crystallization

 $^{^2}$ The H₂O molecules in the composition of complexes **3** and **4** are originated from the initial Mn(OOCMe)₂ · 4H₂O and Zn(OOC-Me)₂ · 2H₂O reagents and/or residual water in solvents.



Fig. 4. Molecular structure of the complex $PdMn(\mu$ -OOCMe)₄(OH₂) (3) with thermal ellipsoids drawn at 50% probability level.



Fig. 5. Molecular structure of the complex $PdZn(\mu\text{-}OOCMe)_4(OH_2)$ (4) with thermal ellipsoids drawn at 50% probability level.

Table 5 Selected bond lengt	ths (Å) and angles	(°) in complex 3	
Pd(1)–Mn(1)	2.6795(10)	Pd(1)–O(1)	
Pd(1) O(3)	2 000(3)	Pd(1) = O(5)	

I u(1) = WIII(1)	2.0795(10)	1 u(1) = O(1)	2.002(3)
Pd(1)–O(3)	2.000(3)	Pd(1)–O(5)	2.004(3)
Pd(1)–O(7)	2.001(3)	Mn(1)–O(2)	2.139(3)
Mn(1)–O(4)	2.141(3)	Mn(1)–O(6)	2.200(3)
Mn(1)–O(8)	2.127(3)	Mn(1)-O(9)	2.070(3)
O(1)-Pd(1)-O(5)	89.91(11)	O(3)–Pd(1)–O(1)	90.25(11)
O(7) - Pd(1) - O(3)	89.90(11)	O(7) - Pd(1) - O(5)	89.93(11)
O(1) - Pd(1) - Mn(1)	90.79(8)	O(3) - Pd(1) - Mn(1)	90.46(8)
O(5)-Pd(1)-Mn(1)	91.60(8)	O(7) - Pd(1) - Mn(1)	89.77(8)
O(2)-Mn(1)-Pd(1)	77.52(7)	O(4) - Mn(1) - Pd(1)	77.77(8)
O(8) - Mn(1) - Pd(1)	78.25(8)	O(6)-Mn(1)-Pd(1)	76.81(7)
O(9)-Mn(1)-Pd(1)	174.58(9)		

2002(2)

Table 6										
Selected	bond	lengths	(Å)	and	angles	(°)	in	com	olex	4

-		• •	
Pd(1)–Zn(1)	2.5811(6)	Zn(1)–O(2)	2.049(3)
Pd(1)–O(1)	2.003(3)	Zn(1)-O(4)	2.068(3)
Pd(1)–O(3)	1.998(3)	Zn(1) - O(6)	2.135(3)
Pd(1)-O(5)	1.998(3)	Zn(1)–O(8)	2.064(2)
Pd(1)-O(7)	1.999(3)	Zn(1)-O(9)	1.968(3)
O(3)-Pd(1)-O(7)	89.83(11)	O(7)-Pd(1)-O(5)	90.02(11)
O(5)-Pd(1)-O(1)	89.94(11)	O(3) - Pd(1) - O(1)	90.21(11)
O(1) - Pd(1) - Zn(1)	88.93(8)	O(2) - Zn(1) - Pd(1)	81.72(8)
O(3) - Pd(1) - Zn(1)	89.52(7)	O(4) - Zn(1) - Pd(1)	80.98(8)
O(5) - Pd(1) - Zn(1)	91.25(7)	O(6) - Zn(1) - Pd(1)	79.65(7)
O(7) - Pd(1) - Zn(1)	90.56(7)	O(8) - Zn(1) - Pd(1)	80.01(7)
O(9)–Zn(1)–Pd(1)	176.08(9)		

molecules (H(1w)···O(10) 1.96 and 1.82 Å; O(9)··· O(10) 2.653(7) and 2.655(7) Å in complexes **3** and **4**, respectively).

Tetranuclear complexes $Pd_2Nd_2(\mu$ -OOCMe)₈ (μ,η^2 -OOCMe)₂(THF)₂ × 2THF (**5**), $Pd_2Eu_2(\mu$ -OOCMe)₈(μ,η^2 -OOCMe)₂(THF)₂ × THF (**6**) and $Pd_2^{II}Ce_2^{IV}(\mu,\eta^2$ -OOCMe)₂(η^1 -OOCMe)₂(μ -OOCMe)₈(H_2O)₂(7) are built of two Pd– Nd(Eu,Ce) "chinese lanthern" binuclear units connected by two μ,η^2 -acetate bridges (Nd···Nd 4.1442(8) and 4.1691(8) Å; Nd–O 2.449(5)– 2.557(5) Å; Eu···Eu 4.0822(9) and 4.0962(9) Å, Eu–O 2.404(7)–2.525(7) Å; Ce···Ce 4.4691(8), Ce–O 2.432(3)–2.527(3) Å) (Figs. 7–9 and Tables 7–9).

In each of the "chinese lanthern" fragment, similarly to complexes **1** and **2**, the Pd–Nd(Eu, Ce) metal distances (Pd–Nd 3.2125(9)–3.2411(10), Pd–Eu 3.2026(10)–3.2170(10) Å, Pd–Ce 3.4022(9) Å) are much shorter than the sum of the van der Waals radii of the corresponding metals, being close to the sum of the metal covalent radii (cf. Pd–Nd 2.92, Pd–Eu 3.11 Å, Pd–Ce 2.93 Å). The coordination sphere of each Nd, Eu atom is complemented with an O-bonded THF molecule, thus gaining a coordination number of eight under assumption of lacking the direct Pd^{II}–Nd^{III}(Eu^{III}) metal–metal bond.



Fig. 6. Structure of complexes 3 and 4 in the crystals (M = Mn, Zn).



 $Fig. \ 7. \ Molecular \ structure \ of \ the \ complex \ Pd_2Nd_2(\mu-OOCMe)_8(\mu,\eta^2-OOCMe)_2(THF)_2 \cdot ({\bf 5}) \ with \ thermal \ ellipsoids \ drawn \ at \ 50\% \ probability \ level.$



Fig. 8. Molecular structure of the complex $Pd_2Eu_2(\mu$ -OOCMe) $_8(\mu,\eta^2$ -OOCMe) $_2(THF)_2 \cdot (6)$ with thermal ellipsoids drawn at 50% probability level.



Fig. 9. Molecular structure of the complex $Pd_2^{II}Ce_2^{IV}(\mu, \eta^2$ -OOCMe) $_2(\eta^1$ -OOCMe) $_2(\mu$ -OOCMe) $_2(H_2O)_2$ (7) with thermal ellipsoids drawn at 30% probability level.

Table 7 Selected geometrical parameters for two independent molecules in crystal **5**

Table 8	
Selected geometrical parameters for two independent molecules in crystal	
6	

Bond lengths (Å)				Molecule A		Molecule B
Molecule A				Bond lengths (\mathring{A})		
Nd(1)-Pd(1)	3.2275(9)	Nd(2)-Pd(2)	3.2125(9)	$E_{11}(1)$ $Pd(1)$	3 2170(10)	$F_{11}(3)$ $P_{1}(3)$
Nd(1)Nd(2)	4.1691(8)	Pd(1)–O(1)	2.002(6)	$E_{11}(2) - Pd(2)$	3.2170(10) 3.2026(10)	Eu(3) - Pd(4)
Pd(1)–O(3)	2.004(6)	Pd(1)–O(5)	1.989(6)	Eu(2) - Fu(2) Eu(1) - Fu(2)	4 0822(9)	Eu(4) = Eu(4) Eu(3) = Eu(4)
Pd(1)–O(7)	2.016(6)	Pd(2)–O(9)	2.016(6)	Pd(1) - O(1)	4.0822(9) 1 999(7)	Pd(3) = Du(4)
Pd(2)–O(11)	2.011(6)	Pd(2)-O(13)	1.987(6)	Pd(1) = O(1)	1.999(7) 1.962(9)	Pd(3) = O(21)
Pd(2)–O(15)	2.007(6)	Nd(1)–O(2)	2.425(6)	Pd(1) = O(5)	1.902(9)	Pd(3) = O(25)
Nd(1)–O(4)	2.394(6)	Nd(1)–O(6)	2.434(5)	Pd(1) = O(3) Pd(1) = O(7)	2.013(8) 1.000(0)	Pd(3) = O(23) Pd(3) = O(27)
Nd(1)–O(8)	2.432(6)	Nd(1)-O(17)	2.449(5)	Pd(1) = O(7) Pd(2) = O(0)	1.999(9)	Pd(3)=O(27) Pd(4)=O(20)
Nd(1)–O(19)	2.557(5)	Nd(1)-O(20)	2.495(5)	Pd(2) = O(9) Pd(2) = O(11)	1.990(8)	Pd(4) = O(29) Pd(4) = O(21)
Nd(1)-O(31)	2.529(5)	Nd(2)-O(10)	2.421(5)	Pd(2) = O(11) Pd(2) = O(12)	1.962(9)	Pd(4) = O(31)
Nd(2)–O(12)	2.397(6)	Nd(2)–O(14)	2.444(5)	Pd(2) = O(15) Pd(2) = O(15)	1.978(10) 2.007(8)	Pd(4) = O(33) Pd(4) = O(25)
Nd(2)-O(16)	2.432(5)	Nd(2)-O(17)	2.561(5)	Pu(2) = O(13) Fu(1) = O(2)	2.007(8)	Fu(4) = O(33) Fu(2) = O(22)
Nd(2) - O(18)	2.512(5)	Nd(2) - O(19)	2.423(5)	Eu(1) - O(2)	2.354(7)	Eu(3) = O(22)
Nd(2) - O(32)	2.501(5)		_(())	Eu(1) - O(4)	2.405(7)	Eu(3) = O(24)
				Eu(1) - O(6)	2.364(8)	Eu(3) - O(26)
Molecule B				Eu(1)-O(8)	2.387(8)	Eu(3) - O(28)
Nd(3)-Pd(3)	3.2411(10)	$Nd(3)Nd(3A)^{a}$	4.1442(8)	Eu(1) - O(17)	2.509(8)	Eu(3) - O(37)
Pd(3)–O(21)	1.995(6)	Pd(3)–O(23)	2.013(6)	Eu(1) - O(18)	2.496(7)	Eu(3) - O(39)
Pd(3)–O(25)	1.970(6)	Pd(3)–O(27)	2.005(5)	Eu(1) - O(19)	2.404(7)	Eu(3) - O(40)
Nd(3)–O(22)	2.416(5)	Nd(3)-O(24)	2.401(6)	Eu(1) - O(41)	2.436(8)	Eu(3) - O(43)
Nd(3)-O(26)	2.440(5)	Nd(3)-O(28)	2.420(5)	Eu(2) - O(10)	2.332(9)	Eu(4)–O(30)
Nd(3)-O(29)	2.445(5)	Nd(3)-O(29A) ^a	2.547(5)	Eu(2) - O(12)	2.395(7)	Eu(4)–O(32)
$Nd(3) - O(30A)^{a}$	2.520(5)			Eu(2)–O(14)	2.421(7)	Eu(4)-O(34)
Nd(3)–O(33)	2.514(6)			Eu(2)-O(16)	2.356(7)	Eu(4)-O(36)
				Eu(2)–O(17)	2.399(7)	Eu(4)-O(37)
Bond angles (°)				Eu(2)–O(19)	2.495(7)	Eu(4)–O(38)
Molecule A				Eu(2)–O(20)	2.469(8)	Eu(4)–O(39)
O(1) - Pd(1) - O(3)	89.4(2)	O(5) - Pd(1) - O(1)	89.1(2)	Eu(2)–O(42)	2.494(8)	Eu(4)-O(44)
O(3) - Pd(1) - O(7)	90.4(2)	O(5) - Pd(1) - O(7)	90.9(2)	Derid and I and (Q)		
O(11) - Pd(2) - O(9)	89.3(3)	O(13) - Pd(2) - O(15)	90.7(3)	Bona angles (2)	00.2(2)	Q(21) D1(2) Q(25)
O(13) - Pd(2) - O(9)	89.0(3)	O(15) - Pd(2) - O(11)	90.8(3)	O(1) - Pd(1) - O(5) O(2) = P I(1) - O(1)	90.2(3)	O(21) - Pd(3) - O(25) O(22) - P1(2) - O(21)
O(2) - Nd(1) - Pd(1)	62.49(13)	O(4) - Nd(1) - Pd(1)	61.84(12)	O(3) - Pd(1) - O(1)	87.0(3)	O(23) - Pd(3) - O(21)
O(6) - Nd(1) - Pd(1)	63 53(13)	O(8) - Nd(1) - Pd(1)	63.72(13)	O(3) - Pd(1) - O(7)	91.6(4)	O(23) - Pd(3) - O(27)
O(17) - Nd(1) - Pd(1)	132.35(12)	O(19) - Nd(1) - Pd(1)	135.90(12)	O(7) - Pd(1) - O(5)	91.1(4)	O(27) - Pd(3) - O(25)
O(20) - Nd(1) - Pd(1)	$117 \ 30(13)$	O(31) - Nd(1) - Pd(1)	130.93(14)	O(11) - Pd(2) - O(9)	90.8(4)	O(31) - Pd(4) - O(29)
O(10) - Nd(2) - Pd(2)	64 14(14)	O(12) - Nd(2) - Pd(2)	62 91(13)	O(9) - Pd(2) - O(15)	90.2(4)	O(33)–Pd(4)–O(29)
O(14) - Nd(2) - Pd(2)	62.96(13)	O(12) = Nd(2) = Pd(2) O(16) = Nd(2) = Pd(2)	63.05(12)	O(13) - Pd(2) - O(11)	87.6(4)	O(35) - Pd(4) - O(33)
O(17) - Nd(2) - Pd(2)	143.00(11)	O(18) - Nd(2) - Pd(2)	$121 \ 37(12)$	O(13) - Pd(2) - O(15)	91.3(4)	O(35) - Pd(4) - O(31)
O(19)-Nd(2)-Pd(2)	126.96(12)	O(10) = Nd(2) = Pd(2) O(32) = Nd(2) = Pd(2)	121.37(12) 128.83(13)	O(2) - Eu(1) - Pd(1)	64.20(1)	O(22)-Eu(3)-Pd(3)
O(17) Hu(2) Hu(2)	120.90(12)	O(32) $IO(2)$ $IO(2)$	120.05(15)	O(4) - Eu(1) - Pd(1)	62.29(19)	O(24) - Eu(3) - Pd(3)
Molecule B				O(6) - Eu(1) - Pd(1)	62.6(2)	O(26) - Eu(3) - Pd(3)
O(21)-Pd(3)-O(23)	90.5(2)	O(25)-Pd(3)-O(21)	87.1(3)	O(8) - Eu(1) - Pd(1)	62.78(18)	O(28)-Eu(3)-Pd(3)
O(27)-Pd(3)-O(23)	90.8(3)	O(25)-Pd(3)-O(27)	91.4(3)	O(17)-Eu(1)-Pd(1)	142.42(17)	O(37)-Eu(3)-Pd(3)
O(22)-Nd(3)-Pd(3)	62.92(13)	O(24)-Nd(3)-Pd(3)	62.19(13)	O(18) - Eu(1) - Pd(1)	122.99(18)	O(39)-Eu(3)-Pd(3)
O(26)-Nd(3)-Pd(3)	63.01(13)	O(28)-Nd(3)-Pd(3)	62.42(12)	O(19)-Eu(1)-Pd(1)	125.63(16)	O(40)-Eu(3)-Pd(3)
O(29) - Nd(3) - Pd(3)	127.45(12)	$O(29A)^{a}-Nd(3)-Pd(3)$	138.66(12)	O(41)-Eu(1)-Pd(1)	128.9(2)	O(43)-Eu(3)-Pd(3)
O(33) - Nd(3) - Pd(3)	128.05(14)	$O(30A)^{a}-Nd(3)-Pd(3)$	122.56(12)	O(2)-Eu(1)-Eu(2)	106.2(2)	O(22)-Eu(3)-Eu(4)
a Symmotory transferr	nations used t-	ganarata aquivalant -t-		O(4) - Eu(1) - Eu(2)	84.24(19)	O(24)-Eu(3)-Eu(4)
symmetry transform	nations used to	generate equivalent ato	5ms: -x + 1,	O(6)-Eu(1)-Eu(2)	150.6(2)	O(26)-Eu(3)-Eu(4)
-y+2, -z+1.				O(8)-Eu(1)-Eu(2)	115.62(19)	O(28)–Eu(3)–Eu(4)
				O(17)–Eu(1)–Eu(2)	32.87(17)	O(37)–Eu(3)–Eu(4)
				O(18) - Eu(1) - Eu(2)	79.56(18)	O(39)-Eu(3)-Eu(4)

O(19)-Eu(1)-Eu(2)

O(41)-Eu(1)-Eu(2)

Pd(1)-Eu(1)-Eu(2)

O(10)-Eu(2)-Pd(2)

O(12)-Eu(2)-Pd(2)

O(16)-Eu(2)-Pd(2)

O(14)-Eu(2)-Pd(2)

O(19)-Eu(2)-Pd(2)

O(17)-Eu(2)-Pd(2)

O(20)-Eu(2)-Pd(2)

O(42)-Eu(2)-Pd(2)

34.26(17)

78.5(2)

146.46(2)

62.3(2)

63.0(2)

63.94(18)

63.70(17)

136.69(16)

129.89(18)

119.56(18)

130.0(2)

The Pd–Ce complex 7 differs from complexes 5 and 6 by chemical composition: unlike the Pd– Nd and Pd–Eu complexes, it contains 12 rather than 10 acetate groups per the Pd_2Ce_2 formula unit. Hence, the cerium atoms in complex 7 are in the oxidation state +4. This is due to the fact that the starting cerium(III) salt is readily oxidized with the air oxygen to cerium(IV) under the synthesis conditions. The additional acetate anions are connected to the cerium atoms by the

3.2043(11) 3.2083(11) 4.0962(9) 1.976(8) 1.976(9) 2.012(8) 1.996(9) 2.019(8) 2.004(8)2.002(8) 1.970(8) 2.374(8) 2.400(7)2.362(8) 2.365(8)2.382(7)2.525(7)2.480(7)2.448(8) 2.366(8) 2.379(8) 2.387(8)2.393(8) 2.497(7) 2.442(8) 2.420(7)2.460(7)

89.7(4)

88.9(4)

92.0(4)

89.3(4)

89.0(3)

90.4(4)

91.7(3)

88.8(3)

64.2(2)

62.80(18)

62.76(19)

63.37(18)

126.58(17)

142.09(17)

122.03(17)

128.5(2)

106.4(2)

84.72(18)

149.50(19)

115.31(19)

33.79(17)

33.24(16)

79.68(17)

78.4(2)

147.47(3)

62.2(2)

62.7(2)

63.6(2)

63.82(19)

117.69(19)

136.84(16)

131.31(18)

129.7(2)

O(40)-Eu(3)-Eu(4)

O(43)-Eu(3)-Eu(4)

Pd(3)-Eu(3)-Eu(4)

O(30)-Eu(4)-Pd(4)

O(32)-Eu(4)-Pd(4)

O(34)-Eu(4)-Pd(4)

O(36)-Eu(4)-Pd(4)

O(38)-Eu(4)-Pd(4)

O(37)-Eu(4)-Pd(4)

O(39)-Eu(4)-Pd(4)

O(44)-Eu(4)-Pd(4)

(continued on next page)

Table 8 (continued)

Molecule A		Molecule B					
Bond angles (°)							
O(10) - Eu(2) - Eu(1)	150.6(2)	O(30) - Eu(4) - Eu(3)	150.0(2)				
O(12)-Eu(2)-Eu(1)	100.5(2)	O(32)-Eu(4)-Eu(3)	99.4(2)				
O(14) - Eu(2) - Eu(1)	82 26(17)	O(34) - Eu(4) - Eu(3)	$121 \ 31(19)$				
O(16) - Eu(2) - Eu(1)	120.04(19)	O(36) - Eu(4) - Eu(3)	83 02(19)				
O(10) = Eu(2) = Eu(1) O(17) = Eu(2) = Eu(1)	34 58(19)	O(30) = Eu(4) = Eu(3) O(37) = Eu(4) = Eu(3)	32.04(16)				
O(19) = Eu(2) = Eu(1)	32 85(16)	O(38) = Eu(4) = Eu(3)	80.03(17)				
O(20) = Eu(2) = Eu(1)	79 48(18)	O(30) = Eu(4) = Eu(3) O(30) = Eu(4) = Eu(3)	34.90(17)				
O(20) - Eu(2) - Eu(1) O(42) Eu(2) Eu(1)	81.8(2)	O(39) = Eu(4) = Eu(3) O(44) = Eu(4) = Eu(3)	34.90(17) 82.20(10)				
Pd(2)-Eu(2)-Eu(1)	144.81(2)	Pd(4) = Eu(4) = Eu(3) Pd(4) = Eu(4) = Eu(3)	145.21(2)				
Table 9							
Selected bond lengths (Å) and angles (°) in complex 7							
$\overline{C_{2}(1)}$ $O(2)$	2 422(2)	$C_{2}(1)$ $O(2)$	2 478(2)				
Ce(1) = O(8)	2.432(3)	Ce(1) = O(2)	2.478(3)				
Ce(1) = O(6)	2.527(3)	Ce(1) = O(9) # 1	2.541(3)				
Ce(1) - O(4)	2.546(3)	Ce(1) - O(12)	2.552(3)				
Ce(1) - O(13)	2.576(4)	Ce(1) - O(10)	2.590(3)				
Ce(1)-O(9)	2.670(3)	Ce(1)-C(9)	3.021(4)				
Ce(1)-Pd(1)	3.4022(9)	Pd(1)-O(1)	1.990(3)				
Pd(1) - O(3)	1.985(3)	Pd(1)–O(7)	1.986(3)				
Pd(1) - O(5)	2.001(3)	O(9)-Ce(1)#1	2.541(3)				
O(8)-Ce(1)-O(2)	117.78(11)	O(8) - Ce(1) - O(6)	75.59(10)				
O(2)-Ce(1)-O(6)	71.05(11)	O(8) - Ce(1) - O(9) #1	75.04(9)				
O(2)-Ce(1)-O(9)#1	144.79(10)	O(6)-Ce(1)-O(9)#1	142.46(10)				
O(8)-Ce(1)-O(4)	76.58(11)	O(2)-Ce(1)-O(4)	76.37(11)				
O(6)-Ce(1)-O(4)	119.29(10)	O(9)#1-Ce(1)-O(4)	75.35(9)				
O(8)-Ce(1)-O(12)	142.29(11)	O(2)-Ce(1)-O(12)	70.25(11)				
O(6)-Ce(1)-O(12)	13617(11)	O(9)#1-Ce(1)-O(12)	80 50(10)				
O(4)-Ce(1)-O(12)	69 68(11)	O(8)-Ce(1)-O(13)	67 09(12)				
O(2) $Ce(1)$ $O(12)$	13373(11)	O(6) - Ce(1) - O(13)	66.00(11)				
O(2) = O(1) = O(13) O(9) = 1 - Ce(1) - O(13)	81 26(10)	O(4)-Ce(1)-O(13)	140.75(11)				
O(12) - Ce(1) - O(13)	13661(12)	O(4) - Ce(1) - O(10)	143.75(11) 143.46(10)				
O(12) = Ce(1) = O(13) O(2) = Ce(1) = O(10)	79.05(10)	O(6) - Ce(1) - O(10)	80.83(10)				
O(2) = O(1) = O(10) O(0) = 0 = 0 = 0 = 0	110.82(8)	O(0) = Cc(1) = O(10) O(4) = Cc(1) = O(10)	130.89(10)				
$O(12) C_{e}(1) O(10)$	72.40(10)	O(4) = O(1) = O(10) $O(13) = C_{0}(1) = O(10)$	77.00(11)				
O(12) = CC(1) = O(10) O(8) = Ca(1) = O(9)	120.74(9)	O(13) = CC(1) = O(10) O(2) = Ce(1) = O(10)	120.07(0)				
O(6) - Cc(1) - O(9)	120.74(9) 116.81(9)	O(2) = O(1) = O(3) $O(0) \# 1 C_{2}(1) O(3)$	61.97(9)				
O(0) = CC(1) = O(9)	110.01(9) 122.84(0)	O(3) = O(1) = O(3)	68 86(10)				
O(4) = Ce(1) = O(9)	67.80(11)	O(12) - Ce(1) - O(9) O(10) - Ce(1) - O(9)	40.05(8)				
O(13) - Ce(1) - O(9)	126.04(11)	O(10) = Ce(1) = O(9) O(2) = Ce(1) = C(0)	49.03(8)				
$O(\delta) - Ce(1) - C(9)$	130.94(10)	O(2) = Ce(1) = C(9)	99.80(11)				
O(6) - Ce(1) - C(9) O(4) - Ce(1) - C(9)	99.38(10)	O(9)#1-Ce(1)-C(9)	80.40(9)				
O(4) = Ce(1) = C(9)	71.02(12)	O(12) - Ce(1) - C(9) $O(10) - C_{2}(1) - C(9)$	07.94(10)				
O(13) - Ce(1) - C(9)	71.93(12)	O(10) - Ce(1) - C(9)	24.39(10)				
O(9) - Ce(1) - C(9)	24.08(9)	O(8) - Ce(1) - Pd(1)	58.54(7)				
O(2) - Ce(1) - Pd(1)	59.31(8) 120.75(6)	O(6) - Ce(1) - Pd(1)	58.84(7)				
O(9)#1-Ce(1)-Pd(1)	120.75(6)	O(4) - Ce(1) - Pd(1)	60.54(7)				
O(12) - Ce(1) - Pd(1)	114.55(8)	O(13) - Ce(1) - Pd(1)	108.64(9)				
O(10) - Ce(1) - Pd(1)	128.44(6)	O(9) - Ce(1) - Pd(1)	1/5.59(6)				
C(9) - Ce(1) - Pd(1)	152.77(7)	O(7) - Pd(1) - O(3)	90.80(16)				
O(7) - Pd(1) - O(1)	1/6.19(13)	O(3) - Pd(1) - O(1)	89.51(16)				
O(7) - Pd(1) - O(5)	88.65(16)	O(3) - Pd(1) - O(5)	1/5.38(13)				
O(1) - Pd(1) - O(5)	90.74(16)	O(7) - Pd(1) - Ce(1)	91.92(9)				
O(3) - Pd(1) - Ce(1)	91.45(10)	O(1)-Pd(1)-Ce(1)	91.88(10)				
O(5) - Pd(1) - Ce(1)	93.16(9)	C(1) - O(1) - Pd(1)	118.5(3)				
C(1)-O(2)-Ce(1)	144.0(3)	C(3)-O(3)-Pd(1)	121.7(3)				
C(3)-O(4)-Ce(1)	140.8(3)	C(5)-O(5)-Pd(1)	118.8(3)				
C(5)-O(6)-Ce(1)	145.4(3)	C(7)-O(7)-Pd(1)	118.0(3)				
C(7)-O(8)-Ce(1)	146.8(3)	C(9)-O(9)-Ce(1)#1	147.9(2)				
C(9)-O(9)-Ce(1)	93.4(2)	Ce(1)#1-O(9)-Ce(1)	118.08(10)				
C(9)-O(10)-Ce(1)	97.4(2)	C(11)-O(12)-Ce(1)	141.6(3)				
O(10)-C(9)-Ce(1)	58.23(19)	O(9)-C(9)-Ce(1)	61.91(19)				
C(10)-C(9)-Ce(1)	1754(3)						

Symmetry transformations used to generate equivalent atoms: #1: -x + 1, -y + 2, -z + 2; #2: -x + 1, -y + 3, -z + 3.

 η^1 -mode (see Fig. 9), supplementing their coordination spheres to a normal coordination number of nine.

The X-ray diffraction study revealed that two of 14 acetate groups belong to the acetic acid molecules of crystallization, whereas the other 12 MeCOO groups are connected to the metal atoms as acido ligands.

Type 3: *double-bridged* Pd₂–Cu *triangle*. Triangle complex $Pd_2Cu(\mu$ -OOCMe)₆ (8). As mentioned above (see Section 2), the reaction between Pd^{II} and Cu^{II} acetates is noticeably different from the other heterometallic systems. The reaction between palladium(II) and copper(II) acetates seems to produce several different complexes depending on the reactants ratio. It was found in earlier work [20,21] that heating of the equimolar amounts of Pd^{II} and Cu^{II} acetates in acetic acid afforded a mixture of Pd^{II} – Cu^{II} acetates with different compositions, including CuPd(OAc)₄ and $CuPd_2(OAc)_6$. We also were not able to prepare the pure 1:1 complex CuPd(OAc)₄ when reacted $Pd_3(OAc)_6$ with $Cu(OAc)_2$. Instead, small crystals of the yellow-green (palladium-copper) and green (purely copper) acetates were seen with an optical microscope in the reaction product. The best preparations were made when using the 2:1 initial Pd:Cu ratio followed by crystallization from benzene to afford adoptable for X-ray diffraction analysis yellow-green crystals of the complex $Pd_2Cu(\mu - OOMe)_6$ (8).



Fig. 10. Molecular structure of the complex $Pd_2Cu(\mu$ -OOCMe)₆ (8) with thermal ellipsoids drawn at 30% probability level. The Pd and Cu atoms are disordered over the coordination triangle (multiplicity of general positions) Pd(0.7)/Cu(0.3) and of special position (mirror plane) Pd(0.3)/Cu(0.2).

Table 10 Selected bond lengths (Å) and angles (°) in complex 8

-		• •	
Bond lengths			
M(1) - O(3)	1.953(7)	M(1) - O(1)	1.981(6)
M(1)–O(6)	1.974(7)	M(1)-M(1)#1	3.1097(17)
M(1)-O(5)	1.982(7)	M(2)–O(2)	1.982(7)
M(1)-M(2)	3.1231(14)	M(2)-O(4)	1.997(7)
Bond angles			
O(3)-M(1)-O(1)	92.1(3)	O(3)-M(1)-O(5)	86.8(3)
O(1)-M(1)-O(6)	86.3(3)	O(6)-M(1)-O(5)	91.7(3)
O(2)-M(2)-O(2A) ^a	84.7(5)	O(2)-M(2)-O(4)	92.5(3)
O(4)-M(2)-O(4A) ^a	87.0(5)		
$M(1A)^{a}-M(1)-M(2)$	60.142(19)	$M(1A)^{a}-M(2)-M(1)$	59.72(4)

M(1)-Pd(0.7)/Cu(0.3); M(2)-Pd(0.3)/Cu(0.2).

^a Symmetry transformation used to generate equivalent atoms x, -y + 3/2, z.

The geometry of complex **8** (Fig. 10) was found to be very close to that of the trinuclear Pd_3 carboxylates [30–33]. The positions of Pd and Cu atoms in the structure of complex **8** are disordered over the coordination triangle (see Section 2). Both palladium(II) and copper(II) atoms have almost identical square-plane coordination with practically equal Pd–O and Cu–O interatomic distances (1.938(4)–1.959(4) Å) and O–Pd(Cu)–O angles (84.7(5)–92.5(3)°, Table 10).

3.3. Behaviour in solution

Most of the synthesized complexes are well soluble in acetic acid and, except for complex **8**, are stable for a long time at room temperature and for at least 3–5 h at 70 °C, as evidenced by the UV–Vis spectra. The formation of heterometallic complexes is accompanied by noticeable changes in the UV–Vis spectra. For instance, the d–d band of palladium(II) shifts from 398 to 335 nm on going from Pd₃(OOCMe)₆ to complex **2** and the extinction coefficient, ε_{max} , increases from 0.24 × 10³ to $1.9 \times 10^3 1 \text{ mol}^{-1} \text{ cm}^{-1}$ (Table 11).

The UV–Vis spectrum of complex **8** dissolved in acetic acid do not obey the Beer–Lambert law in the concentration range from 3×10^{-3} to 0.5×10^{-3} mol l⁻¹, and the complex slowly transforms to the monometallic components and other Pd^{II}–Cu^{II} complexes. Unlike this, the posi-

Table 11 UV–Vis spectral characteristics for complexes 1–3 and 8

Complex	d–d band		CT band	
	λ (nm)	$\varepsilon (1 \text{ mol}^{-1} \text{ cm}^{-1})$	λ (nm)	$\varepsilon (1 \text{ mol}^{-1} \text{ cm}^{-1})$
Pd ₃ (OOCMe) ₆	398	245	256	1900
1	335	1600	250	3000
2	325	1900	250	3000
3	340	1100	250	2012
8 ^a	385	680	265	1500

^a The initial λ_{max} and ε_{max} values for complex 8 measured within 3–5 min after dissolution in acetic acid.

4. Conclusions

Our study showed that the double-bridged trinuclear structure of palladium(II) acetate can easily undergo a nucleophilic attack by a terminal acetate group of the mononuclear complexes of divalent transition metals (e.g., Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}) and trivalent rare-earth metals (e.g., Nd^{III}, Eu^{III}, Ce^{III}) to give rise to the mixedmetal di-, tri- and tetranuclear complexes in which the square-planar moiety $[Pd(\mu - OOCMe)_4]$ serves a function of the structure-determining building block. The fact that the prepared mixed-metal complexes involve not only the 3d- but also 4f-metals suggests the reaction to be of general occurrence. In most cases (except for Cu^{II}) the complexes have a "face-to-face" arrangement of the Pd^{II} and M^{II,III} coordination planes. Unlike this, in the Pd^{II}-Cu^{II} acetate complexes the Pd^{II} and Cu^{II} coordination planes are turned 60° to each other.

The Pd^{II} and Cu^{II} acetates are known to be a basis of the catalyst for homogeneous olefin oxidation and oxidative acetoxylation [6–12]. We believe that the found Pd^{II}–Cu^{II} complexation in this catalytic system should be taken into account when analysing the kinetic and mechanistic data on the catalytic reactions.

The metal–metal interatomic distances in the complexes under question also engage our attention. According to the X-ray diffraction data, the $Pd^{II}-M^{II,III}$ distances in the four-bridged complexes are very close to the sum of the corresponding covalent radii, whereas in the double-bridged $Pd^{II}-Cu^{II}$ complexes the distances have a normal value of ~3.1 Å. The formation of direct metal–metal bonds between the divalent palladium and two- or three-valent transition metals seem to be unlikely. Meanwhile, a weak electron interaction cannot a priori be ruled out and, therefore, needs a special investigation.

The above-examined heterodimetallic Pd^{II} -based complexes are of interest not only for catalysis and the coordination chemistry of these metals but also as promising starting materials for the synthesis of heterometallic nanomaterials. Earlier [34,35] we have synthesized a palladium giant cluster with the idealized formula Pd_{561} phen₆₀(OAc)₁₈₀ by the reduction of Pd_3 (OOCMe)₆ in acetic acid containing a dozed amount of 1,10-phenanthroline (phen) as stabilizing ligand. The Pd giant cluster and its derivatives containing different acido ligands (PF_6^- , OH^- , O^{2-} , etc.) but preserving the [Pd_{561} phen₆₀] cluster core exhibited high catalytic performance in various reactions under mild conditions [34] and specific thermomagnetic behaviour [36].

A similar synthetic approach can be used for the preparation of bimetallic nanoclusters starting from the Pd^{II}based heterodimetallic complexes. In particular, it would be of interest to reveal whether the complementary metal can enter the cluster core to form an alloy nanoparticle or it will serve as extra ligand for the Pd giant cluster. These studies are in progress in our group now.

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References

- [1] J.H. Sinfelt, Bimetallic Catalysts. Discoveries, Concepts and Applications, Wiley, New York, 1983.
- [2] K.I. Zamaraev, Pure Appl. Chem. 69 (1997) 865.
- [3] M. Heemeier, A.F. Carlsson, M. Naschitzki, M. Schmal, M. Bäumer, H.-J. Freund, Angew. Chem., Int. Ed. Engl. 41 (2002) 4073.
- [4] O. Savadogo, K. Lee, S. Mitsushima, N. Kamiya, K.-I. Ota, J. New Mat. Electrochem. Systems 7 (2004) 77.
- [5] J.L. Fernandez, D.A. Walsh, A.J. Bard, J. Am. Chem. Soc. 127 (2005) 357.
- [6] J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Rüttinger, H. Kojer, Angew. Chem. 71 (1959) 176.
- [7] I.I. Moiseev, M.N. Vargaftik, Ya.K. Syrkin, Doklady Akad. Nauk SSSR 130 (1960) 820.
- [8] I.I. Moiseev, M.N. Vargaftik, Ya.K. Syrkin, Doklady Akad. Nauk SSSR 133 (1960) 377 (in Russian).
- [9] I.I. Moiseev, π-Complexes in Liquid-Phase Olefin Oxidation, Nauka, Moscow, 1970 (in Russian).
- [10] P.M. Maitlis, The Organic Chemistry of Palladium, Academic Press, New York, 1971.
- [11] P.M. Henry, in: Palladium Catalyzed Oxidation of Hydrocarbons, D. Reidel, Dordrecht, 1980, p. 41.

- [12] R. Jira, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, Wiley-VCH, Weinheim, 2002, p. 386.
- [13] U. Thewalt, S.Z. Müller, Natuforsch. B: Chem. Sci. 44 (1989) 1206.
- [14] M. Kujime, S. Hikichi, M. Akita, J. Chem. Soc., Dalton Trans. (2003) 3506.
- [15] Y. C Neo, J.J. Vittal, T.S. Hor, J. Chem. Soc., Dalton Trans. (2002) 337.
- [16] F.-E. Hong, C.-P. Chang, Yu.-C. Chang, J. Chem. Soc., Dalton Trans. (2003) 3892.
- [17] R.W. Brandon, D.V. Claridge, Chem. Commun. (1968) 677.
- [18] A.L. Balch, B.J. Davis, E.Y. Fung, M.M. Olmstead, Inorg. Chim. Acta 212 (1993) 149.
- [19] S. Adam, A. Bauer, O. Timpe, U. Wild, G. Mestl, W. Bensch, R. Schlögl, Chem. Eur. J. 4 (1998) 1458.
- [20] R.J. Pandey, P.M. Henry, Can. J. Chem. 52 (1974) 1241.
- [21] R.J. Pandey, P.M. Henry, Can. J. Chem. 53 (1975) 1833.
- [22] N.Yu. Kozitsyna, M.N. Vargaftik, I.I. Moiseev, J. Organometal. Chem. 593–594 (2000) 274.
- [23] N.Yu. Kozitsyna, A.A. Bukharkina, M.V. Martens, M.N. Vargaftik, I.I. Moiseev, J. Organometal. Chem. 636 (2001) 69.
- [24] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd ed., Pergamon Press, Oxford, 1988.
- [25] T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer, G. Wilkinson, J. Chem. Soc. (1965) 3632.
- [26] G.M. Sheldrick, SADABS, Bruker AXS Inc., Madison, WI-53719, USA, 1997.
- [27] SMART V5.051 and SAINT V5.00, Area Detector Control and Integration Software, 1998, Bruker AXS Inc., Madison, WI-53719, USA..
- [28] G.M. Sheldrick, SHELXTL-97 V5.10, Bruker AXS Inc., Madison, WI-53719, USA, 1997.
- [29] Preliminary communication see: N.Yu. Kozitsyna, S.E. Nefedov, N.V. Cherkashina, V.N. Ikorski, M.N. Vargaftik, I.I. Moiseev, Russ. Chem. Bull. 1 (2005) 9.
- [30] A.C. Skapski, M.L. Smart, J. Chem. Soc. D (1970) 658.
- [31] F.A. Cotton, S. Han, Revue de Chimie Mineral 20 (1983) 496.
- [32] F.A. Cotton, S. Han, Revue de Chimie Mineral. 22 (1985) 277.
- [33] N.Yu. Kozitsyna, M.V. Martens, I.P. Stolarov, S.E. Nefedov, M.N. Vargaftik, I.L. Eremenko, I.I. Moiseev, Russ. J. Inorg. Chem. 44 (1999) 1823.
- [34] M.N. Vargaftik, V.P. Zagorodnikov, I.P. Stolarov, I.I. Moiseev, D.I. Kochubey, V.A. Likholobov, A.L. Chuvilin, K.I. Zamaraev, J. Mol. Catal. 53 (1989) 315.
- [35] M.N. Vargaftik, I.I. Moiseev, in: F.A. Cotton, R. Adams (Eds.), Catalysis by Di- and Polynuclear Metal Complexes, Wiley-VCH, NewYork, 1998, p. 395.
- [36] Y. Volokitin, J. Sinzig, L.J. de Jongh, G. Schmidt, M.N. Vargaftik, I.I. Moiseev, Nature 384 (1996) 621.