First crystalline palladium(II) carboxylate complex with divalent 3d metal, PdCo(μ-OOCMe)$_4$(NCMe): synthesis and structure*

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The first heterometallic palladium(II) acetate complex with divalent 3d metal, PdCo(μ-OOCMe)$_4$(NCMe) • 3 MeCN, was synthesized and structurally characterized.

Key words: palladium, cobalt, heterometallic complex, structure, magnetic susceptibility, spectra.

Coordination compounds of palladium(II) with transition metals are both of theoretical and practical interest, in particular, as the starting compounds for the preparation of bimetallic nanoalloys[1] and catalysts.[2] Published data on these complexes are scarce. Most of known compounds contain halide, hydroxy, and/or organic N- and P-donor ligands. These liagnds substantially complicate the preparation of polymetallic nanomaterials. Heterometallic palladium(II)—transition metal complexes with readily removable carboxylate ligands (acetate, pivalate, *etc.*) could be very convenient for this purpose as the starting compounds.

The Cambridge Structural Database contains crystal structure information on two palladium(II) acetate complexes with post-transition metals only, *viz.*, Pd$_2$Cd$_2$(μ-OOCMe)$_8$(HOOCMe)$_2$ [3] and PdTl(μ-OOCMe)$_4$(OCOMe),[4] whereas data on complexes with transition metals are lacking. Earlier, the synthesis of the complexes of composition PdCo(OOCMe)$_4$ • 2HOOCMe • 2H$_2$O, PdNi(OOCMe)$_4$ • HOOCMe • H$_2$O, PdCu(OOCMe)$_4$, and PdCd(OOCMe)$_4$ • H$_2$O • HOOCMe has been briefly described.[5] However, neither strong evidence for the chemical nature of these compounds nor X-ray diffraction data have been reported.

We synthesized and structurally characterized the first palladium(II) carboxylate complex with 3d transition metal in oxidation state +2. The complex PdCo(μ-OOCMe)$_4$(NCMe) • 3MeCN (**1**) was characterized by X-ray diffraction, elemental analysis, electronic spectroscopy, and IR spectroscopy.

Results and Discussion

After the addition of cobalt(II) acetate Co(OOCMe)$_2$ • 4H$_2$O to a solution of palladium(II) acetate Pd$_3$(μ-OOCMe)$_6$ in acetic acid heated to 70 °C, the color of the solution gradually changed from red to yellow-orange and cobalt(II) acetate (which is poorly soluble in acetic acid) dissolved. Attempts to isolate the resulting compound in the crystalline state failed. Crystals suitable for X-ray diffraction were grown by crystallization from acetonitrile, and the heterometallic complex PdCo(μ-OOCMe)$_4$(NCMe) • 3MeCN (**1**) was isolated.

Single-crystal X-ray diffraction study of complex **1** demonstrated that the molecule of **1** has a lantern-type structure (Fig. 1).

The Pd and Co atoms are linked by four bridging acetate groups. The Pd—Co distance (2.515(3) Å) is substantially smaller than the sum of the van der Waals radii of the palladium and cobalt atoms and is only slightly larger than the sum of the covalent radii of these atoms (Pd—Co, 2.44 Å) (Table 1).

One of three solvent MeCN molecules is located much closer to the molecule of the complex than two other MeCN molecules, and there is a short contact between the palladium atom and the nitrogen atom of this MeCN molecule (Pd(1)—N(1), 2.509 Å). As a consequence, the Pd and Co atoms are disordered over two positions with

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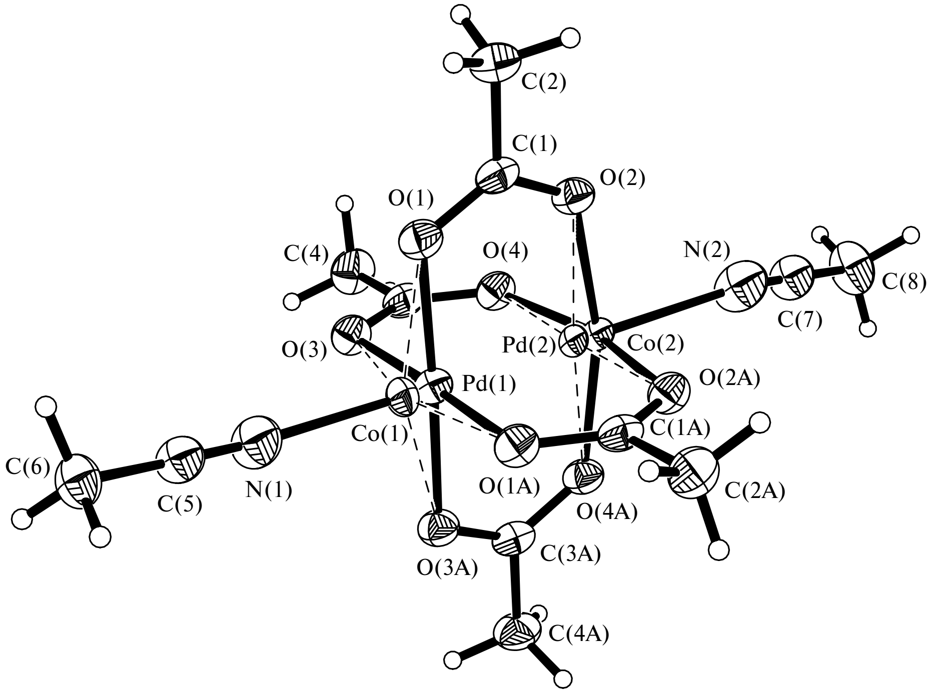


Fig. 1. Molecular structure of the complex $PdCo(\mu\text{-}OOCMe)_4(NCMe) \cdot 3\ MeCN$ (**1**) with displacement ellipsoids drawn at the 50% probability level. The Pd and Co atoms are disordered over two positions with equal occupancies (two of three MeCN molecules of crystallization are omitted).

Table 1. Selected geometric characteristics of heterometallic complex **1**

Bond	d/Å	Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Pd(1)—Co(2)	2.515(3)	Pd(2)—Co(1)	2.551(3)	O(1)—Pd(1)—O(3)	90.69(9)	O(2)—Pd(2)—O(4)	90.67(9)
Pd(1)—O(1)	2.025(3)	Pd(2)—O(2)	2.013(3)	O(1A)[a]—Pd(1)—O(1)	89.78(15)	O(2A)[a]—Pd(2)—O(2)	89.58(16)
Pd(1)—O(3)	2.041(3)	Pd(2)—O(4)	2.037(3)	O(3)—Pd(1)—O(3A)[a]	88.74(14)	O(4)—Pd(2)—O(4A)[a]	88.72(16)
Co(2)—O(2)	2.070(4)	Co(1)—O(1)	2.091(4)	O(1)—Pd(1)—Co(2)	91.18(11)	O(2)—Pd(2)—Co(1)	93.56(11)
Co(2)—O(4)	2.027(4)	Co(1)—O(3)	2.050(4)	O(3)—Pd(1)—Co(2)	91.27(12)	O(4)—Pd(2)—Co(1)	90.97(11)
Co(2)—N(2)	2.279(6)	Co(1)—N(1)	2.073(5)	N(2)—Co(2)—Pd(1)	176.7(3)	N(1)—Co(1)—Pd(2)	177.1(3)
Pd(1)...N(1)	2.509(5)	Pd(2)...N(2)	2.678(6)				

[a] The symmetry code for equivalent atoms: $x - y + 3/2z$.

virtually equal occupancies. The distance between two positions in the structure of **1** is ~0.4 Å (alternative positions are shown in Fig. 1 by dashed lines).

The relatively short Pd—Co distance (see above) could be indicative of the presence of the metal—metal bond, although an electronic interaction between the Pd^{II} (d^8) and Co^{II} (d^7) atoms is unlikely to occur.

The effective magnetic moment of complex **1** weakly depends on the temperature (4.846 μ_B at 300 K, 3.710 μ_B at 2 K, S = 3/2) and is almost equal to the magnetic moment of the mononuclear complex $Co(H_2O)_6^{2+}$ (4.9 μ_B at 300 K).

Solutions of complex **1** in acetic acid are stable at room temperature for an indefinitely long time and at 70 °C for at least 3 h. In the visible and UV regions, the spectrum differs substantially from both the spectra of the starting palladium and cobalt complexes (Fig. 2) and the sum of these spectra.

The formation of the heterometallic complex is accompanied by a substantial hypsochromic shift of the d—d band of palladium from 400 to 335 nm and an increase in its intensity, whereas the position and intensity of the charge-transfer band are changed only slightly (Table 2).

The formation of the heterometallic complex occurs, apparently, through the nucleophilic attack of the terminal carboxylate groups of the mononuclear complex $Co(OOCMe)_2 \cdot 4H_2O$ on the palladium(II) atoms of the trinuclear complex $Pd_3(OOCMe)_6$, resulting in the cleavage of the carboxylate bridges and open-

Table 2. Characteristics of the electronic absorption spectra of the starting complexes and complex **1** (AcOH as the solvent, $C = 1.5 \cdot 10^{-3}$ mol L^{-1}, 25 °C)

Complex	d—d Transition		Charge-transfer transition	
	λ/nm	ε/L mol^{-1} cm^{-1}	λ/nm	ε/L mol^{-1} cm^{-1}
$Pd_3(OOCMe)_6$	400	240	255	1800
$Co(OOCMe)_2 \cdot 4H_2O$	258	35	~200	—
$PdCo(OOCMe)_4(NCMe)$ (**1**)	335	1600	260	2000

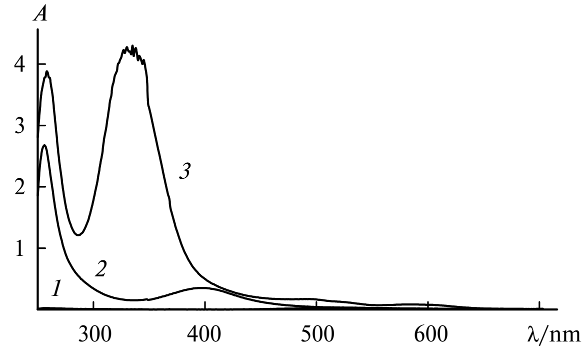
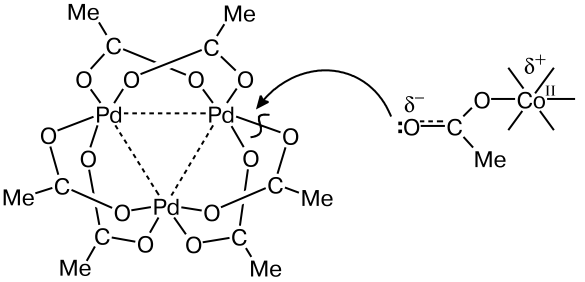


Fig. 2. Absorption spectra of solutions of the starting complexes $Co(OOCMe)_2 \cdot 4H_2O$ ($C = 1.5 \cdot 10^{-3}$ mol L^{-1}) (*1*); $Pd_3(OOCMe)_6$ ($C = 1.5 \cdot 10^{-3}$ mol L^{-1}) (*2*); and PdCo(μ-OOCMe)$_4$(NCMe)$\cdot$3MeCN ($C = 3 \cdot 10^{-3}$ mol L^{-1}) (*3*) in AcOH at 25 °C.

ing of the cyclic structure of the starting palladium complex.



Earlier,[6] analogous reactions have been observed for $Pd_3(OOCMe)_6$ with acetates of monovalent cations, *viz.*, alkali metals, NR_4^+, and $[(Ph_3P)_2N]^+$. These reactions rapidly proceed (during a few minutes) in acetic acid solutions at room temperature. The coordination vacancies that appear are occupied by the attacking carboxylate groups.

$$2\,Pd_3(OOCMe)_6 + 6\,M^+MeCOO^- \rightleftharpoons 3\,M_2{}^+[Pd_2(OOCMe)_6]^{2-}$$

$$M_2[Pd_2(OOCMe)_6]^{2-} + 2\,M^+MeCOO^- \rightleftharpoons 2\,M_2{}^+[Pd(OOCMe)_4]^{2-}$$

$$M^+ = Na^+,\ K^+,\ NR_4{}^+,\ [(Ph_3P)_2N]^+$$

Mono- and dinuclear palladium(II) complexes were found[6] in solutions of acetates of monovalent cations as tight ion pairs with the corresponding cations. An analogous reaction with the cobalt(II) complex proceeds substantially more slowly (refluxing in acetic acid for 1.5 h) and affords the covalently bound heterometallic complex as the final product, which was isolated as the crystal solvate PdCo(μ-OOCMe)$_4$(NCMe)$\cdot$3MeCN.

Experimental

Elemental microanalysis was carried out on an automated Carlo Erba Strumentazione C,H,N-analyzer. The magnetic susceptibility was measured on a SQUID Quantum Design magnetometer in the temperature range 2—300 K. The UV-Vis spectra of solutions of the complexes were recorded on a Varian Cary 100 spectrophotometer. The IR spectra were measured on a Nicolet Nexus spectrophotometer (KBr pellets).

The solvents (glacial acetic acid, acetonitrile, and benzene) of reagent grade (Reakhim) were dried and purified according to standard procedures.[7] Palladium(II) acetate $Pd_3(OOCMe)_6$ was synthesized by oxidation of Pd black (prepared by reduction of $PdCl_2$ (reagent grade, the Voikov Plant, Russia) with sodium borohydride) with concentrated HNO_3 in glacial acetic acid according to a known procedure,[8] purified from impurities of nitrite complexes by refluxing in glacial acetic acid containing a new portion of Pd black over a long period of time until elimination of NO_2 ceased, and then recrystallized from acetic acid. Cobalt(II) acetate $Co(OOCMe)_2 \cdot 4H_2O$ of reagent grade (Acros, Belgium) was used without additional purification.

Complex PdCo(μ-OOCMe)$_4$(NCMe)$\cdot$3MeCN (1). Palladium(II) acetate $Pd_3(OOCMe)_6$ (448 mg, 2 mmol based on Pd) and cobalt(II) acetate $Co(OOCMe)_2 \cdot 4H_2O$ (498 mg, 2 mmol) were suspended in acetic acid (20 mL) and refluxed with stirring until the precipitate was completely dissolved (~1.5 h). The solvent was evaporated to dryness on a rotary evaporator. The dry residue was dissolved in benzene (15 mL) and the solution was concentrated to dryness. The latter operation was repeated three times until the acetic acid was completely removed. The resulting pink-beige powder was dissolved in acetonitrile (20 mL), concentrated to 5 mL, and kept at ~20 °C for one day. The cherry-colored crystals of complex **1** that precipitated (320 mg) were separated by decantation and studied by X-ray diffraction. The complex rapidly loses a large portion of MeCN molecules of crystallization during storage in air. Found (%): C, 27.34; N, 3.23; H, 3.49. $C_{10}H_{15}O_8NPdCo$ (MeCN molecules of crystallization are not taken into account).

Calculated (%): C, 27.14, N, 3.16; H, 3.42. IR, ν/cm^{-1}: 2945, 2882, 2822, 1610 s (ν_{as}(CO)), 1409 (ν_s(CO)), 1385, 1345, 1051, 1029, 698, 624.

X-ray diffraction study of complex 1. X-ray diffraction study was carried out at the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences) on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (Mo-Kα radiation, graphite monochromator, ω scanning technique with a scan step of 0.3°, frames were exposed for 10 s, $2\theta_{max} = 60°$) according to standard procedures.[9] For single crystals of complex **1**: $C_{16}H_{24}CoN_4O_8Pd$, M = 565.72, orthorhombic system, space group *Pnma*, a = 13.602(2) Å, b = 16.786(3) Å, c = 10.3033(17) Å, V = 2352.4(7) Å^3 (200 K), Z = 8 (Z' = 4), 18044 measured reflections, of which 3451 reflections were with $F^2 > 2\sigma(I)$, ρ_{calc} = 1.597 g cm^{-3}, μ = 1.515 cm^{-1}, R_1 = 0.0535, wR_2 = 0.1336.

Semiempirical absorption corrections were applied using the SADABS program.[10] The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic displacements parameters for all nonhydrogen atoms. Fourier analysis of the electron density distribution showed that the Pd and Co atoms in molecule **1** are disordered over two positions with equal occupancies. The distance between two positions in the structure of **1** is ~0.4 Å. All calculations were carried out with the use of the SAINT [9] and SHELXTL-97 [11] program packages.

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References

1. N. Kioussis and J. W. Garland, *Phys. Rev. Lett.*, 1991, **67**, 366; K. J. Bryden and J. Y. Ying, *Acta Materialia*, 1996, **44**, 3847; H. Okamoto, *J. Phase Equilibria*, 2001, **22**, 364; N. S. Sobal and M. Giersig, *Austral. J. Chem.*, 2005, **58**, 307.
2. J. H. Sinfelt, *Bimetallic Catalysts. Discoveries, Concepts and Applications*, Wiley, New York, 1983; K. I. Zamaraev, *Pure Appl. Chem.*, 1997, **69**, 865; (c) M. Heemeier, A. F. Carlsson, M. Naschitzki, M. Schmal, M. Bäumer, and H.-J. Freund, *Angew. Chem., Int. Ed. Engl.*, 2002, **41**, 4073; J. L. Fernandez, D. A. Walsh, and A. J. Bard, *J. Am. Chem. Soc.*, 2005, **127**, 357.
3. S. Adam, A. Bauer, O. Timpe, U. Wild, G. Mestl, W. Bensch, and R. Schlögl, *Chem. Eur. J.*, 1998, **4**, 1458.
4. A. L. Balch, B. J. Davis, E. Y. Fung, and M. M. Olmstead, *Inorg. Chim. Acta*, 1993, **212**, 149.
5. R. W. Brandon and D. V. Claridge, *J. Chem. Soc., Chem. Commun.*, 1968, 677.
6. R. J. Pandey and P. M. Henry, *Can. J. Chem.*, 1974, **52**, 1241; 1975, **53**, 1833; N. Yu. Kozitsyna, M. N. Vargaftik, and I. I. Moiseev, *J. Organometal. Chem.*, 2000, **593—594**, 274; N. Yu. Kozitsyna, A. A. Bukharkina, M. V. Martens, M. N. Vargaftik, and I. I. Moiseev, *J. Organomet. Chem.*, 2001, **636**, 69.
7. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon, Oxford, 1988.
8. T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.
9. *SMART (V5.051) and SAINT (V5.00), Area Detector Control and Integration Software*, Bruker AXS Inc., Madison (WI), USA, 1998.
10. G. M. Sheldrick, *SADABS*, Bruker AXS Inc., Madison (WI), USA, 1997.
11. G. M. Sheldrick, *SHELXTL-97, V5.10*, Bruker AXS Inc., Madison (WI), USA, 1997.

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