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Dedicated to the memory of Professor Sergey Evgen'evich Nefedov

Chemical Transformations of $[Pd(OOCMe)_4Mn]$ in the Reactions with 1,10-Phenanthroline and Pivalic Acid

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Abstract—A series of new Pd–Mn bimetallic acetate and pivalate complexes were synthesized and structurally characterized. The starting $[Pd(OOCMe)_4Mn]$ complex reacts with N-donor ligands such as 1,10-phenanthroline (phen) to give $[Pd(OOCMe)_4Mn(phen)]\cdot MeCN$ (**I**) (CCDC no. 2217716). The replacement of acetate bridges in the heterometallic Pd–Mn carboxylate complexes with pivalate bridges was investigated. It was shown that complete replacement of all acetate bridges with pivalate ones can occur both in heterometallic complex **I**, which contains a ligand coordinated to the second metal atom, to give the compound $[Pd(Piv)_4Mn(phen)]\cdot C_6H_6$ (**II**) (CCDC no. 2217717), structurally related to the initial acetate complex, and in the acetate complex $[Pd(OOCMe)_4Mn]$. The heterometallic co-crystallized pivalate $[Pd(Piv)_4Mn\cdot 2HPiv]$ (**III**) (CCDC no. 2217718) formed in the latter case can react with 5-nitro-1,10-phenanthroline to give the complex $[Pd(Piv)_4Mn(Nphen)]$ (**IV**) (CCDC no. 2217719).

Keywords: palladium, manganese, heterometallic complexes, synthesis, X-ray diffraction, crystal chemistry

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INTRODUCTION

Molecular bimetallic complexes based on platinum group metals are convenient precursors of supported heterometallic systems possessing better catalytic performance than monometallic analogues [1]. Study of the thermal transformations of these complexes revealed special properties of phases formed under different heat treatment conditions; a benefit of carboxylate-bridged systems is the ability to be reduced under mild conditions to metal oxide systems [2, 3] or bimetallic nanoalloy particles [4–8]. An additional advantage is the stoichiometric ratio of noble and non-noble metal strictly specified by the structure of the precursor complex.

The chemical properties of the binuclear $[Pd(OOCMe)_4M]$ complex with the "Chinese lantern" structure attest to the stability of heterometallic system and the ability to retain the binuclear structure upon treatment with bidentate nitrogenous bases such as 1,10-phenanthroline in the case of $[Pd(OOCMe)_4Co]$ [9] and to change the structure towards the formation of trinuclear [10, 11], pentanuclear [12], and polynuclear carboxylate-bridged complexes [13]. The possibility of simultaneous introduction of a nitrogen-containing ligand into the complex and the previously demonstrated possibility of replacement of the acetate bridging groups with other carboxylates [14, 15], in particular by metal-containing carboxylic acid residues [16–19], opens up broad synthetic opportunities for influencing the composition and structure [20] of bimetallic complexes and obtaining compounds with specified properties, e.g., solubility, for subsequent investigation of their behavior in solutions and on solid catalyst supports.

Previously, it was shown that 1,10-phenanthroline coordination in the heterometallic complex $[PdCo(OOCMe)_4(NCMe)]\cdot 3MeCN$ occurs selectively to the additional cobalt metal atom, which is accompanied by Co–O bond cleavage in the bridging acetate group [9]; in other words, one of the bridging acetate groups switches to a terminal position. However, the possibilities of further modification of these compounds on treatment with N- and O-donor ligands were addressed only in a few studies [21–23].

This paper describes the synthesis of new coordination compounds and study of the reactivity of mixed-metal carboxylates reported previously [24] by considering the heterometallic palladium and manga-

nese system [Pd(OOCR)$_4$Mn] in reactions with pivalic acid (HPiv), 1,10-phenanthroline (phen), and 5-nitro-1,10-phenanthroline (Nphen).

EXPERIMENTAL

Commercial 1,10-phenanthroline (99%, Alfa Aesar), HPiv (99%, Sigma-Aldrich), 5-nitro-1,10-phenanthroline (97%, Sigma-Aldrich), and acetonitrile (MeCN, HPLC Plus, Sigma-Aldrich) were used as received. Benzene was purified by standard procedures [25]. Palladium(II) acetate [Pd$_3$(OOCMe)$_6$] (high-purity grade, Reakhim) for the preparation of [Pd(OOCMe)$_4$Mn] was refluxed in glacial acetic acid with freshly prepared palladium black and recrystallized from acetic acid.

Elemental analysis was performed on a EuroVector EA3000 automatic C,H,N-analyzer. Infrared spectra were recorded on a Bruker Alpha FTIR spectrometer by the attenuated total reflectance (ATR) method in the 4000–400 cm^{-1} frequency range. The melting (decomposition) points of the complexes were determined using a Linkam DSC600 DSC system.

The initial compound [Pd(OOCMe)$_4$Mn] was synthesized by a known procedure [24], without the stage of isolation of the THF crystal solvate, and used as a dry powder that formed immediately after the removal of excess acetic acid and water by distillation with benzene followed by the removal of benzene at a reduced pressure on a rotary evaporator.

Synthesis of [Pd(OOCMe)$_4$Mn(phen)]·MeCN (I). A powder of [Pd(OOCMe)$_4$Mn] (150 mg, 0.377 mmol) was dissolved in MeCN (7 mL), and the solution was filtered through a paper filter into a flask to remove the possible insoluble impurities. Then a solution of phen (68 mg, 0.377 mmol) in MeCN (5 mL) was added to the resulting solution. The formation of crystals was observed almost immediately. The yield of yellow crystals was 102 mg (44% in terms of Pd). T_m = 160.4°C (decomposition).

For $C_{22}H_{23}N_3O_8MnPd$

Anal. calcd., %	C, 42.70	H, 3.75	N, 6.79
Found, %	C, 42.39	H, 3.42	N, 6.55

IR (ATR; ν, cm^{-1}) 3061 w ν_{as}(C–H), 2932 w ν_s(C–H), 1619 s ν(C=O), 1514 m, 1389 s ν_s(C–H (–CH_3)), 1338 s, 1223 m, 1143 m, 1102 m, 1046 m, 1021 m, 845 s, 773 m, 724 s, 688 s, 624 m, 421 m.

Synthesis of [Pd(Piv)$_4$Mn(phen)]·C$_6$H$_6$ (II). A solution of pivalic acid (41 mg, 0.4 mmol) in benzene (15 mL) was added to compound **I** (62 mg, 0.1 mmol). The reaction took place with stirring and heating to 60°C for 1 h and was accompanied by complete dissolution of the initial complex **I**. After cooling, the solution was filtered through a paper filter and concentrated on a rotary evaporator to a volume of 3 mL. The solution thus formed was left for crystallization at room temperature. The yield of yellow crystals was 76 mg (92% in terms of Pd). T_m = 93.2°C (decomposition).

For $C_{38}H_{50}N_2O_8MnPd$

Anal. calcd., %	C, 55.38	H, 6.11	N, 3.40
Found, %	C, 54.92	H, 5.85	N, 3.61

IR (ATR; ν, cm^{-1}) 2953 m ν_{as}(C–H), 2868 w ν_s(C–H), 1620 s ν(C=O), 1516 w, 1479 s, 1401 s ν_s(C–H (–$C(CH_3)_3$)), 1355 s ν_s(C–H (–$C(CH_3)_3$)), 1219 s, 1144 m, 1102 w, 1034 w, 893 m, 865 w, 841 m, 785 m, 726 m, 682 s, 639 m, 578 w, 448 m.

Synthesis of [Pd(Piv)$_4$Mn·2HPiv] (III). A solution of HPiv (69 mg, 0.679 mmol) in benzene (15 mL) was added to [Pd(OOCMe)$_4$Mn] (45 mg, 0.113 mmol). The reaction took place with stirring and heating to 60°C for 1 h. After the reaction was completed, the solution was cooled down, filtered through a paper filter, and concentrated to dryness on a rotary evaporator. The yield of **III** as yellow crystals was 84 mg (97% in terms of Pd). T_m = 115.2°C (decomposition).

For $C_{30}H_{56}O_{12}MnPd$

Anal. calcd., %	C, 46.79	H, 7.33
Found, %	C, 46.65	H, 7.60

IR (ATR; ν, cm^{-1}) 2966 m (ν(C–H) + ν(O–H)), 2932 w ν_{as}(C–H), 2872 w ν_s(C–H), 1676 s ν(C=O, (HPiv)), 1592 s ν(C=O), 1508 m, 1482 s, 1405 s ν_s(C–H (–$C(CH_3)_3$), 1362 s ν_s(C–H (–$C(CH_3)_3$), 1310 s ν(C–O), 1201 s, 1031 w, 937 m, 896 m, 787 m, 646 s, 617 m, 593 m, 536 m, 452 s.

Synthesis of [Pd(Piv)$_4$Mn(Nphen)] (IV). A solution of Nphen (15 mg, 0.065 mmol) in acetonitrile (15 mL) was added to compound **III** (50 mg, 0.065 mmol). The resulting solution was evaporated under reduced pressure to a minimum volume of 1 mL and left to crystallize at room temperature. The yield of **IV** as yellow crystals was 20 mg (39% in terms of Pd). T_m = 158.3°C (decomposition).

For $C_{32}H_{43}N_3O_{10}MnPd$

Anal. calcd., %	C, 48.59	H, 5.48	N, 5.31
Found, %	C, 48.72	H, 5.37	N, 5.08

IR (ATR; ν, cm^{-1}) 2959 m ν_{as}(C–H), 2928 m ν_{as}(C–H), 2868 w ν_s(C–H), 1616 s ν(C=O), 1585 s, 1534 m, 1516 s ν_{as}(NO_2), 1479 s, 1399 s ν_s(C–H (–$C(CH_3)_3$), 1361 s (ν_s(C–H (–$C(CH_3)_3$) + ν_s(NO_2)), 1219 s, 1151 m, 1114 m, 1056 w, 1031 w, 991 w, 939 w, 892 m, 818 m, 785 m, 730 m, 642 s, 580 m, 533 m, 448 s.

X-ray diffraction study of complexes **I**, **II**, and **IV** was performed on a Bruker D8 Venture Photon single-

Table 1. Crystallographic data and structure refinement details for complexes **I**–**IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Molecular formula	$C_{22}H_{23}MnN_3O_8Pd$	$C_{38}H_{50}MnN_2O_8Pd$	$C_{30}H_{56}MnO_{12}Pd$	$C_{32}H_{43}MnN_3O_{10}Pd$
M	618.77	824.14	770.08	791.03
Color, habit	Yellow prisms	Colorless plates	Yellow prisms	Yellow prisms
Crystal size, mm	0.230 × 0.200 × 0.120	0.190 × 0.180 × 0.020	0.250 × 0.210 × 0.190	0.340 × 0.190 × 0.110
Temperature, K	100(2)	150(2)	100(2)	150(2)
System	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$	$Pbca$
a, Å	8.0770(3)	11.6473(5)	12.0320(5)	19.9184(7)
b, Å	19.3059(7)	16.6133(7)	20.0594(9)	11.7690(4)
c, Å	15.8478(5)	20.5497(8)	16.2027(7)	30.0041(10)
α, Å	90	90	90	90
β, Å	94.1833(12)	104.7591(15)	108.1340(10)	90
γ, Å	90	90	90	90
V, Å^3	2464.62(15)	3845.2(3)	3716.4(3)	7033.6(4)
Z	4	4	4	8
ρ(calcd.), g/cm^3	1.668	1.424	1.376	1.494
μ, mm^{-1}	1.293	1.424	0.877	0.928
F(000)	1244	1708	1612	3256
θ_{min}–θ_{max}, deg	2.472–30.555	1.837–26.515	2.423–26.733	1.357–27.878
Ranges of reflection indices	$-11 \le h \le 11$, $-27 \le k \le 27$, $-22 \le l \le 22$	$-14 \le h \le 14$, $-20 \le k \le 20$, $-25 \le l \le 25$	$-15 \le h \le 15$, $-25 \le k \le 25$, $-20 \le l \le 20$	$-26 \le h \le 26$, $-15 \le k \le 15$, $-39 \le l \le 39$
Number of measured reflections	41865	47983	24468	94953
Number of unique reflections (R_{int})	7554 (0.0378)	7992 (0.0675)	3948 (0.0583)	8399 (0.0934)
Number of reflections with $I > 2\sigma(I)$	6542	5653	3282	5723
Reflections/constraints/parameters	7554/50/350	7992/219/534	3948/0/213	8399/228/498
GOOF	1.091	1.036	1.063	1.019
R-factors for $I > 2\sigma(I)$	$R_1 = 0.0376$, $wR_2 = 0.0818$	$R_1 = 0.0451$, $wR_2 = 0.0973$	$R_1 = 0.0375$, $wR_2 = 0.0669$	$R_1 = 0.0420$, $wR_2 = 0.0963$
R-factors for all reflections	$R_1 = 0.0468$, $wR_2 = 0.0852$	$R_1 = 0.0753$, $wR_2 = 0.1091$	$R_1 = 0.0519$, $wR_2 = 0.0740$	$R_1 = 0.0744$, $wR_2 = 0.1096$
Residual electron density (min/max), e Å^{-3}	−1.881/1.444	−0.790/0.545	−0.826/1.138	−0.803/0.638

crystal X-ray diffractometer in the φ- and ω-scan mode at the Center for Collective use of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences. The reflections were collected at 150 K (or 100 K for the crystals of **I**) at X-ray radiation wavelength λ = 0.71073 Å using an Incoatec IμS 3.0 micro-focus X-ray source. The set of X-ray diffraction data for complex **III** was collected on a Bruker APEX-II diffractometer (λ = 0.71073 Å) at 100 K. The initial determination of the unit cell parameters, their refinement, and integration of reflection intensities were performed using the Bruker APEX3 software package [26]. The absorption corrections for the experimental reflection intensities were applied using the SADABS program [27].

The structures of **I**–**IV** were solved by direct methods [28] and refined in the anisotropic approximation by the full-matrix least-squares method on F^2 [29] for

all non-hydrogen atoms. The disordered positions of the solvent (acetonitrile) atoms in **I** were refined using geometric constraints (SADI instruction) and constraints on the thermal displacement of atoms (SIMU, ISOR instructions). The disordered carbon atoms of the *tert*-butyl groups of the pivalate anions in **II** and **IV** were refined using constraints on the geometric parameters (SADI) and thermal displacements (SIMU, RIGU).

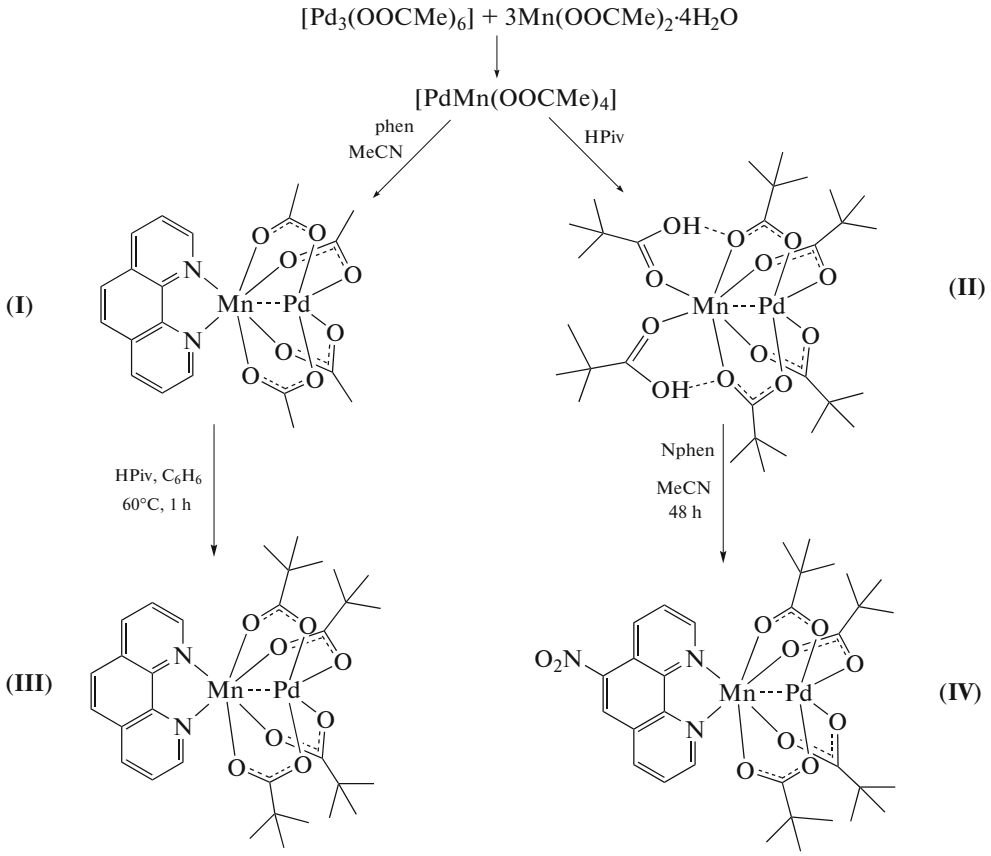
In the refinement of all structures, the hydrogen atoms were placed into the calculated positions and refined in the riding model with U_{iso}(H) equal to $1.5U_{equiv}$(C) for the methyl hydrogen atoms and to $1.2U_{equiv}$(C) for the hydrogen atoms of 1,10-phenanthroline and 5-nitro-1,10-phenanthroline. The hydrogen atom position in the coordinated pivalic acid forming the hydrogen bond in **III** was revealed from the electron density map and refined in the isotropic approximation freely without the use of geometric or thermal constraints.

The calculations were carried out using the SHELXTL program package [29] in the OLEX2 structural data visualization and processing medium [30]. The crystallographic parameters and structure refinement details are summarized in Table 1.

The structures of **I**–**IV** were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2217716–2217719, respectively) and are available at ccdc.cam.ac.uk/structures (deposit@ccdc.cam. ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The binuclear heterometallic Pd(II) complexes with the general structure [Pd(OOCMe)$_4$M], where M is an additional metal atom, are more reactive towards N-donor ligands [21] and more active catalysts [31] than trinuclear palladium acetate. Furthermore, depending on the nature of the additional metal, the bidentate ligand can be coordinated, under certain conditions, either to palladium to give trinuclear complexes (e.g., the reaction of [Pd(OOCMe)$_4$Ni] with 1,10-phenanthroline [10]), or, alternatively, to the additional metal atom (e.g., [Pd(OOCMe)$_4$Co] [9]). Unlike cobalt(II) atom with the d^7-electronic configuration, the manganese(II) atom has two electrons less and the d^5 electron configuration, which leads to even higher acceptor properties of the Mn atom in the [Pd(OOCMe)$_4$Mn] binuclear system relative to the phenanthroline type N-donor ligands. The chemical transformations of [Pd(OOCMe)$_4$Mn] in the reactions with various ligands are summarized in Scheme 1.



Scheme 1.

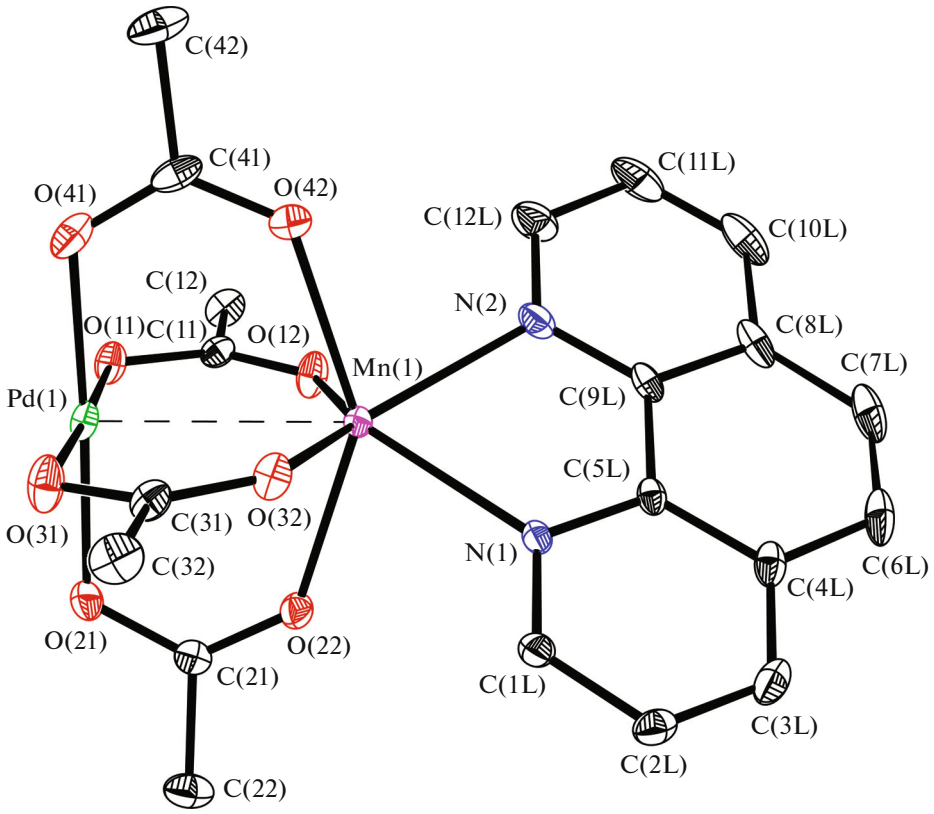


Fig. 1. Structure of complex **I**. The thermal displacement parameters of atoms are shown at 35% probability level. The disordered acetonitrile molecules and hydrogen atoms of methyl groups and 1,10-phenanthroline are not shown.

As shown in relation to the reaction of $[Pd(OOCMe)_4Mn]$ with 1,10-phenanthroline, the reaction equilibrium is shifted towards the formation of the expected product, $[Pd(OOCMe)_4Mn(phen)]\cdot MeCN$ (**I**), which was isolated in the crystalline state. According to X-ray diffraction data (Fig. 1), compound **I** crystallizes in the monoclinic space group $P2_1/c$ as a solvate with an acetonitrile molecule. The independent part of the unit cell contains one molecule of complex **I** as the crystal solvate with one acetonitrile molecule; in general, the binuclear tetrabridged structure of the $\{Pd(OOCMe)_4Mn\}$ moiety is retained, being only slightly different from the structure of the starting compound. The Pd(1) palladium atom is in a square planar environment formed by oxygen atoms (the details of the local coordination environment of the central atoms are given in Table 2) and virtually does not deviate from the O(11)O(21)-O(31)O(41) plane (by not more than 0.0465(9) Å). The Pd(1)–Mn(1) interatomic distance is relatively short (2.8599(4) Å), but is still considerably longer than that in the initial $[Pd(OOCMe)_4Mn(OH_2)]$ complex (2.6570(12) Å) [32]. In turn, the manganese atom deviates from the plane of the oxygen environment (O(12)O(22)O(32)O(42)) by 1.1675(12) Å away from the palladium atom towards the N(1) and N(2) atoms of the phenanthroline molecule, which are located at nearly equal distances from Mn(1) (2.293(2) and 2.296(2) Å, respectively). The coordination environment of manganese is a trigonal prism, as found by coordination polyhedron analysis with the SHAPE algorithm [33, 34]. It is noteworthy that the 1,10-phenanthroline molecule in **I** is not planar, since the dihedral angle between the N(1)C(1L)C(2L)-C(3L)-C(4L)C(5L) and N(2)C(12L)C(11L)-C(10L)-C(8L)C(9L) planes is 3.720(14)°. In the crystal structure, the molecules of **I** are assembled in stacks (Fig. 2) oriented along the crystallographic *a* axis and formed by partially overlapping 1,10-phenanthroline moieties with an average interplanar spacing of 3.521(3)–3.581(4) Å, typical of π–π stacking interactions for systems containing [35].

Treatment of the poorly soluble complex **I** with pivalic acid, taken in a slight excess relative to the stoichiometric amount, in benzene leads to complete replacement of the acetate bridging ligands with pivalate ligands under mild conditions to give the complex $[Pd(Piv)_4Mn(phen)]\cdot C_6H_6$ (**II**) in a high yield. Complex **II** was isolated as a benzene solvate (Fig. 3) and crystallized in space group $P2_1/n$. The molecular geometry of **II** and the coordination environment of palladium and manganese are generally similar to those in **I** (Table 2); however, the introduction of bulky *tert*-butyl groups into the structure changes the

Table 2. Selected interatomic distances in the structures of complexes **I**–**IV**

Distances, Å	I	II	III	IV
Pd(1)–O(11)	2.0009(18)	1.980(3)	2.0146(18)	2.001(2)
Pd(1)–O(21)	1.9970(19)	2.005(3)	1.9956(18)	2.002(2)
Pd(1)–O(31)	1.9985(19)	1.978(3)		2.006(2)
Pd(1)–O(41)	1.985(2)	2.011(3)		2.003(2)
Mn(1)–O(12)	2.1977(18)	2.243(3)	2.1094(19)	2.162(2)
Mn(1)–O(22)	2.1938(18)	2.144(3)	2.3371(19)	2.163(2)
Mn(1)–O(32)	2.1908(18)	2.227(3)	2.218(2)	2.175(2)
Mn(1)–O(42)	2.2157(19)	2.150(3)		2.190(2)
Mn(1)–N(1)	2.296(2)	2.296(3)		2.306(3)
Mn(1)–N(2)	2.293(2)	2.300(3)		2.315(3)
Pd(1)–Mn(1)	2.8599(4)	2.8557(6)	2.8601(7)	2.8227(5)

nature of the intermolecular interaction between the phenanthroline ligands. This gives rise to pairs of molecules (Fig. 4) bound by the π–π-stacking interaction between the aromatic systems of the coordinated 1,10-phenanthroline molecules with interplanar spacing of 3.412(4) Å, which attests to a fairly strong interaction. A similar pairwise structure organization is also encountered in mononuclear palladium complexes [36]; each pair of molecules of this type in compound **II** is also surrounded by benzene molecules of crystallization (Fig. 4).

On the other hand, on treatment with excess pivalic acid, the bridging ligands in the binuclear complex [Pd(OOCMe)$_4$Mn] can be replaced rather easily to give [Pd(Piv)$_4$Mn·2HPiv] (**III**) (Fig. 5), which was also isolated in the crystalline state. Like in the case of addition of 1,10-phenanthroline, the coordination polyhedron of palladium does not change (Table 2), while the coordination polyhedron of manganese (without taking account of the palladium atom as an additional ligand) resembles most closely a distorted trigonal prism, according to the analysis of its local environment. The Mn(1)–O distances are not equivalent, being considerably different for the bridging pivalic acid and for coordinated neutral HPiv (Mn(1)–O(12), 2.1094(19), and Mn(1)–O(31), 2.218(2) Å, respectively). Neutral pivalic acid not only completes the coordination environment of manganese by the carbonyl oxygen atom of the carboxy group, but also forms a relatively strong [37] hydrogen bond (1.69(4) Å) with the bridging oxygen atom of the bidentate pivalic acid via the hydroxyl group (O(32)–H(32)...O(22). The distance between the donor and acceptor oxygen atoms is 2.564(3) Å).

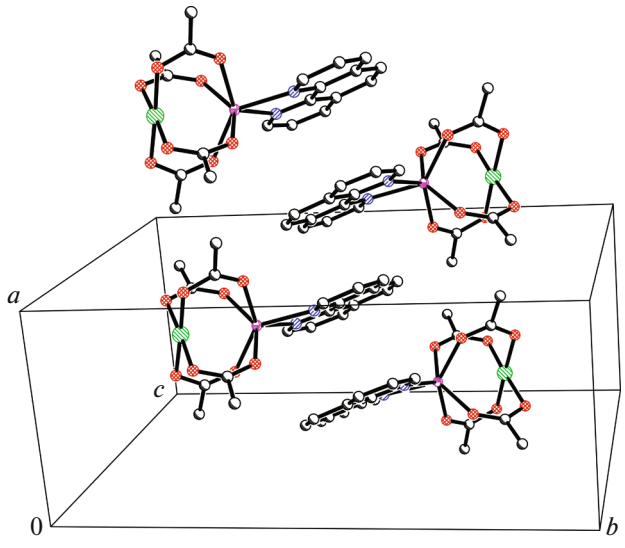


Fig. 2. Fragment of the crystal packing of complex **I**.

It was shown that compound **III** can also react with N-donor ligands, despite the greater steric restrictions to the reaction with the additional metal atom (manganese). In relation to a 1,10-phenanthroline derivative, 5-nitro-1,10-phenanthroline, it was shown that displacement of two coordinated pivalic acid molecules gives rise to the unsolvated complex [Pd(Piv)$_4$Mn(Nphen)] (**IV**) (Fig. 6), which crystallizes in the orthorhombic space group *Pbca*. Like in the previously described cases, the ligand coordination to Mn(1) is still preferred and is not accompanied by a significant distortion of the molecular geometry of either the tetra-bridged structure or Nphen. The nitrogen atoms of 5-nitro-1,10-phenanthroline, like the nitrogen atoms of unsubstituted phenanthroline in structures **I** and **II**, complete the coordination envi-

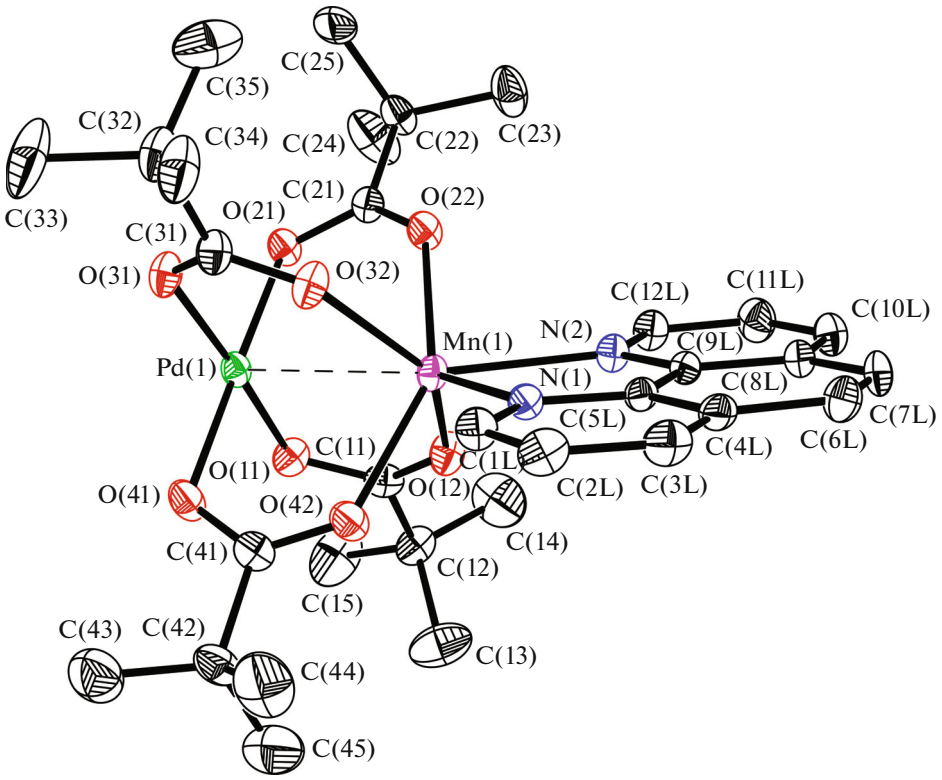


Fig. 3. Structure of complex **II**. The thermal displacement parameters of atoms are shown at 30% probability level. The disordered *tert*-butyl groups, benzene solvate molecules, and hydrogen atoms are not shown.

ronment of manganese to a trigonal prism. Unlike the above compounds containing 1,10-phenanthroline, according to crystal packing analysis, 5-nitro-1,10-phenanthroline is not involved in the π–π stacking with neighboring molecules (Fig. 7), most likely, because of the presence of bulky *tert*-butyl groups in the complex and because of the electron-withdrawing NO_2 group at the ligand aromatic system.

Thus, in relation to the heterometallic Pd–Mn system, it was shown that aromatic N-donor ligands, 1,10-phenanthroline and 5-nitro-1,10-phenanthroline, can be coordinated in the bidentate fashion to the additional metal atom, while the bridging coordination of both acetate and pivalate groups is retained to give compounds $[Pd(OOCMe)_4Mn(phen)]\cdot MeCN$ (**I**) and $[Pd(Piv)_4Mn(Nphen)]$ (**IV**), respectively. The replacement of the bridging acetate ligands in the complexes with coordinated N-donor ligands leads to a substantial increase in the solubility compared to that of the initial heterobimetallic acetate systems, which have low solubility due to specific features of their crystal packing, mainly intermolecular π–π stacking, which is manifested in the pivalate-bridged complex $[Pd(Piv)_4Mn(phen)]\cdot C_6H_6$ (**II**) only as inter-

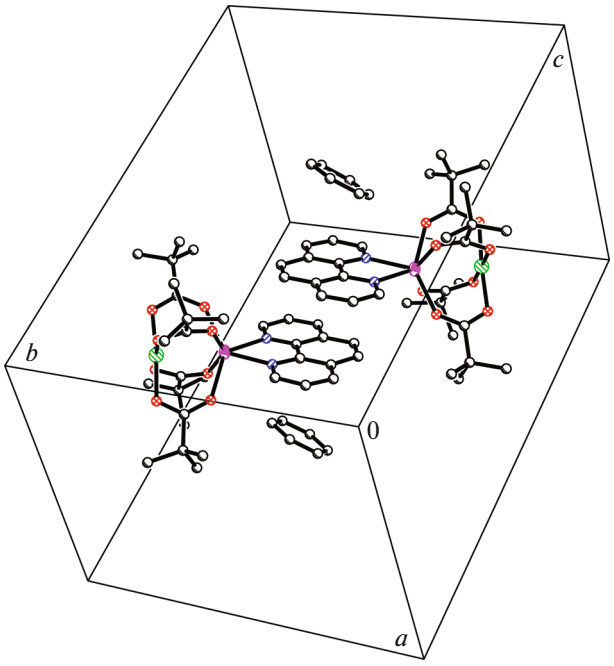


Fig. 4. Fragment of the crystal packing of compound **II**.

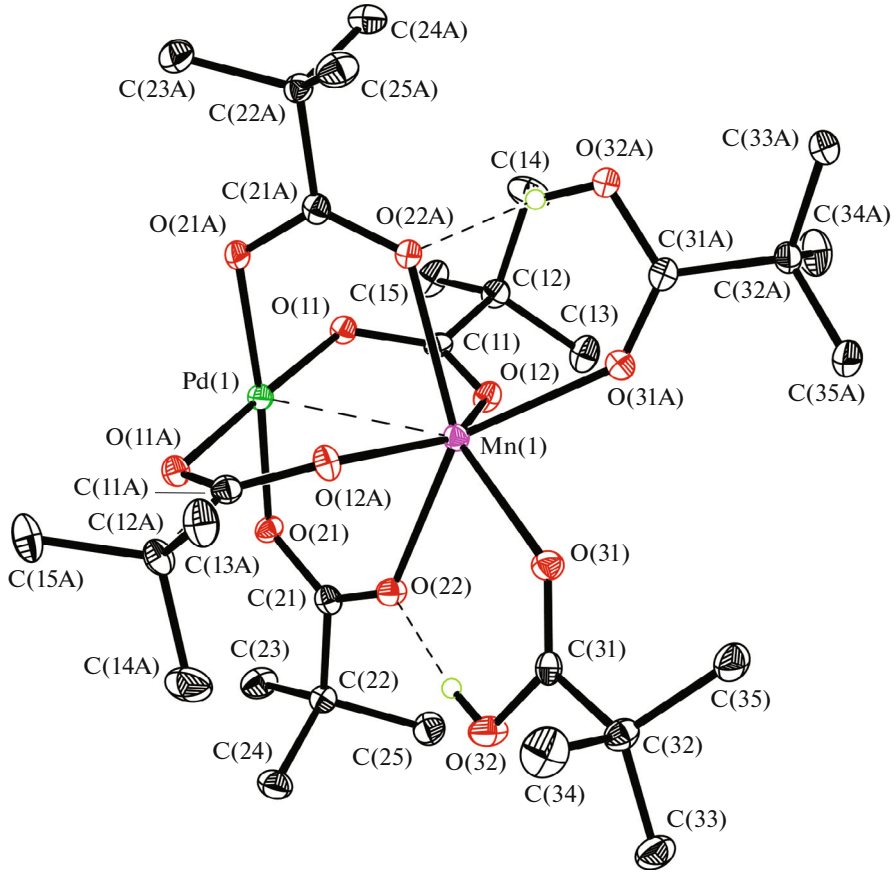


Fig. 5. Molecular structure of complex **III**. The hydrogen atoms of methyl groups are omitted. The thermal ellipsoids are shown at 35% probability level.

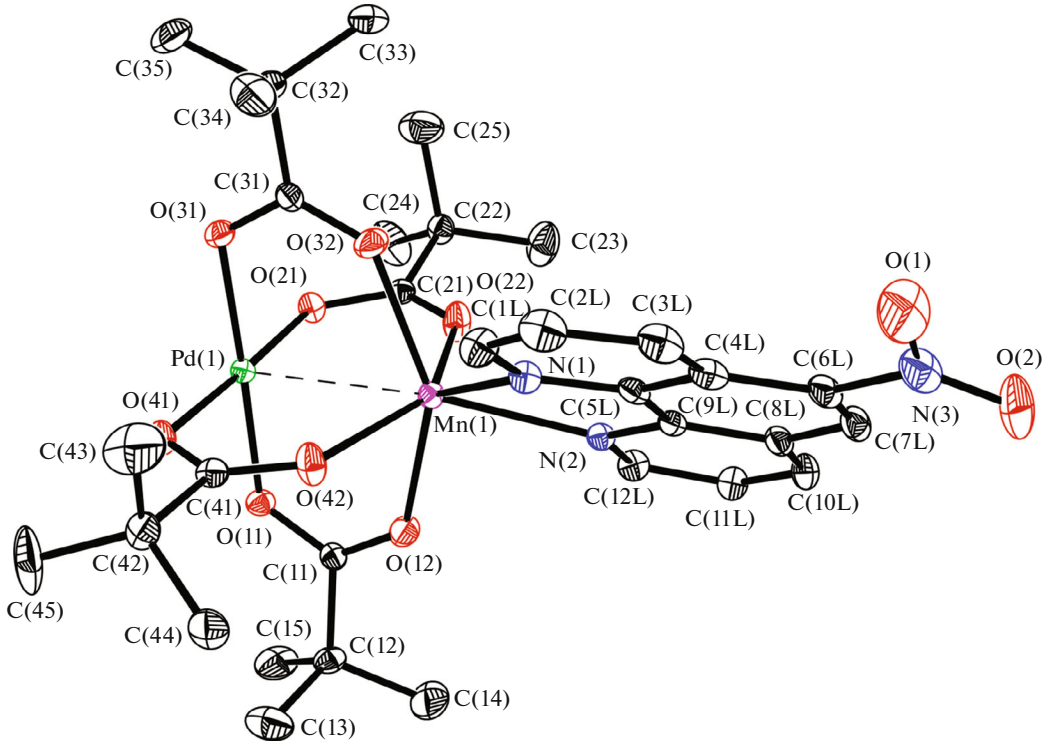


Fig. 6. Molecular structure of complex **IV**. The disordered *tert*-butyl groups and hydrogen atoms are omitted. The thermal ellipsoids are shown at 30% probability level.

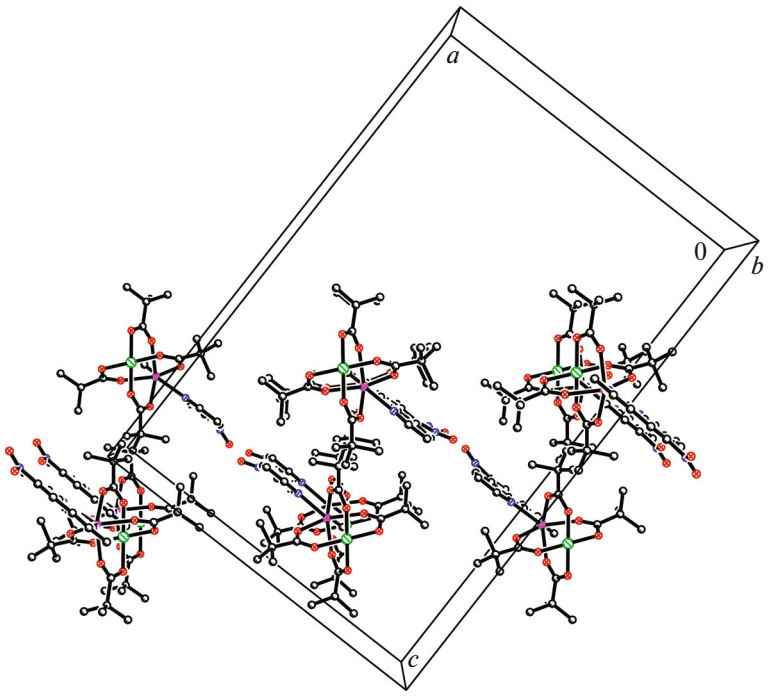


Fig. 7. Fragment of the crystal packing of compound **IV**.

action between pairs of molecules, while in the case of $[Pd(Piv)_4Mn(Nphen)]$, it is not detected.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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