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# Synthesis, structural, vibrational and DFT investigation of new binuclear molecular Pd—Cu and Cu—Cu complexes formed by Schiff base and hexafluoroacetylacetonate building blocks



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# ABSTRACT

In this work, the first binuclear molecular noble metal-contained complex from the Schiff base (SB) and  $\beta$ -diketonate building blocks, *viz.* [Pd(acacen)Cu(hfac)<sub>2</sub>], has been synthesized and investigated in comparison with the homometallic binuclear analog [Cu(acacen)Cu(hfac)<sub>2</sub>]. The detailed comparative characterization of the structure of these new compounds as well as their molecular SB components [M(acacen)] was performed using crystallography, vibrational spectroscopy and DFT calculations. Experimental IR bands have been assigned based on DFT calculations. The Hirshfeld surface analysis was used as a tool for the better insight into intermolecular contacts. It was shown that despite both bimetallic complexes had similar molecular structure and packing style, the nature of the closest intermolecular contacts in [M(acacen)] and [M(acacen)Cu(hfac)<sub>2</sub>] complexes was carried out and the most probable paths of bond cleavage during decomposition of the compounds were revealed. The binding energies of the molecular components in binuclear complexes were also calculated.

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# 1. Introduction

1D and 2D nanomaterials of Pd–Cu bimetallic system are widely used in different industrial processes. For example,  $Pd_xCu_{(1-x)}$ nanoparticles are utilized as catalysts for CO<sub>2</sub>, nitrite and nitrate hydrogenation [1,2], while palladium-containing thin films are one of the most effective membranes for the high purity hydrogen production [3,4]. Chemical vapor deposition methods, in particular metal-organic chemical vapor deposition (MOCVD), are used to produce multicomponent materials with specified properties [5]. However, in addition to general requirements (high volatility, thermal stability, "thermal window" between the vapor sublimation and its decomposition) the MOCVD precursors used for these purposes must have certain physicochemical properties such as compatible deposition temperatures, and contain identical ligands

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to prevent their exchange in the gas phase. Recently the idea of bimetallic single-source precursors has attracted attention because their application enables to avoid the selection of precursor combinations, to simplify the experimental procedure and to control the gas phase composition.

While chemistry of heteropolynuclear complexes is widely covered in the literature, data on molecular compounds suitable as precursors in MOCVD processes are sporadic [6]. Different synthetic procedures based on alkoxides [7–9], carboxylates [10,11], glyoximates [12] etc. have already been described in the literature. In particular, for Pd–Cu volatile compounds, there was no information about bimetallic palladium-containing complexes with these types of ligands until 2014 due to their insufficient thermal stability. Indeed, the first bimetallic Pd–Cu precursor was formed due to as a result of specific intermolecular interactions of functionalized metal  $\beta$ -diketonates [13–15]. However, such intermolecular interactions were weak, and the compounds mostly had a polymer structure. In addition, when heated, dissociation of such

heterometallic compounds can occur. Thus, the design of a new type of Pd–Cu bimetallic molecular compounds is of current importance.

One of the promising approaches is coordination of one metal atom in a complex containing a Schiff's tetradentate base (SB) or similar ligand with another metal atom in the β-diketonate environment. For instance, the pioneering work was devoted to the synthesis and crystal structure of  $[Cu(salen)Cu(hfac)_2]$  (salen<sup>2-</sup> – N,N'-ethylenebis(salicylidenaminato), hfac<sup>-</sup> hexafluoroacetylacetonato) [16]. Later syntheses, crystal structures, and magnetic characterizations of a number of  $[M(SB)Ln(\beta-diket)_3]$  (M - Ni, Cu) compounds were reported by Gleizes, Rayzanov, Kuzmina and coauthors [17-20], and the obtained results were mainly presented in the light of comparing the structural features and magnetic properties of these bimetallic complexes. In the case of  $[Ni(SB)La(\beta-diket)_3]$  thermal behavior has been studied and some principles of changes in the thermodynamic and thermal stability in dependence on their crystal structures have been formulated [17]. This work [17] was the most complete study in the field of thermochemistry of such compounds. Thus, the attractiveness of this synthetic approach lies in the possibility of controlling the thermal properties of complexes by varying the nature of SB or  $\beta$ diketonate components in a bimetallic molecule. The ranges of changes in the volatility of individual palladium and copper chelates with SB or β-diketonate ligands demonstrated in the literature [21-24] provide a promising basis for obtaining effective precursors of this type.

In this work, we first combine the Schiff base and  $\beta$ -diketonate building blocks to prepare a heterobimetallic Pd-Cu compound. For this purpose, [Pd(acacen)] (acacen<sup>2–</sup> – N,N'-(ethylene)-*bis*(acetylacetoneiminato-) was chosen as an initial SB molecular component because in contrast to the above mentioned [M(salen)] it is not prone to  $\pi$ - $\pi$  or M- $\pi$  stacking interactions. Copper (II) hexafluoroacetylacetonate,  $[Cu(hfac)_2]$ , was used as a  $\beta$ -diketonate component since it exhibits high ability to coordinate donor molecules to copper center due to the presence of electronwithdrawing groups in the ligand [25,26]. Herein, we focus on the study of the structure of the bimetallic heteronuclear complex [Pd(acacen)Cu(hfac)<sub>2</sub>] in comparison with its homonuclear analogue [Cu(acacen)Cu(hfac)<sub>2</sub>]. Both the new compounds and the corresponding mononuclear components were characterized by the methods of elemental analysis, single-crystal X-ray diffractometry and vibrational spectroscopy. DFT calculations were employed for topological analysis of the electron density distribution and estimation of binding energies of the complex binuclear molecules.

# 2. Experimental and computational details

#### 2.1. Chemicals and methods

All the chemicals were analytical grade reagents and were used without additional purification. The elemental analysis was carried out using the Carlo-Erba 1106 analyzer. IR-spectra of the complexes in KBr and polyethylene pellets were recorded on a Vertex 80 FTIR spectrometer. NMR spectra were recorded on an Avance 500 spectrometer at 500 MHz for <sup>1</sup>H NMR and 125 MHz for <sup>13</sup>C NMR in CDCl<sub>3</sub> solution. Melting points (*m.p.*) were determined by visual method on the Koffler's table.

### 2.2. Syntheses and characterization

**H**<sub>2</sub>*acacen* was synthesized according to the previously described method [27] by condensation of ethylenediamine (0.67 mL, 10 mmol) with acetylacetone (2.04 mL, 20 mmol) with

subsequent recrystallizations from hexane. Yield: 1.35 g (60%). *m.p.* 110 °C. Anal. calc. for  $C_{12}H_{20}N_2O_2$ : C, 64.3; H, 9.0; N, 12.5. Found: C, 64.0; H, 9.1; N, 12.5.

**[Pd(acacen)].** PdCl<sub>2</sub> (0.80 g, palladium content 59.845%, 4.5 mmol) was dissolved in 90 mL of acetonitrile upon heating to ~50 °C, and then the solution of H<sub>2</sub>acacen (1.00 g, 4.5 mmol) in 30 mL acetonitrile was added. After stirring during 10 min the solution was mixed with the equimolar amount of KOH (0.51 g, 9.1 mmol) dissolved in a minimum amount of water and kept for 10 min. Then water was added in the ratio of 5:1 (vol.). Finally, the product was filtered and purified by double sublimation in vacuum (P =  $5 \cdot 10^{-2}$  Torr, T = 170-200 °C). Yield: 0.92 g (62%) m.p. 226 °C. Anal. Calc. for C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>Pd: C, 43.9; H, 5.5; N, 8.5. Found: C, 44.1; H, 5.7; N 8.3. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.93 s (6H, 2CH<sub>3</sub>), 1.98 s (6H, 2CH<sub>3</sub>), 3.39 s (4H, 2CH<sub>2</sub>), 4.83 s (2H, CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 20.64 (CH<sub>3</sub>), 25.37 (CH<sub>3</sub>), 55.89 (NCH<sub>2</sub>), 99.01 (CH), 161.81 (C=N), 177.51 (C=O).

**Cu(II) complexes.** [Cu(acacen)] and [Cu(hfac)<sub>2</sub>] were synthesized according to the method described in the literature [28] by interaction of H<sub>2</sub>acacen (1.00 g, 4.5 mmol) or Hhfac (1.28 ml, 9.0 mmol) with as-precipitated Cu(OH)<sub>2</sub> (0.50 g, 5.1 mmol, 13% excess) in the presence of acetone (15 mL). Cu(OH)<sub>2</sub> was obtained by mixing aqueous solutions of CuCl<sub>2</sub>(0.68 g, 5.1 mmol) and KOH(0.58 g, 10.3 mmol). After acetone evaporation, Cu (II) complexes were extracted with chloroform and purified by double vacuum sublimation.

[*Cu*(*acacen*]). Sublimation parameters: T = 110-120 °C,  $P = 5 \cdot 10^{-2}$ Torr. Yield: 1.09 g (85%). *m.p.*136–138 °C. Anal. Calc. for  $C_{12}H_{18}N_2O_2Cu$ : C, 50.5; H, 6.4; N, 9.8. Found: C, 50.7; H, 6.3; N, 9.7.

[*Cu*(*hfac*)<sub>2</sub>].Sublimation parameters: T = 60-70 °C,  $P = 5 \cdot 10^{-2}$ Torr. Yield: 1.38 g (64%). *m.p.* 131–132 °C. Anal. Calc. for C<sub>10</sub>H<sub>2</sub>F<sub>12</sub>O<sub>4</sub>Cu: C, 25.2; H,0.4; F, 47.8. Found: C, 25.3; H, 0.3; F, 47.8.

**[M(acacen)Cu(hfac)<sub>2</sub>], (M** = **Pd, Cu).** Both bimetallic complexes were obtained according to the procedure described in the literature [18]. The chloroform solution (20 mL) of [Pd(acacen)] (0.40 g, 1.2 mmol) or [Cu(acacen)] (0.35 g, 1.2 mmol) was slowly added to the chloroform solution (20 mL) of [Cu(hfac)<sub>2</sub>] (0.58 g, 1.2 mmol) and the mixture was refluxed for 1 h. The brown crystals of the complexe were grown during solvent evaporation. The yield was close to 100%.

[ $Pd(acacen)Cu(hfac)_2$ ]. m.p. 172–174 °C. Anal. Calc. for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>F<sub>12</sub>O<sub>6</sub>CuPd: C, 32.8; H, 3.5; N, 3.5; F, 28.3. Found: C, 32.5; H, 3.4; N, 3.4; F, 28.1.

[ $Cu(acacen)Cu(hfac)_2$ ]. m.p. 177 °C. Anal. Calc. for  $C_{22}H_{20}N_2F_{12}O_6Cu_2$ : C, 34.6; H, 2.6; N, 3.7; F, 29.9. Found: C, 34.2; H, 2.3; N, 3.7; F, 29.6.

# 2.3. X-ray diffraction studies

Crystals of [Cu(acacen)], [Pd(acacen)] and bimetallic complexes were selected under a microscope and then mounted to the tip of a thin glass fiber with epoxy resin. X-Ray data were collected using a Bruker DUO single-crystal diffractometer (Mo-anode sealed tube with graphite monochromator ( $\lambda = 0.71073$  Å), APEX II CCD detector) using standard 0.5° frame width  $\phi$  and  $\omega$  scans. The frames were collected at 150 K for all compounds except [Cu(acacen) Cu(hfac)<sub>2</sub>], while for the latter complex the temperature was held at 250K because of crystal splitting during cooling. The Apex2 software package (SAINT, SADABS, RLATT) [29] was used for unit cell determination, integration and absorption correction. The obtained hkl datasets were processed in the Olex2 [30] software using SHELXT [31] and SHELXL [31] for the structure solution and subsequent refinement. All non-hydrogen atoms were refined anisotropically. ISOR 0.01 0.02 restraints were placed on C8 atom in [Pd(acacen)Cu(hfac)<sub>2</sub>].

#### 2.4. Computational details

Quantum-chemical calculations of molecular and electronic structures, as well as IR-spectra of [M(acacen)] and [M(acacen) Cu(hfac)<sub>2</sub>] molecules, where M = Cu, Pd, were carried out by DFT BLYP-D3/def2-SVP method [32–37] using the ORCA software package [38,39]. The topological analysis of electron density distribution functions obtained as a result of these computations was performed in the framework of Richard Bader "atoms in molecules" theory [40–42] using the AIMAII software package [43] in order to identify chemical bonds in these compounds along which the cleavage more likely to occur.

The geometry optimization of considered compounds was carried out without any symmetry restrictions (e.g. the point group symmetry was  $C_1$ ). The spin multiplicity in the series of [Cu(acacen)], [Pd(acacen)], [Cu(acacen)Cu(hfac)<sub>2</sub>] and [Pd(acacen)Cu(h $fac)_2$  molecules was equal to 2, 1, 3 and 2, respectively. The spin states of all molecules were defined with the use of single point calculations of the structures obtained from the experimental XRD data without their geometries optimization. The energy gaps between these spin states and multiplicities 4, 3, 1 and 4 in this series of molecules are equal to 2.83 eV, 2.62 eV, 0.69 eV and 2.57 eV. It means that all spin states considered in this work are the most energetically favorable (see Fig. S1, Supporting Information for the more details). Therefore, all calculations were performed in the framework of spin unrestricted Kohn-Sham (UKS) theory. Additionally, RI approximation [44-49] was used for IR-spectra calculations.

# 3. Results and discussion

# 3.1. Synthesis

New binuclear heteroleptic complexes were synthesized by cocrystallization of pre-prepared monometallic components [M(acacen)] and [Cu(hfac)<sub>2</sub>] in the equimolar ratio in chloroform (Scheme 1). Both Pd–Cu and Cu–Cu complexes are formed as brown crystals when the solvent evaporates and are stable in air. These compounds can be repeatedly recrystallized from organic solvents such as chloroform and toluene without changing their characteristics (IR spectra, melting points, and elemental composition).

#### 3.2. Crystal structures of SB molecular components

To identify the features of the formation of binuclear compounds, the individual molecular components were first investigated. As for the components of synthesized heteroleptic complexes, only the structure of [Cu(hfac)<sub>2</sub>] was studied before [50]. Crystal structure of [Cu(acacen)] complex has already been described by Hall et al. [51], however the published structure had a relatively high R-factor (12%) and hydrogen atoms were not determined. For this reason, the crystal structure of [Cu(acacen)] were refined again using single-crystal X-ray diffraction. The resulting structure is identical to the one previously reported [51], but has all hydrogen atoms arranged with a much better R-factor of 2.81%. Here the crystal structure of the compound [Pd(acacen)] was determined for the first time. The obtained crystallographic data along with the selected refinement details are given in Table 1.

According to the single-crystal X-ray analysis, [Pd(acacen)] crystallizes in a monoclinic P2<sub>1</sub>/c space group with 4 molecules in the asymmetric unit. The molecular structure of the complex is shown in Fig. 1, while the most relevant bond distances and angles related to the Pd coordination sphere are listed in Table 2. The central Pd atom has nearly square-planar coordination geometry formed by two N and two O donor atoms belonging to the *acacen* ligand. The maximum deviation of Pd atom from the mean N<sub>2</sub>O<sub>2</sub> plane is only 0.009 Å. The Pd–O and Pd–N bond lengths, as well as bond distances and angles within the ligand, are similar to those previously reported for related palladium complexes with aliphatic Schiff bases [21,52].

Six-membered metallocycles do not show a significant deviation from planarity, which makes the whole molecule almost flat (the maximal deviation from the mean plane is 0.071 Å). The methyl groups are slightly displaced from their "parent" rings; the angle between C–C bridge and the mean plane is in range from 18.33 to 22.89°. The unit cell volume of [Pd(acacen)] is 4 times larger compared to that of [Cu(acacen)] with 16 molecules per unit cell. The asymmetric unit contains 4 molecules arranged in two pairs which in turn form alternating parquet layers parallel to the plane (100) (Fig. 1, b). The molecules in pairs are almost parallel (the angles between two molecules are equal to 1.83° and 1.94°) and are rotated 180° relative to each other. The distance between two molecules in pairs is ~3.75 Å. The angle between two adjacent pairs of molecules is 37.36°.

Hirshfeld surface analysis was used for the visualization of intermolecular interactions and identification of close contacts between molecules in the investigated crystals. Fig. 2 shows the Hirshfeld surfaces [53] obtained using Crystal Explorer [54] for [Cu(acacen)] and [Pd(acacen)] complexes, mapped with  $d_{\text{norm}}$ , curvedness and shape index properties. Since [Pd(acacen)] has 4 individual molecules in the unit cell, separate Hirshfeld surfaces were generated for each of them. Surfaces mapped with  $d_{norm}$ property with  $(-0.1 \div 1.4)$  scale range show that both complexes have no close contacts between adjacent molecules. Weak red spots indicate several C····H, H···H and O···H contacts with interatomic distances between two atoms *ca*.0.1 Å less than the sum of their van der Waals radii. At the same time, in the case of [Cu(acacen)] pairs of red and blue triangles arranged in the form of an hourglasses on the surface mapped with the shape index property (Fig. 2, bottom row) indicate  $\pi$ - $\pi$  interaction between two metallocycles of adjacent [Cu(acacen)] molecules. This  $\pi$ - $\pi$  interaction also appears as a large flat area on the surface, mapped with the curvedness property (Fig. 2, middle row). In contrast, no  $\pi$ - $\pi$  interactions are observed in the case of [Pd(acacen)].

# 3.3. Crystal structures of binuclear complexes

Molecular structures and packing diagrams of  $[Cu(acacen) Cu(hfac)_2]$  and  $[Pd(acacen)Cu(hfac)_2]$  are shown in Fig. 3. The obtained crystallographic data together with the selected refinement

$$PdCl_{2} \xrightarrow{CH_{3}CN} Pd(CH_{3}CN)_{2}Cl_{2} \xrightarrow{H_{2}acacen, KOH} CH_{3}CN} [M(acacen)] \xrightarrow{Cu(hfac)_{2}} [M(acacen)Cu(hfac)_{2}]$$

$$CuCl_{2} \xrightarrow{KOH} Cu(OH)_{2} \xrightarrow{H_{2}acacen} (CH_{3})_{2}CO} [M(acacen)] \xrightarrow{Cu(hfac)_{2}} [M(acacen)Cu(hfac)_{2}]$$

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Crystallographic data and selected refinement details.

Compound	[Cu(acacen)]	[Pd(acacen)]	[Cu(acacen)Cu(hfac) <sub>2</sub> ]	[Pd(acacen)Cu(hfac) <sub>2</sub> ]
Formula	$C_{12}H_{18}CuN_2O_2$	$C_{12}H_{18}N_2O_2Pd$	$C_{22}H_{20}Cu_2F_{12}N_2O_6$	C22H20N2O6F12CuPd
F.W.	285.82	328.68	763.48	806.34
Temperature/K	150	150	250	150
Space group	P21/c	P2 <sub>1</sub> /c	C2/c	C2/c
a/Å	10.9580(3)	13.6878(6)	18.6599(9)	17.8001(7)
b/Å	8.9714(2)	19.5327(12)	19.2046(11)	18.3194(7)
c/Å	12.8174(3)	21.9344(9)	8.5667(4)	8.6028(3)
β/°	93.4770(10)	119.446(3)	109.706(2)	92.2600(10)
Volume/Å <sup>3</sup>	1257.74(5)	5106.8(5)	2890.1(3)	2803.08(18)
Z	4	16	4	4
$\rho_{calc}/g \cdot cm^{-3}$	1.509	1.710	1.755	1.911
F(000)	596	2656	1520	1588
Reflections/Independent reflections	8446/3115	31659/11422	7592/3612	11663/3501
R <sub>int</sub> /R <sub>sigma</sub>	2.33%/3.15%	5.59%/8.28%	1.87%/2.95%	2.68%/2.41%
Data/restraints/parameters	3115/0/158	11422/0/629	3612/0/202	3501/6/202
Goodness-of-fit on F <sup>2</sup>	1.032	0.968	1.027	1.079
Final R indexes $[I \ge 2\sigma (I)]/\%$	$R_1 = 2.81 \text{ w} R_2 = 6.77$	$R_1 = 4.57 \text{ w}R_2 = 7.48$	$R_1 = 4.89 \text{ w} R_2 = 13.10\%$	$R_1 = 5.08 \ wR_2 = 12.08$
Final R indexes [all data]/%	$R_1 = 3.62 \ wR_2 = 7.10$	$R_1 = 9.46 \text{ w}R_2 = 9.17$	$R_1 = 7.19 \; wR_2 = 14.90$	$R_1 = 6.18 \ wR_2 = 13.21$
CCDCN <sup></sup>	1961113	1961114	1961115	1961116



Fig. 1. Molecular structure of [Pd(acacen)] complex (a) and packing diagram (b, view along a axis).

# Table 2

Bond lengths and angles of Cu(acacen) and Pd(acacen) fragments as individual complexes and in bimetallic complexes. DFT results are presented as italic in brackets.

Parameter	[Cu(acacen)]	<i>Cu(acacen)</i> in [Cu(acacen)Cu(hfac) <sub>2</sub> ]	[Pd(acacen)]	Pd(acacen) in [Pd(acacen)Cu(hfac) <sub>2</sub> ]
M–O/Å	1.919–1.925 (1.965-1.966)	1.925 (1.967)	1.997-2.006 (2.066)	2.004 (2.053)
<m-0>/Å</m-0>	1.922 (1.966)	1.925 (1.967)	2.002 (2.066)	2.004 (2.053)
M—N/Å	1.938-1.941 (1.981-1.982)	1.920 (1.964)	1.956-1.976 (2.022-2.023)	1.953 (2.006)
<m-n>/Å</m-n>	1.940 (1.982)	1.920 (1.964)	1.965 (2.023)	1.953 (2.006)
∠N–M–O/°	93.18-93.64 (93.40-93.47)	95.14 (94.21)	94.55-94.88 (93.56)	95.96 (94.77)
$\angle < N-M-O > /^{\circ}$	93.41 (93.43)	95.14 (94.21)	94.71 (93.56)	95.96 (94.77)
$\angle$ (C–C/"mean plane")/°	21.57 (21.90)	15.32 (21.35)	18.33–22.89 (22.27)	19.58 (21.86)

details are given in Table 1. The distance between two metal atoms is 3.191 Å in  $[Cu(acacen)Cu(hfac)_2]$  and 3.264 Å in  $[Pd(acacen)Cu(hfac)_2]$ .

Bond distances and angles related to the M(acacen) fragments are given in Table 2. It should be noted that no significant changes in bond lengths are observed in M(acacen) fragment, and these molecules retain their flat structure when coordinated. At the same time, N–Cu–O and N–Pd–O angles become larger, as the M(acacen) fragment becomes more elongated towards the Cu atom of Cu(hfac)<sub>2</sub>. On the other hand,  $Cu(hfac)_2$  fragment changes its geometry dramatically (Table 3). The individual complex [Cu(hfac)<sub>2</sub>] is characterized by a planar geometry [50] with all atoms (except fluorine) deviating from the mean squared plane by no more than 0.08 Å, whereas the *Cu(hfac)*<sub>2</sub> fragment in the bimetallic complexes is not planar, because the coordination of Cu changes from square to distorted octahedral. O–Cu–O angles vary from 72.37° to 102.34° in [Cu(acacen)Cu(hfac)<sub>2</sub>] and from 74.00° to 101.56° in [Pd(acacen)Cu(hfac)<sub>2</sub>]. In both complexes the O–Cu–O angle that deviates most from 90° is formed by two oxygen atoms belonging to the M(acacen) fragment.

While *hfac*-ligands remain flat, Cu atoms deviate significantly from the mean planes of both ligands. As a consequence, the bend angles of chelate metallocycle along the line between (OO) donor atoms are equal to  $156.13^{\circ}$  in [Cu(acacen)Cu(hfac)<sub>2</sub>] and  $162.59^{\circ}$  in



Fig. 2. Hirshfeld surfaces for [Cu(acacen)] and [Pd(acacen)] complexes, mapped with d<sub>norm</sub> (top row), curvedness (middle row) and shape index (bottom row).



Fig. 3. Molecular structure (a) and packing diagram (b) of [Cu(acacen)Cu(hfac)<sub>2</sub>] complex and molecular structure (c) and packing diagram (d) of [Pd(acacen)Cu(hfac)<sub>2</sub>].

 $[Pd(acacen)Cu(hfac)_2]$ , whereas in  $Cu(hfac)_2$  they are equal to 177.46°. The chelate bond lengths also change significantly. While in the individual  $[Cu(hfac)_2]$  complex they vary slightly from 1.885 to 1.930 Å, in bimetallic  $[M(acacen)Cu(hfac)_2]$  molecules Cu-O

bonds attain the 4 + 2 configuration: four long Cu–O bonds lie in the plane of M(acacen), and two short Cu–O bonds are perpendicular to the M(acacen) plane. This asymmetric geometry can be attributed to multiple ligands with low-symmetric structures.

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Bond lengths and angles for [Cu(hfac)<sub>2</sub>] molecule and Cu(hfac)<sub>2</sub> fragments in binuclear complexes. DFT results are presented as *italic* in brackets.

Parameter	[Cu(hfac) <sub>2</sub> ] [50]	Cu(hfac) <sub>2</sub> in [Cu(salen)Cu(hfac) <sub>2</sub> ] [16]	Cu(hfac) <sub>2</sub> in [Cu(acacen)Cu(hfac) <sub>2</sub> ] [this work]	Cu(hfac) <sub>2</sub> in [Pd(acacen)Cu(hfac) <sub>2</sub> ] [this work]
Cu-O/Å <cu-o>/Å</cu-o>	1.885–1.930 1.912	1.937–2.288 2.043	1.934–2.136 (1.976-2.163) 2.035 (2.070) 87 48 (88 51 00 21)	1.936–2.114 (1.962-2.141) 2.025 (2.052) 00.05 (20.60, 0.1, 62)
$\angle <0-Cu-O/^{\circ}$ $\angle <0-Cu-O>/^{\circ}$ $\angle (metallocycle folding along (0,0) line)/^{\circ}$	92.20–93.88 92.94 177.46	87.71 149.34–172.82	87.48 (89.41) 156.13° (158.29°)	90.05 (90.79) 162.59° (166.66°)

Similar distortions to Cu(hfac)<sub>2</sub> fragment are also observed in the homobinuclear complex with *salen*-type Schiff base [Cu(salen)] Cu(hfac)<sub>2</sub>][16], however, in this structure they are noticeably larger. In particular, the difference between shortest and longest Cu-O bonds is 0.35 Å, and the angle of metallocycle bend along the line between donor atoms can be as low as 149.34°, which is 28° different from the individual [Cu(hfac)<sub>2</sub>] complex. Another noticeable difference is the lengths of Cu–O bridge bonds between Cu atom of  $Cu(hfac)_2$  fragment and two oxygen atoms of M(acacen). In both [M(acacen)Cu(hfac)<sub>2</sub>] complexes these bridge bonds are symmetrically equivalent and equal to 2.179 Å for M = Cu and 2.211 Å for M = Pd, while in  $[Cu(salen)Cu(hfac)_2]$  the lengths of these Cu–O bonds are 2.031 Å/2.375 Å and 1.995 Å/2.493 Å for two symmetrically independent molecules in the unit cell [16]. Both [Cu(acacen)Cu(hfac)<sub>2</sub>] and [Pd(acacen)Cu(hfac)<sub>2</sub>] compounds have columnar packing style along the *c* axis (Fig. 3 (b, d)) with M(acacen) parts stacked parallel to each other and facing "inward" the column, while the bulky *Cu(hfac)*<sup>2</sup> fragments face "outward". The distance between mean planes of two adjacent Pd(acacen) fragments is 3.68 Å, and 3.91 Å between *Cu(acacen)* fragments. The stacking angle (the angle between the stacking direction, the *c* axis in this case, and the normal to the mean square plane of the stacked molecule) is 24.25° for the *Cu(acacen)* fragment and 31.14° for the *Pd(acacen)* fragment.

Fig. 4 shows Hirshfeld surfaces mapped with the  $d_{norm}$  property for [Cu(acacen)Cu(hfac)<sub>2</sub>] and [Pd(acacen)Cu(hfac)<sub>2</sub>]. Despite the fact that both compounds have the same molecular structure and packing style, the nature of their close intermolecular contacts differs considerably. There are several short (2.85 Å) F…F contacts between hfac-ligands in the adjacent stacks of [Cu(acacen)Cu(h $fac_{2}$ , while  $[Pd(acacen)Cu(hfac_{2})]$  has weak C-H···O hydrogen bonds (2.5 Å) between neighbor *M*(*acacen*) fragments. These weak intermolecular interactions apparently have a noticeable effect on the crystal structure of bimetallic complexes. Despite the fact that the hkl data set with slightly better quality was obtained for the  $[Cu(acacen)Cu(hfac)_2]$  complex with  $R_{int}=$  1.87% and  $R_1=4.89\%$  $(R_{int} = 2.68\%$  and  $R_1 = 5.08\%$  for  $[Pd(acacen)Cu(hfac)_2])$ , the Pd(acacen) fragment of [Pd(acacen)Cu(hfac)<sub>2</sub>] has significantly smaller thermal ellipsoids (Fig. 3c) than the Cu(acacen) fragment of [Cu(acacen)Cu(hfac)<sub>2</sub>] (Fig. 3a), which means that the Pd(acacen) fragments are packed more rigidly within the stack. At the same time, *hfac*-ligands of both bimetallic complexes have large thermal ellipsoids with weakly localized F atoms, which is typical for -CF<sub>3</sub> groups.

#### 3.4. Vibrational analysis

The vibrational spectra of the prepared bimetallic complexes were studied and compared with those of their monometallic precursor molecules. The experimental IR and far IR spectra of all complexes are given in Fig. 5. The experimental and calculated IR spectra of [Pd(acacen)] and [Pd(acacen)Cu(hfac)<sub>2</sub>] are presented in Fig. 6 as an example. The assignment and comparison of the most intense experimental and calculated bands in the IR spectra of complexes are given in Tables S1—S4 (Supporting Information). The experimentally measured vibrational wavenumbers of the molecules coincide well with DFT theoretical predictions. The RMS difference between the calculated and experimental wavenumbers was 20 cm<sup>-1</sup>.

In the spectra of all derivatives the group of intense bands in the range of 1600-1500  $\text{cm}^{-1}$  corresponds mainly to the C=C, C=O, C=N ring stretching vibrations. The bands in two regions of 1445-1354 cm<sup>-1</sup> and 1040-990 cm<sup>-1</sup> are mainly attributed to bending vibrations of -CH<sub>3</sub> and -CH<sub>2</sub> groups. The CH out-of-plane vibrations appear as strong bands at 740-760 cm<sup>-1</sup>. The bands with the high contribution of M-O and M-N lie below 700 cm<sup>-1</sup>. For instance, the most intense bands corresponding to Pd-N and Pd-O stretching vibrations lie at 469, 331,  $252 \text{ cm}^{-1}$  in the spectrum of [Pd(acacen)], while the bands corresponding to Cu-N and Cu-O are 458 and 362 cm<sup>-1</sup>. The experimental IR spectrum of [Cu(hfac)<sub>2</sub>] has already been discussed in the literature [55]. In its spectrum, the strong bands in the range 1100–1300 cm<sup>-1</sup> were mainly assigned to C–F stretching vibrations. Cu-O stretching vibrations mixed with deformations of F-C-C in substituents and ring out-of-plane bending vibrations appeared at ~530 and 325, while the deformations of O-Cu-O and O-Cu-N are observed in the range from 230 to 260 cm<sup>-1</sup>. In the IR spectra of bimetallic complexes, the region above 700 cm<sup>-1</sup> comprises the combination of bands corresponding to the vibrations of both counterparts, whereas bands involving Pd-O, Cu-O stretching and O-Cu-O deformation vibrations in the range from 200 to 700 cm<sup>-1</sup> are most sensitive to the formation of new Cu–O1 bonds (Fig. 5, Tables S3–S4). For example, the bands at 692, 671, 585, 333, 256, and 235 cm<sup>-1</sup> in the IR spectrum of  $[Pd(acacen)Cu(hfac)_2]$  exhibit noticeable shifts (3-5 cm<sup>-1</sup>) compared to the corresponding bands in spectra of initial [Pd(acacen)] and [Cu(hfac)<sub>2</sub>] compounds due to the formation of Cu-O1 bond. Two new bands at 492 and 212 cm<sup>-1</sup> with the high contribution of Cu–O1 stretching and  $\delta(OCuO_1)$  vibrations also appear in the [Pd(acacen)Cu(hfac)<sub>2</sub>] spectrum. Similar shift of several bands at 670, 587, 464, 218, 208 and 218 cm<sup>-1</sup> and the change of their intensities compared to the spectra of the initial counterparts are observed in the spectrum of [Cu(acacen)Cu(hfac)<sub>2</sub>]; the new bands at 484 and 292 cm<sup>-1</sup> appear in the spectra. All these changes indicate the formation of new bonds in bimetallic complexes.

# 3.5. Topological analysis based on DFT calculations

Although studies of  $[M(SB)M'(\beta-diket)_2]$  complexes of 3d metals have been carried out since the 1980s, they were mainly focused on structures and magnetic properties [56], and no works have been found illuminating the binding energy of molecular components in bimetallic complexes. Currently, this information is necessary both for fundamental understanding of the coordination ability of the metals M' which can form bimetallic compounds of this type, and for the development of approaches to the molecular design of such compounds, because it provides a key to determining the stability of a binuclear molecule. Moreover, the stability factor is crucial for the application of bimetallic complexes in vapor phase deposition



Fig. 4. Hirshfeld surfaces mapped with d<sub>norm</sub> property (-0.1 ÷ 1.7 range) and fingerprint plots for [Cu(acacen)Cu(hfac)<sub>2</sub>] (a) and [Pd(acacen)Cu(hfac)<sub>2</sub>] (b).

methods with the formation of inorganic films (MOCVD) [57] or molecular metal-organic magnetic films (physical vapor deposition) [58]. For related 3d-4f [M(SB)M'( $\beta$ -diket)<sub>3</sub>] compounds, it was shown that the binding energies calculated by the DFT method were in good agreement with the dissociation enthalpy values obtained by experimental methods [19]. Therefore, we applied the DFT method to the theoretical study of the synthesized complexes [M(acacen)Cu(hfac)<sub>2</sub>] to reveal the influence of the metal M on the stability of binuclear complexes.

As for the use of bimetallic complexes in vapor-phase deposition, it should also be noted that the nature of the bonds stabilizing the binuclear complex molecule in crystals and in the gas phase may differ. For this reason, we also performed the topological analysis as the most appropriate and highly informative tool for determining most significant intramolecular interactions [40–42]. In addition, this approach allows us to identify the most likely bonds for cleavage, which gives the first step to understanding the mechanism of precursor decomposition, which is the key to controlling the MOCVD process [59,60]. This is necessary for monitoring the MOCVD process and determining the effect of the precursor on the composition and characteristics of the resulting materials obtained. Finally, since mononuclear complexes [M(acacen)] are not only components of binuclear complexes, but also promising MOCVD precursors [21,22], they were also the objects of detailed topological study.

The experimental and theoretical geometries of individual molecules of mono- and binuclear complexes were in good agreement (Tables 2 and 3). The calculated metal-oxygen and metal-nitrogen bond lengths exceed the experimental ones by only 0.04–0.06 Å (Tables 2 and 3), which is less than 2%. The corresponding theoretical valence angles are slightly larger than those determined experimentally, but the difference in the most cases is no more than  $1-4^{\circ}$ .

As the result of topological analysis of the function of electron density distribution in the [Cu(acacen)] and [Pd(acacen)] complexes, the bond critical points (3,-1) (or BCP) were established and their parameters were estimated (Fig. 7, Table 4). These BCP indicate the accumulation of electron density exactly in the space between two atoms, since this is characterized by the positive curvature of the electron density along one direction (from one atom to another) and two negative curvatures along two perpendicular directions. Therefore, the presence of BCP (3,-1) between atoms is an indicator of the formation of a chemical bond, while the values of the electron density  $\rho(\mathbf{r})$  and its Laplacian  $\nabla^2 \rho(\mathbf{r})$  give information about the nature of this bond [40-42]. In all cases, the interaction between atoms in C-C, C-N and C-O chemical bonds refers to the type of "shared interaction", and bonds themselves refer to the covalent type because the  $\rho(\mathbf{r})$  and  $\nabla^2 \rho(\mathbf{r})$  values are sufficiently high, and the last parameters are negative (Table S5).

The chemical bonds between metal atoms and nitrogen and oxygen atoms are of most interest because the values of their interatomic interaction energy E, estimated as  $\frac{1}{2}$  of potential energy density according to the previously published data [61], are the lowest compared to all other chemical bonds (Table 4, Table S5). In



Fig. 5. Experimental IR (a) and far IR spectra (b): 1 – [Cu(hfac)<sub>2</sub>], 2 – [Pd(acacen)], 3 – [Cu(acacen)], 4 – [Pd(acacen)Cu(hfac)<sub>2</sub>], 5 – [Cu(acacen)Cu(hfac)<sub>2</sub>],



Fig. 6. Experimental and calculated IR spectra of [Pd(acacen)] and [Pd(acacen)Cu(hfac)<sub>2</sub>].

the case of M-N bonds, the interaction between these two atoms is of "intermediate" type because of the negative values of  $h_e(\mathbf{r})$  in the corresponding critical points. However, the interaction between metal and oxygen atoms refers to the type of "closed-shell interaction" realized through electrostatic attraction, because the values of  $\nabla^2 \rho(\mathbf{r})$  and  $h_e(\mathbf{r})$  are positive. At the same time, the M-O1 and M- O2 atom pairs in the case of both molecules possess the lowest values of interatomic interaction energy; therefore, the cleavage of these bonds is the most probable. The same conclusion was made for a series of the related *bis*-chelated (O^N)-coordinated palladium(II) complexes [62], indicating that the trend to the preferred cleavage of M-O bonds rather than M-N ones may be common for



Fig. 7. Structural formula of [M(acacen)], where M = Cu, Pd (left) and the positions of bond critical points (green balls) in the [Pd(acacen)] structure (right).

**Table 4** Topological parameters of the  $\rho(\mathbf{r})$  function in the critical points (3,-1) of metal-nitrogen and metal-oxygen bonds of M(acacen) molecules.

Bond	Cu(acacen)				Pd(acacen)			
	$\rho(\mathbf{r}), e/Å^3$	$ abla^2  ho(\mathbf{r}),  e/\text{\AA}^5$	<i>h<sub>e</sub></i> (r), au	E, eV	$\rho(\mathbf{r}), e/Å^3$	$ abla^2  ho(\mathbf{r}),  e/\mathrm{\AA}^5$	<i>h<sub>e</sub></i> (r), au	E, eV
M-N1	0.592	11.39	$-3.84 \cdot 10^{-3}$	1.71	0.742	11.73	$-1.70 \cdot 10^{-2}$	2.12
M-N2	0.590	11.35	$-3.77 \cdot 10^{-3}$	1.70	0.742	11.73	$-1.70 \cdot 10^{-2}$	2.12
M-01	0.519	12.56	$8.59 \cdot 10^{-3}$	1.54	0.568	12.48	5.69·10 <sup>-3</sup>	1.61
M-02	0.519	12.56	$8.59 \cdot 10^{-3}$	1.54	0.568	12.48	$5.69 \cdot 10^{-3}$	1.61

the considered metals in the near square-planar coordination environment.

Topological analysis of the electron density distribution function in the  $[Cu(acacen)Cu(hfac)_2]$  and  $[Pd(acacen)Cu(hfac)_2]$  compounds (Fig. 8) shows that the nature of interaction between atom pairs such as carbon-carbon, carbon-nitrogen and carbon-oxygen is identical to that observed in [Cu(acacen)] and [Pd(acacen)] molecules. Similar situation is also observed for M-O1, M-O2, M-N1  $\mu$  M-N2 bonds (Table S6).

The bridge Cu–O1 and Cu–O2 bonds between both parts in  $[Cu(acacen)Cu(hfac)_2]$  and  $[Pd(acacen)Cu(hfac)_2]$  molecules possess the lower values of electron density in the corresponding critical points (3,-1) and, as a consequence, the lower values of interatomic interaction energy (Table 5). For this reason, the

cleavage of Cu-O1 and Cu-O2 bonds is most probable.

The detected values of the electron density and its Laplacian at the bond critical points between copper or palladium atoms and oxygen or nitrogen atoms are in good agreement with the results of other works (Tables 4, 5 and S6). For example, it was shown for dipeptide Cu(glygly)(OH<sub>2</sub>)<sub>2</sub> complex on the basis of topological analysis of experimental data that  $\rho(\mathbf{r})$  in the BCPs in the atomic pairs Cu–O and Cu–N are in the range 0.3–0.8  $e/Å^3$ , while  $\nabla^2 \rho(\mathbf{r})$ has a value from 3 to 13  $e/Å^5$  [63]. In the case of other type of compounds, e.g. Cu(H<sub>2</sub>O)<sub>5</sub> and Cu(H<sub>2</sub>O)<sub>6</sub>, where copper atom interacts with oxygen atoms of water molecules, the values of electron density and its Laplacian in the corresponding bond critical points lie in the ranges of 0.31–0.57  $e/Å^3$  and 4.92–12.36  $e/Å^5$ , respectively [64,65]. The values of  $\rho(\mathbf{r})$  in the BCPs in the Pd–O and



Fig. 8. Structural formula of [M(acacen)Cu(hfac)<sub>2</sub>], where M = Cu, Pd, (*left*); the positions of the bond critical points (green balls) in [Cu(acacen)Cu(hfac)<sub>2</sub>] (*right*).

<b>Table 5</b> Topological p	arameters of the $ ho({f r})$ function in the c	ritical points $(3,-1)$ of metal-oxygen and hydrogen bonds of $[M(acacen)Cu(hfac)_2]$ molecules.
Bond	[Cu(acacen)Cu(hfac) <sub>2</sub> ]	[Pd(acacen)Cu(hfac) <sub>2</sub> ]

Bond	[Cu(acacen)Cu	(hfac) <sub>2</sub> ]			[Pd(acacen)Cu	(hfac) <sub>2</sub> ]		
	$\rho(\mathbf{r}), e/Å^3$	$ abla^2  ho(\mathbf{r}),  e/\mathrm{\AA}^5$	$h_e(\mathbf{r})$ , au	E, eV	$\rho(\mathbf{r}), e/Å^3$	$ abla^2  ho(\mathbf{r}),  e/\mathrm{\AA}^5$	$h_e(\mathbf{r})$ , au	E, eV
Cu-01	0.292	5.13	$2.57 \cdot 10^{-3}$	0.65	0.268	4.48	$1.57 \cdot 10^{-3}$	0.59
Cu-02	0.292	5.13	$2.56 \cdot 10^{-3}$	0.65	0.268	4.48	$1.57 \cdot 10^{-3}$	0.59
Cu-03′	0.341	6.36	$4.01 \cdot 10^{-3}$	0.79	0.358	6.97	$4.75 \cdot 10^{-3}$	0.85
Cu-03″	0.498	11.79	$9.05 \cdot 10^{-3}$	1.42	0.516	12.41	$8.90 \cdot 10^{-3}$	1.51
Cu-04′	0.341	6.36	$4.01 \cdot 10^{-3}$	0.79	0.358	6.97	$4.75 \cdot 10^{-3}$	0.85
Cu-04"	0.498	11.79	$9.05 \cdot 10^{-3}$	1.42	0.516	12.41	8.90·10 <sup>-3</sup>	1.51
03′-H	0.076	0.92	$8.23 \cdot 10^{-4}$	0.11	0.065	0.81	$9.03 \cdot 10^{-4}$	0.09
04′-H	0.076	0.92	$8.23 \cdot 10^{-4}$	0.11	0.065	0.81	$9.03 \cdot 10^{-4}$	0.09
O3″-H	0.042	0.57	$8.92 \cdot 10^{-4}$	0.06	_	_	_	_
04″-H	0.042	0.57	$8.92 \cdot 10^{-4}$	0.06	_	_	_	_
F—H	0.042	0.59	$8.21 \cdot 10^{-4}$	0.06	_	_	_	_
F—H	0.042	0.59	$8.21 \cdot 10^{-4}$	0.06	_	-	-	-

Pd—N atomic pairs of the Pd(II)-salen complex are in the ranges of 0.66–0.73  $e/Å^3$  and 0.68–0.85  $e/Å^3$ , while the corresponding values of  $\nabla^2 \rho(\mathbf{r})$  are in the ranges of 12.68–15.04  $e/Å^5$  and 10.68–13.88  $e/Å^5$ , correspondingly [66].

Six additional bond critical points are also observed in [Cu(acacen)Cu(hfac)<sub>2</sub>] (Fig. 8). Four of them are between four hydrogen atoms of two CH<sub>3</sub>-groups of Cu(acacen) and four oxygen atoms of  $Cu(hfac)_2$ , while the other two points are between two hydrogen atoms of two CH<sub>3</sub>-groups of Cu(acacen) and two fluorine atoms of two CF<sub>3</sub>-groups. At the same time, there are only two such points between two hydrogen atoms of two CH<sub>3</sub>-groups of Pd(acacen) and two oxygen atoms of  $Cu(hfac)_2$  in [Pd(acacen)Cu(hfac)\_2]. These bond critical points indicate the existence of hydrogen bonds between the mentioned pairs of atoms. The values of  $\rho(\mathbf{r})$  and  $\nabla^2 \rho(\mathbf{r})$ for typical hydrogen bonds are in the range of 0.013–0.236  $e/Å^3$  and 0.578–3.350  $e/Å^5$ , correspondingly [42]. The sum of energies of interatomic interactions between atoms in the bridge Cu-O bonds is 5.72 eV in the case of [Cu(acacen)Cu(hfac)<sub>2</sub>] and 5.90 eV in the case of [Pd(acacen)Cu(hfac)<sub>2</sub>]. However, they increase to 6.18 eV and 6.08 eV, respectively, if hydrogen bonds are taken into account. Therefore, the binding between Cu(hfac)<sub>2</sub> and Cu(acacen) fragments is stronger than that between  $Cu(hfac)_2$  and Pd(acacen). This fact was also confirmed by the results of calculation of the binding energy between *M*(*acacen*) and *Cu*(*hfac*)<sub>2</sub> fragments in bimetallic compounds according to equation (1)

$$E_{\rm b} = E_{\rm M(acacen)} + E_{\rm Cu(hfac)2} - E_{\rm M(acacen)Cu(hfac)2}$$
(1)

The binding energy  $(E_b)$  was calculated as the difference of the total energies of the corresponding compound and its initial components. It was shown that  $E_b$  was equal to 1.64 eV for M = Cu, and 1.44 eV when M = Pd, indicating the higher stability of [Cu(acacen) Cu(hfac)<sub>2</sub>] in comparison with [Pd(acacen)Cu(hfac)<sub>2</sub>]. These values are little bit higher compared to the binding energy of 1.31 eV (30.2 kcal/mol) obtained for  $[Cu(salen)La(ptac)_3]$  (ptac - pivaloyltrifluoroacetonato) [19] (the only data available for such systems). The binding energy values are rather low and indicate that such binuclear complexes may dissociate to monometallic precursors in gas phase upon heating. The experimental investigations of the behavior of bimetallic complexes in gas phase and their application as MOCVD precursors are of great interest and will be a subject of future works. In addition, the binuclear complexes synthesized here can be used to obtain molecular metal-organic films by physical vapor deposition [67,68], and due to the proximity of metal centers the molecules of this type can exhibit interesting magnetic properties [26,69].

#### 4. Conclusion

In this work, the binuclear  $[Pd(acacen)Cu(hfac)_2]$  complex was synthesized and investigated as the first example of heterobimetallic molecular compounds formed by Schiff base and  $\beta$ diketonate building blocks with noble metals. The detailed characterization of the structure of this compound in comparison with the homometallic binuclear analogue  $[Cu(acacen)Cu(hfac)_2]$  and the corresponding molecular SB components [M(acacen)] was performed by single crystal X-ray diffraction, vibrational spectroscopy and DFT calculations.

It was shown that the structure of SB complex molecules was almost unchanged after coordination of these molecules to  $Cu(hfac)_2$ . Despite both bimetallic complexes had similar molecular structure and packing style, the nature of the closest intermolecular contacts in [M(acacen)Cu(hfac)\_2] differed considerably. In particular, Hirshfeld surface analysis revealed several short (2.85 Å) F···F contacts between *hfac*-ligands in the [Cu(acacen)Cu(hfac)\_2] crystals, while the weak C–H···O hydrogen bonds (2.5 Å) between neighbor M(acacen) fragments were found for [Pd(acacen) Cu(hfac)\_2].

The topological analysis shown that the strong bridge interaction of Cu–O is strengthen by the formation of weak hydrogen bonds between hydrogen atoms of CH<sub>3</sub>-groups of M(acacen) and oxygen atoms of Cu(hfac)<sub>2</sub> in the both bimetallic complexes. Additional hydrogen bonds involving CF<sub>3</sub>-groups were observed in the case of [Cu(acacen)Cu(hfac)<sub>2</sub>], which caused slightly stronger binding between Cu(acacen) and Cu(hfac)<sub>2</sub> fragments in this binuclear complex (1.64 eV) compared to [Pd(acacen)Cu(hfac)<sub>2</sub>] (1.44 eV).

The demonstrated ability of palladium(II) SB complexes to coordinate to fluorinated  $\beta$ -diketonates with acceptor metal centers opens up a new way for the development of bimetallic Pd-M complexes for various applications. The approach to the preparation of binuclear complexes described in this work can be a starting point for the creation of homo- and heterobimetallic complexes with other 3*d*-transition metals.

#### **CRediT authorship contribution statement**

**Evgeniia S. Vikulova:** Conceptualization, Writing - original draft. **Nataliya S. Nikolaeva:** Investigation, Writing - original draft. **Pavel O. Krasnov:** Investigation, Visualization. **Alexander A. Sukhikh:** Investigation, Visualization. **Anton I. Smolentsev:** Formal analysis. **Evgenia A. Kovaleva:** Formal analysis. **Natalya B. Moro-zova:** Supervision. **Tamara V. Basova:** Writing - review & editing.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2020.128341.

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12