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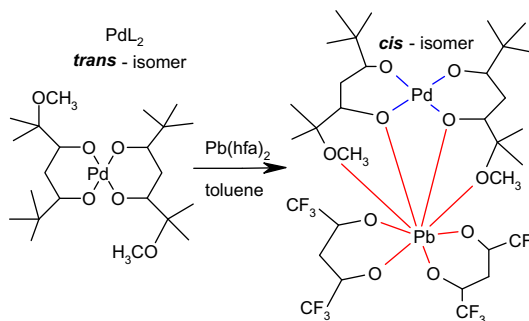


Volatile Pd–Pb and Cu–Pb heterometallic complexes: structure, properties, and *trans*-to-*cis* isomerization under cocrystallization of Pd and Cu β -diketonates with Pb hexafluoroacetylacetonate

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Preparation of volatile heterometallic precursors is a significant step on the way to advanced multi-component materials. Study of molecular transformations in solution upon precursor synthesis is of importance to optimize the preparation of the stable solid product of desired composition. Two new volatile heterobimetallic complexes, *cis*-PdL₂*Pb(hfa)₂ and *cis*-CuL₂*Pb(hfa)₂, were obtained (L = 2-methoxy-2,6,6-trimethylheptane-3,5-dionate, hfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) under cocrystallization of *trans*-bis-beta-diketonates of Pd(II) and Cu(II) with Pb(hfa)₂ from organic solvents. Crystals of these compounds are built of discrete bimetallic molecules where transition metal complex isomerized from *trans*-to-*cis* form. Complexation followed by isomerization was studied by solution NMR. The bimetallic molecular species were formed early in solution. Enthalpy and activation energy of isomerization were estimated to be 49 and 93 kJ mol⁻¹, respectively. A new synthesis technique of Pd(II) beta-diketonates which is distinguished by simplicity and selectivity as well as the crystal structure of *trans*-PdL₂ is described. Volatility of all obtained compounds was confirmed by thermogravimetric analysis and fractional sublimation in vacuum; Pd-containing heterobimetallic complex appeared to be more volatile than both the initial monometallic complexes and Cu-containing complex.

Keywords: Heterometallic complexes; Metal beta-diketonates; Bimetallic precursors; Volatile metal–organic complexes

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1. Introduction

Large flexibility exists for choice of ligands to prepare heterometallic complexes which can be used as single-source molecular (SSM) precursors for multicomponent (composite) materials, catalysts, etc. [1]. Increased solubility, stability, sometimes volatility, better control of composition, and microstructure of the material are among major benefits of such precursors. Most heterobimetallic compounds represent Lewis base–acid adducts and may be obtained by association of substructures with the stoichiometry under thermodynamic control [1(b), 2]. Among a great number of heterometallic complexes, only a few evaporate at elevated temperatures without decomposition.

Meanwhile, there is a considerable interest in the creation of stable precursors having high volatility to allow transport through the gas phase and reasonable thermal stability to deposit multicomponent inorganic film materials on large surfaces with complex shape as well as on non-planar (tubular, porous) substrates as a result of vapor thermolysis. For volatile heterometallic complexes of various compositions and structures, the possibility of preparation of different multicomponent inorganic materials as well as thin film materials by chemical vapor deposition (CVD) techniques was demonstrated [1(a), 3(a), (b)].

The most volatile and thermally stable are binuclear heterometallic complexes wherein bridging ligands combine two metal ions in contrast to complexes formed by direct metal–metal interactions and complexes having ionic structure with e.g. the transition d-metal as a cation and non-transition or f-metal as an anion [3(c)]. Among ligands containing O- and N-anionic donors (e.g. carboxylates, beta-diketonates, beta-ketoesterates, beta-ketoiminates, alkoxides, etc.) and neutral (glymes, bipyridine, etc.) ligands, it was demonstrated that metal β -diketonates represent the predominant type of building blocks to assemble stable and volatile heterometallic complexes.

Previously, we reported formation of heterometallic coordination polymers in the course of the cocrystallization of some Cu(II) [4(a)–(c)] or Pd(II) [4(d)] and Pb(II) β -diketonates and their derivatives from organic solvents. As for initial monometallic complexes, these heterometallic compounds are volatile and sublime on heating in vacuum. These compounds are formed by incorporation of monometallic complexes binding to each other through different bridging interactions. Their structural diversity, thermal behavior, and ability to sublime retaining their composition and suprastructure largely depend on the composition of the initial monometallic complexes. Varying the structure of the building blocks, supramolecular structures with different topologies including coordination polymers built of infinite chains of neutral molecules or tetranuclear and binuclear species were prepared. As a result of cocrystallization of *trans*-CuL₂ with Pb(hfa)₂ (hfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate), we isolated the linear coordination polymer [*cis*-CuL₂*Pb(hfa)₂]_n (L = 2-methoxy-2,6,6-trimethylheptane-3,5-dionate) [4(c)], i.e. geometrical isomerization occurred upon cocrystallization. Unsymmetrical beta-diketones can form *trans* or *cis* square-planar complexes depending on the position of terminal substituents in the ligand. This isomerism is connected with geometry of the complex or an arrangement of the entire ligand in the complex. We report isomerization of the complex when this arrangement is changed. Although isomerization is an important aspect of coordination chemistry, geometrical isomerization under formation of heterometallic complexes was not reported before. Geometrical isomerization has been studied extensively for octahedral monometal tris-diketonates and to considerably less extent for square-planar bis-complexes with unsymmetrical ligands [5(a)–(f)]. For heterobimetallic compounds, only coordination position isomerism was described [5(g), (h)]. We study the geometrical isomerization phenomenon

under formation of heterometallic complexes to clarify whether such an isomerization manifested in other metal complexes with the same ligand. For this purpose, we synthesized a new monometallic complex, *trans*-PdL₂ (**1**), for which we report here a novel synthesis and crystal structure. Starting from this complex, we have obtained a bimetallic complex built of discrete molecules, *cis*-PdL₂*Pb(hfa)₂ (**2**). Moreover, we have obtained an analogous copper-containing complex, *cis*-CuL₂*Pb(hfa)₂ (**3**), which has discrete structure in contrast to an earlier reported [4(c)] coordination polymer. How such molecular assemblies could be formed, and how the isomerization of transition metal complexes occurs when the molecules stay in solution, as well as properties of the Cu–Pb and Pd–Pb beta-diketonate complexes with regard to materials chemistry, are discussed in this article. Study of mechanism of the main processes which accompany intermolecular interaction in solution can help synthesize SSM precursors with controlled structure and composition for multicomponent materials. These systems might be interesting for biochemistry, since it can be regarded as a model in the study of the mutagenic effect of heavy metal compounds on the biomolecule.

2. Experimental

2.1. Materials and physical measurements

Preparation and identification of 2-methoxy-2,6,6-trimethylheptane-3,5-dione (HL), CuL₂, and Pb(hfa)₂ are described [6(a)–(c)], respectively. Metal complexes were purified by vacuum sublimation before using.

NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer for ¹H and ¹³C at 500 MHz and 125.7 MHz, respectively, with CDCl₃ or C₆D₆ as solvent. ¹⁹F NMR spectra were recorded on a Bruker Avance III/500 spectrometer at 470 MHz with C₆D₆ as solvent. To study kinetics of complexation, monometal complexes were dissolved in C₆D₆ and signal of CF₃ groups was recorded. Initial concentration of each component was ~8 × 10^{−6} M.

Thermogravimetric-differential thermal analysis (TG-DTA) was performed under atmospheric pressure in a helium flow (30–40 mL min^{−1}) with a heating rate of 10 °C/min from 25–380 °C using a TG 209 F1 Iris/ (NETZSCH) thermobalance. A standard open crucible was used.

Elemental microanalyses for carbon and hydrogen were performed by a Euro EA 3000 device.

2.2. Synthesis

Two hundred milligram of PdCl₂ was dissolved in 30 mL of acetonitrile on heating. Five hundred and sixty milligram of 2-methoxy-2,6,6-trimethylheptane-3,5-dione (HL) in 10 mL of acetonitrile was added under stirring. PdCl₂ and HL molar ratio is 1/2.5. An equivalent amount (by ligand) of KOH dissolved in a minimum amount of distilled water was added to the resulting solution. Then, water was added by portions under stirring until complete precipitation of product occurred. The resulting mixture was filtered, washed with water, and dried in air. The yield was 95%. After vacuum sublimation (*T* = 170 °C, *p* = 10^{−2} Torr), the product *trans*-PdL₂ (**1**) represented well-faceted orange crystals. MP – 188 °C (in capillary). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 5.98 (2H, s, γ-CH), 3.16 (6H,

d, $J = 3.5$ Hz, $-\text{OCH}_3$), 1.29 (12H, d, $J = 5$ Hz, $-\text{C}(\text{CH}_3)_2$), 1.14 (18H, d, $J = 4$ Hz, $-\text{C}(\text{CH}_3)_3$). ^{13}C NMR (125.7 MHz, CDCl_3 , 25 °C): δ 198.7 ($-\text{CO}-\text{C}(\text{CH}_3)_3$), 193.1 ($-\text{CO}-\text{C}(\text{CH}_3)_2\text{OCH}_3$), 92.9 ($\gamma\text{-CH}$), 80.7 ($-\text{C}(\text{CH}_3)_2\text{OCH}_3$), 52.4 ($-\text{OCH}_3$), 41.5 ($-\text{C}(\text{CH}_3)_3$), 29.2 ($-\text{C}(\text{CH}_3)_3$), 25.7 ($-\text{C}(\text{CH}_3)_2\text{OCH}_3$). Anal. Calcd for $\text{C}_{22}\text{H}_{38}\text{O}_6\text{Pd}$ (%): C, 52.3; H, 7.6. Found: C, 52.3; H, 7.5.

cis- $\text{PdL}_2^*\text{Pb}(\text{hfa})_2$ (**2**) and *cis*- $\text{CuL}_2^*\text{Pb}(\text{hfa})_2$ (**3**) were obtained by simultaneous dissolution of monometallic complexes in toluene. To accelerate dissolution, the solution was heated slightly. After slow evaporation of solvent under nitrogen at room temperature, yellow and blue crystals were obtained for **2** and **3**, respectively. The products were recrystallized from heptane and purified by vacuum sublimation ($T = 100$ °C, $p = 10^{-2}$ Torr).

Compound **2** sublimed into one zone: MP 100 °C (in capillary). ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ 6.21 (2H, s, $\gamma\text{-CH}$), 2.88 (6H, s, $-\text{OCH}_3$), 1.19 (12H, s, $-\text{C}(\text{CH}_3)_2$), 0.98 (18H, s, $-\text{C}(\text{CH}_3)_3$), δ 5.88 (2H, s, $\gamma\text{-CH}$, $\text{Pb}(\text{hfa})_2$). ^{19}F NMR (470 MHz, C_6D_6 , 25 °C): δ -500.08 and -500.14 against the signal of CF_3COOH at δ -504. Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{O}_{10}\text{PbPd}$ (%): C, 34.1; H, 3.6. Found: C, 34.9; H, 4.0.

Compound **3** sublimed into two zones. The less volatile one is predominant and corresponds to bimetallic **3**: MP 95 °C (in capillary). Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{O}_{10}\text{CuPb}$ (%): C, 35.5; H, 3.7. Found: C, 36.0; H, 4.1. More volatile compound corresponds to heteroligand $\text{Cu}(\text{hfa})\text{L}$: MP 125 °C. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_5\text{Cu}$ (%): C, 40.9; H, 4.3; F, 24.2. Found: C, 40.4; H, 3.9; F, 24.0.

2.3. X-ray diffraction study

The powder XRD of the polycrystals was carried out using a Shimadzu XRD-7000 diffractometer (CuK_α radiation, Ni filter, 2θ angle range from 5° to 50°, and step 0.03° 2θ) at room temperature and atmospheric pressure. The products were ground in the presence of vaseline oil; the suspension was deposited onto the polished side of a standard quartz cuvette. In the study, a polycrystalline silicon sample similarly prepared was used as the external standard. The diffraction pattern of the compound was completely indexed by the results of the single-crystal study to find no extra lines, which indicated that the product was a single phase. The unit cell parameters and experimental intensities to solve the crystal structure were measured with a Bruker Apex Duo four-circle diffractometer with a 2-D CCD detector (MoK_α radiation and graphite monochromator). The structures were solved by direct methods and refined in an anisotropic (isotropic for H and F) approximation. The positions of hydrogens are defined geometrically. One CF_3 group and one $\text{C}(\text{CH}_3)_3$ group in **2** are disordered by rotation. All the calculations used the SHELX-97 software [7]. CCDC 908765 for **1**, CCDC 987817 for **2**, and CCDC 695761 for **3** contain the supplementary crystallographic data for this article. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

3. Results and discussion

3.1. Crystal structures

The crystallographic data and experiment details are given in table S1.1 (see online supplemental material at <http://dx.doi.org/10.1080/00958972.2015.1035653>); the packing of the

molecules is demonstrated in figures S1.1–S1.3 (Supplementary material), and all intermolecular interactions are van der Waals. The crystal structure of **1** is molecular (figure 1), built of isolated molecules of *trans*-PdL₂. Pd is located in the center of symmetry and has square coordination by four oxygens of two beta-diketonate ligands. The average value of the coordination bond lengths is 1.976 Å. Chelate angle O–Pd–O is 92.46° (table S1.2 in the Supplementary material). With the exception of terminal CH₃ groups, the molecule is of almost planar structure, $\Delta = 0.01$ Å. The resulting geometry of the reported complex is similar to that one of the well-studied complex Pd(tmhd)₂ (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate) [6(d)]. Each molecule is surrounded by six identical molecules with four Pd···Pd distances of 8.5 and two of 9.9 Å.

The structure of bimetallic **2** is molecular, built from neutral homoligand complexes PdL₂ and Pb(hfa)₂ united into binuclear molecules. The structure of the complexes with the numbering of atoms is demonstrated in figure 2. In this article, for the synthesis of the heterometallic complex, we took *trans*-Pd complex as the starting compound; however, the resulting compound exhibits the Pd(II) complex having *cis* structure, i.e. *trans*-to-*cis* isomerization occurred in the course of the synthesis of heterometallic compound. The Pd ion exhibits square-type coordination formed by four oxygens of two beta-diketonate ligands, and the average value of the O–Pd–O chelate bond angles is 94.3°. The complex has no elements of symmetry, the difference in the Pd–O bond length from the side of different substituents is insignificant, but demonstrates that the Pd complex is slightly compressed in plane in the direction toward Pb (figure 2). The molecule of Pb(hfa)₂, as well as all the other Pb(II) complexes with beta-diketonates exhibits a non-planar structure and has no symmetry elements [6(c)]. Pb coordinates four oxygens of two chelating hfa ligands, the length values of these covalent Pb–O bonds are 2.403–2.461 Å, the chelate angles O–Pb–O have a mean value of 73.5°, and the angle between the normals to the planes of the chelate rings is 67.4°. Coordination of Pb is completed (4 + 2 + 2) by interactions with oxygens of the Pd complex: the bond length values for Pb-methoxy oxygen are 2.851 and 2.938 Å, those for Pb-chelate ring oxygen of the Pd complex are 3.050 and 3.076 Å. At the expense of the coordination complement, the Pb and Pd ions approach to 4.212 Å, with formation of a binuclear complex. Thus, oxygens of the chelate ring and of the methoxy-groups of PdL₂ bridge.

XRD single-crystal analysis has shown that **3** consists of bimetallic molecules built of two monometallic complexes CuL₂ and Pb(hfa)₂ without exchange but with sharing their ligands (figure 3). Two crystal modifications of the initial *trans*-CuL₂ have been described before [6(e)]. In the present work, α -modification of *trans*-copper complex was used. In the reported compound, it isomerizes into *cis*-complex when Cu coordinates four oxygens of its ligands and one oxygen from Pb complex retaining coordination number five with distorted square pyramidal coordination (figure S1.4, Supplementary material) in contrast to palladium coordination in **2**. In this case, Cu is out of the plane and the angle between O5Cu1O6 and O7Cu1O8 planes is 2.2°. For the vertex bridging, Cu1–O4 is 2.44 Å. Two oxygens of Cu chelates are coordinated by Pb. In asymmetric *cis*-complex, Cu–O distances with shared oxygens are elongated in comparison with other ones. Chelate angles of O5Cu1O6 and O7Cu1O8 are 93.4° and 92.5°, respectively. In addition to oxygens and its ligands, Pb coordinates two oxygens of Cu chelates and two oxygens of methoxy groups in the terminal substituents of Cu complex which are now *cis*. Thus, the coordination number for Pb reaches eight and Pb(hfa)₂ molecule is transformed. In the reported bimetallic compound, this molecule is flattened. Pb–O distances are longer and chelate angle is smaller in the hfa-ligand whose oxygen is coordinated by Cu (Cu1–O4). As a result, binuclear molecule has Cu···Pb distance of 3.44 Å.

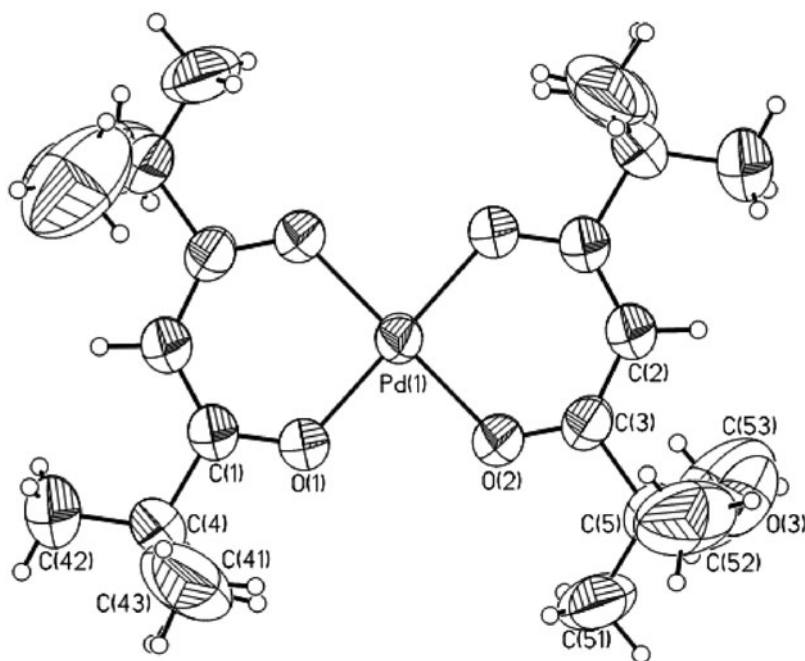


Figure 1. Molecular structure of **1**. Selected bond lengths (Å): Pd(1)–O(1) 1.9738(17), Pd(1)–O(2) 1.9774(18), O(1)–C(1) 1.273(3), O(2)–C(3) 1.261(4), C(1)–C(4) 1.526(4), C(2)–C(1)#1 1.373(4), C(2)–C(3) 1.406(5), C(3)–C(5) 1.531(5), C(5)–O(3) 1.381(6), and O(3)–C(53) 1.618(13).

3.2. Synthesis, structure, and volatility of the compounds

Among numerous Pd(II) beta-diketonates, **1**, the complex with 2-methoxy-2,6,6-trimethylheptane-3,5-dionate, was not described. We used an original technique to synthesize isomerically pure **1** in high yield. In contrast to known methods of preparation of Pd(II) beta-diketonates [5(b), 6(f)], the developed technique is simple and does not result in a mixture of *cis*- and *trans*-complexes in the case of unsymmetrical diketonate ligands. Only the *trans*-isomer was obtained. The developed synthesis is also suitable for the synthesis of Pd complexes with other beta-diketonates and ketoiminates [8]. We believe that the selective synthesis of the particular geometric isomer in this case is promoted by formation of an asymmetric intermediate complex between Pd(II) chloride and strong coordinating solvent acetonitrile, whereas the methods described in the literature presented the synthesis proceeding via formation of symmetric ions such as $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{PdCl}_4]^{2-}$.

The structural data demonstrate that **1** forms molecular crystals wherein the molecules of *trans*-PdL₂ do not form coordination polymers as observed in the structure of CuL₂. It should be noted that CuL₂ forms α -*trans*-modification (3-D-polymer) from the solution, but sublimation results in a metastable β -*trans*-modification with 1-D coordination polymeric structure [6(e)]. Obtained *trans*-PdL₂ does not convert into the *cis*-isomer upon dissolving or sublimation. As revealed by NMR spectra, *trans*-PdL₂ does not isomerize to *cis* in benzene or toluene solution during 12 h at 55 °C and during at least 3 weeks at room temperature. However, in the presence of Pb(hfa)₂, complex formation occurs with isomerization of the Pd complex resulting in a stable binuclear **2** (figure 4). A similar discrete bimetallic **3**

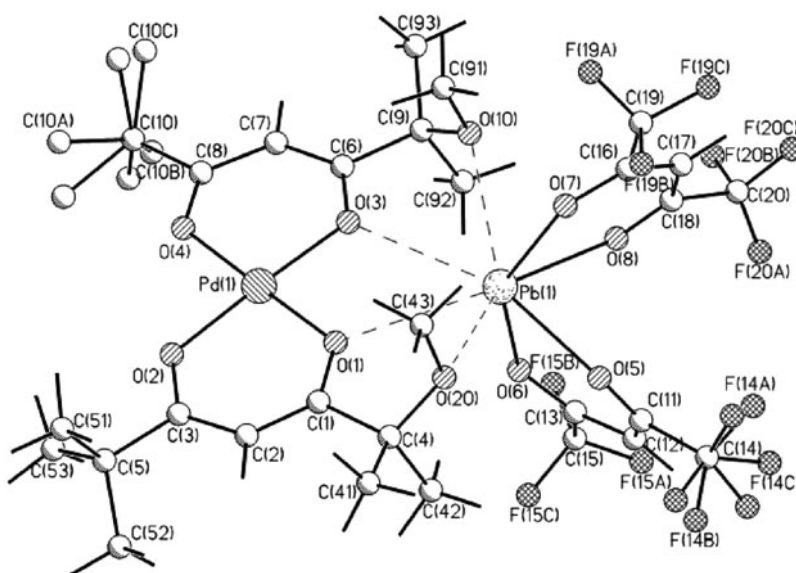


Figure 2. Molecular structure of **2**. Selected bond lengths (Å): Pd(1)–O(3) 1.973(3), Pd(1)–O(1) 1.976(3), Pd(1)–O(4) 1.980(3), Pd(1)–O(2) 1.981(3), Pb(1)–O(5) 2.404(4), Pb(1)–O(8) 2.416(3), Pb(1)–O(7) 2.448(4), Pb(1)–O(6) 2.461(4), O(1)–C(1) 1.283(5), O(5)–C(11) 1.245(6), O(2)–C(3) 1.274(5), O(6)–C(13) 1.240(6), O(3)–C(6) 1.279(5), O(7)–C(16) 1.246(7), O(4)–C(8) 1.268(5), O(8)–C(18) 1.234(6), C(9)–O(10) 1.428(6), C(4)–O(20) 1.415(6), Pb(1)–O(10) 2.93, and Pb(1)–O(20) 2.85.

can be obtained with *trans*-CuL₂ using the same non-coordinating solvents (e.g. toluene or heptane), whereas formation of linear coordination polymer [*cis*-CuL₂*Pb(hfa)₂]_n [**4(c)**] is observed using chloroform. Compounds **2** and **3** were isolated via solvent evaporation in separate experiments. Owing to their molecular structure, **2** and **3** are soluble both in polar and non-polar solvents. Binuclear complex formation is not the only product in the system CuL₂ – Pb(hfa)₂ with a certain amount of heteroligand complex Cu(hfa)L, whose structure and properties are to be discussed in a separate article, is formed. Compound **3** in this case could be considered as an intermediate in the ligand exchange reaction between Pb and Cu complex. No formation of heteroligand product was observed for much less labile Pd complex at the same conditions. The separation of heterometallic **3** and heteroligand Cu complex can be readily carried out via a gradient sublimation of the mixture.

Monometallic Pb(hfa)₂ has “butterfly” geometry [6(c)] which is also characteristic for the Pb-containing moiety in **2** where Pd does not form additional coordination bonds and hence, monometallic complexes are less bound. In **3**, we observe the situation when Lewis interactions between different central and donor atoms provide tight intermolecular bonding between structural units leading to noticeable reconstruction of the coordination sphere as for Cu and Pb. Sharing of donor atoms leads to shorter bridging bonds when comparing **2** and **3**. As a result, Cu...Pb distance is much shorter in **3** than Pd...Pb distance in **2**. Compared with [*cis*-CuL₂*Pb(hfa)₂]_n [**4(c)**], **3** involves Pb(hfa)₂ molecules flattened to a considerable extent and the bridging oxygens of the methoxy groups of the Cu complex in the axial position are coordinated to the Pb, whereas in **2**, the methoxy groups belonging to the Pd complex are in an equatorial position and oriented on the same side of the plane of the Pd complex. This position of methoxy groups might indicate that the process of



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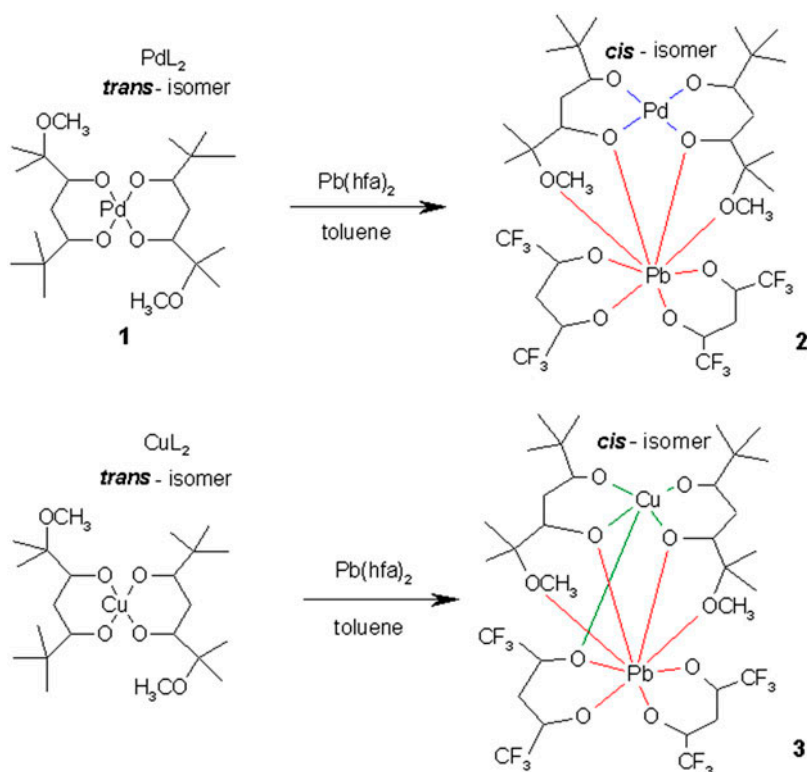


Figure 4. Schematic representation of heterobimetallic compound formation followed by the isomerization of initial monometallic complex.

more volatile than both initial complexes and **3** [figure 5(b)]. This effect could be explained by the fact that **2** has a looser packing of the molecules in the crystal than the initial monometallic **1**: the intermolecular Pd–Pd distance in **1** is equal to 8.5 Å, whereas in **2**, this value is greater than 10 Å. The intermolecular Cu–Cu distance is 7.6 Å for **3** as against 7.8 Å for CuL_2 . As far as **3** is concerned, there could be isolated the shortest intermolecular contact such as $\text{Pb}\cdots\text{F}$ distance equal to 3.5 Å, whereas **2** has no pronounced intermolecular contacts between the metal atoms and either atom of the adjacent binuclear molecules.

That mass transfer of **2** and **3** into the vapor phase can be achieved at $T = 100^\circ\text{C}$, whereas one possible dissociation product, such as PdL_2 does not sublime in a noticeable amount, might indicate the presence of heterometallic complex in the gas phase. Indeed, molecular ion peak $[\text{CuL}_2\text{Pb}(\text{hfa})_2]^+$ of low intensity and its fragment $[\text{CuL}_2\text{Pb}(\text{hfa})_2 - \text{C}(\text{CH}_3)_2\text{OCH}_3]^+$ at m/z 1010 were recorded by mass spectrometry (time-of-flight mass analyzer, electron impact ionization, ca. 70 eV) for **3** vapor at evaporation temperature of 130°C . This excludes occurrence of a synergistic effect exerting on the volatility of low volatile compound in the case of adding a highly volatile complex, which was observed for lanthanide acetylacetonates [9(c)].

3.3. NMR study of complexation

In most cases, heterometallic complexes were isolated as final products and their crystal structures determined regardless of attention to complexation processes which may happen in solution. We tried to find out how temperature influences the formation of bimetallic complex in solution and isomerization phenomena. We believe formation of a heterometallic complex from *trans*-ML₂ involves several successive stages presented by Equation (1): (1) a reversible stage of forming the molecular complex *trans*-ML₂*Pb(hfa)₂, and (2) a slow isomerization stage to form molecular complex *cis*-ML₂*Pb(hfa)₂. Such a process occurs much faster in the case of more labile Cu complexes.

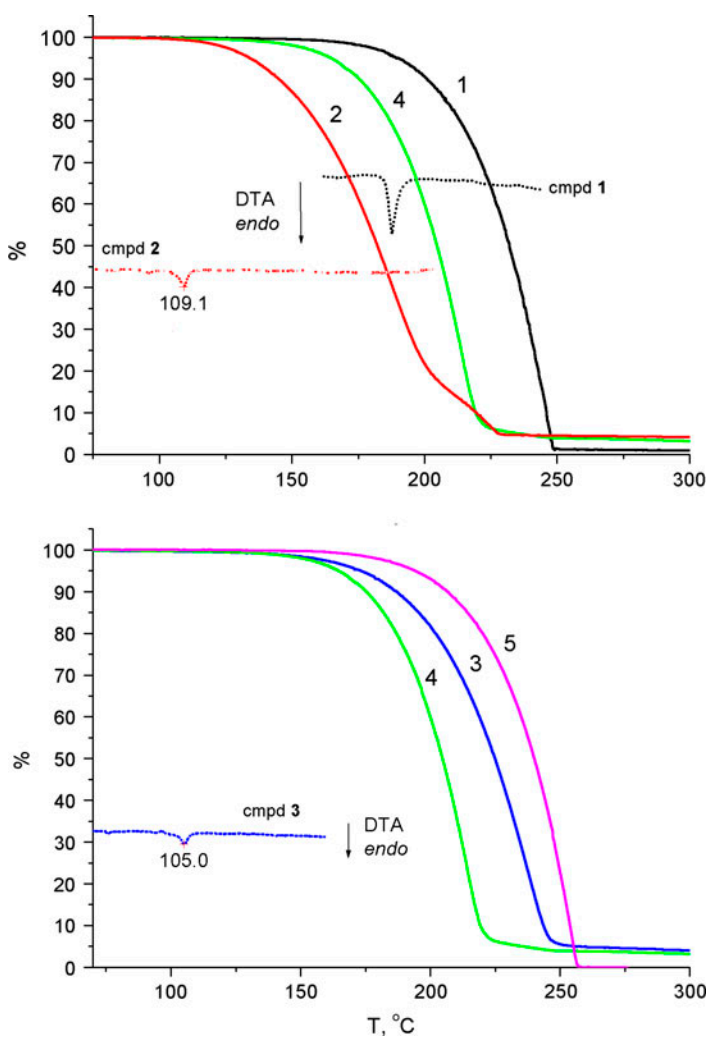
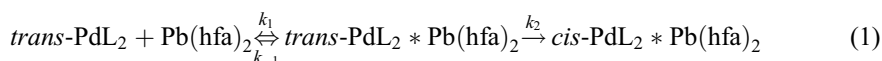


Figure 5. [(a) and (b)] TG-DTA data for PdL₂ (1), PdL₂*Pb(hfa)₂ (2), CuL₂*Pb(hfa)₂ (3), Pb(hfa)₂ (4), and CuL₂ (5).

Pd-containing complexes proved suitable to study complexation and isomerization in solution by NMR. For *trans*-PdL₂, the following set of ¹H NMR (500 MHz, C₆D₆, 25 °C) signals is observed: 6.22 (2H, s, γ-CH), 2.97 (6H, s, -OCH₃), 1.33 (12H, s, -C(CH₃)₂), and 1.10 (18H, s, -C(CH₃)₃). In ¹H NMR spectrum of **2**, the signals of the Pd complex are shifted to stronger field and are not split upon complexation. Monometallic Pb(hfa)₂ gives one ¹⁹F NMR signal at -502.93 ppm (470 MHz, C₆D₆, 25 °C), while Pb(hfa)₂ in **2** gives a doublet: at -500.08 and -500.14 ppm (against the signal of CF₃COOH at δ -504) (NMR spectra are available in figures S2.1–S2.4, Supplementary material). It was also established that **2** does not dissociate into initial monometallic complexes in C₆D₆ from 25 to 55 °C.

Based on the measurement of the intensity of ¹⁹F NMR signal from free Pb(hfa)₂ and from that associated in heterometallic complex, we have estimated the equilibrium constant $K = [AB]/[A][B]$ for the reaction $A + B \rightleftharpoons AB$. We assumed that the intensity of the NMR spectral signal is in direct proportion to the concentration of corresponding components and that $[A] = [B]$. Kinetic curves obtained at $T = 298, 308, 318$, and 328 K are available as figure S3.1, Supplementary material. Since the equilibrium was not reached at room temperature within a reasonable time, for plotting the curve $\ln K \sim 1/T$, we used the three points $T = 308, 318$, and 328 K (table S3.1 and figure S3.2, Supplementary material). At this stage, we did not attempt accurate thermodynamic study of this reaction with the involvement of statistical processing a wide range of the experimental data. From the line slope, we estimated the reaction enthalpy ΔH as $+49.15 \pm 0.8$ kJ mol⁻¹.

We believe that the kinetics of reaction (1) could be described within the framework of Michaelis–Menten approach for homogeneous catalytic reactions [10(a)] as well as that in our case, it should follow equation (2),

$$d[P]/dt = K_1 k_2 [A]([B] + [C]) / (1 + K_1 [A]) \quad (2)$$

Mathematical treatment and extraction of parameters from such functions are not easy. Hence, kinetic curves were treated using a simpler model developed for the isomerization of other palladium complexes [10(b)]. Isomerization reaction can be treated by linearization of the regression (3):

$$[P] = [B](1 - \exp(-k_{\text{obs}}t)) + [P]_0 \quad (3)$$

The observed rate constant k_{obs} may be approximated as $k_{\text{obs}} = k_2 + k_1[B]_0$, where k_2 represents the monomolecular and k_1 is the bimolecular path to *cis* isomer in (1); $k_{\text{obs}}(T)$ were derived from the plot $\ln([B] - [P])/[B]$ against t . This function linearized well at 298 K, but for other temperatures, we used only the first 10 points from kinetic curves. Activation energy of the process was estimated by standard treating of the linear regression when $\ln(k_{\text{obs}})$ versus $1/T$ making $E_a \sim 93$ kJ mol⁻¹ $\pm 10\%$ (figure S3.3, Supplementary material). This value is relatively high (comparable with the energy of Pd–O bonding in the complex) and may explain the slowness of the isomerization of the palladium complex.

4. Conclusion

Volatile heterobimetallic coordination complexes *cis*-ML₂*Pb(hfa)₂ (M = Cu or Pd) have been obtained by direct Lewis acid–base adduct formation from metal beta-diketonates in organic solvents. The Pd-containing heterobimetallic complex is more volatile than both

initial monometallic complexes and Cu-containing complex. The complexes obtained represent discrete binuclear complexes formed by chelate beta-diketonate moieties. The phenomenon of *trans*-to-*cis* isomerization of the initial transition metal complex has been revealed in formation of heterobimetallic complexes. Bimetallic molecular complexes are formed early in solution. The mentioned process is endothermic and the conversion level exhibits an increase with increasing temperature within the temperature range under investigation. It could be proposed that formation of such bimetallic species may represent a transient stage in the reactions of ligand exchange between labile metal complexes. Thus, we described new molecular compounds with specific intermolecular interaction which can be utilized as a tool in crystal engineering of volatile heterometallic complexes.

Supplementary material

Supplementary material related to this article: figures, tables, and CIF files giving structural data for **1–3** and kinetic study details for **2**.

Disclosure statement

No potential conflict of interest was reported by the authors.

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