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Palladium Acetate Complexes in the Gas Phase

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Abstract—New palladium acetate complexes, $Pd_2(OOCMe)_4^+$, $Pd_2(OOCMe)_3^+$, $Pd_2(OOCMe)_2^+$, and $Pd_2(OOCMe)^+$ were detected in the thermal decomposition products of *trans*-$Pd(Py)_2(OOCMe)_2$ by mass spectrometry with direct ion source. The geometric and electronic structures of the $Pd_2(\mu\text{-}OOCMe)_4^+$ cation and the $Pd_2(OOCMe)_4$ molecule were established by quantum chemical calculations (DFT with the PBE1PBE hybrid exchange correlation potential in the 6-31G*/SDD basis set) and natural orbital analysis.

Keywords: palladium, coordination compounds, carboxylates, mass spectrometry, quantum chemical calculations

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INTRODUCTION

Studies of palladium carboxylate complexes have played an important role in the development of the modern coordination chemistry [1] and metal complex catalysis [2]. A typical representative of this class of coordination compounds, crystalline palladium(II) acetate, is the trinuclear complex $Pd_3(\mu\text{-}OOCMe)_6$ [3, 4], as opposed to tetranuclear platinum(II) acetate $Pt_4(\mu\text{-}OOCMe)_8$ [5, 6]. Recently, palladium(II) acetate was obtained as a polymeric complex $[Pd(OOCMe)_2]_n$, and studied by powder X-ray diffraction [7, 8]. Solutions in glacial acetic acid containing alkali metal acetate (M = Li, Na, Rb, Cs) comprise mono- and binuclear anionic complexes, $M_2[Pd(OOCMe)_4]$ and $M_2[Pd_2(OOCMe)_6]$ [9, 10], which play a key role in the catalysis of oxidative transformations of olefins and aromatic hydrocarbons [11–13].

In this work, a direct injection mass spectrometric study of the thermal decomposition of *trans*-$Pd(Py)_2(OOCMe)_2$ (**I**) resulted in the detection of new palladium acetate complexes, $Pd_2(OOCMe)_4^+$ (**II**), $Pd_2(OOCMe)_3^+$, $Pd_2(OOCMe)_2^+$, and $Pd_2(OOCMe)^+$, in the gas phase, apart from the organic thermolysis products, pyridine and 2,2'-dipyridine. The geometric and electronic structures of cation **II** and the corresponding $Pd_2(OOCMe)_4$ molecule were studied by quantum chemistry methods.

EXPERIMENTAL

The initial complex $Pd(Py)_2(OOCMe)_2$ (**I**) was synthesized by a reported procedure [14] using special purity grade pyridine (Sigma-Aldrich) and high-purity palladium(II) acetate obtained from palladium metal (99.99%) by a known procedure [15].

Direct injection mass spectrometry. Mass spectra were run on a Thermo/Finnigan MAT Incos 50 mass spectrometer. Experimental conditions: direct insertion probe (DIP) with programmed sample heating from 50 to 290°C (15°C/min); $EI = 70$ eV; ion source temperature, 240°C; calibration against the FC-43 standard (reference peaks, *m/z:* 18, 28, 69, 100, 131, 219, 264, 414, 502); 50–600 a.m.u range of masses. The isotope distribution of detected ionic clusters was analyzed by calculation software [16].

Calculation procedure. The geometric and electronic structures of $[Pd_2(\mu\text{-}OOCMe)_4]^{n+}$ (n = 0, 1) were studied by DFT with the hybrid exchange-correlation PBE1PBE potential [17] in the 6-31G*/SDD basis set [18, 19]. The Gaussian-03 software was used [20]. The calculations included full optimization of all geometric parameters without symmetry constraints.

RESULTS AND DISCUSSION

The mass spectra of metal-containing products formed upon thermolysis of complex **I** in the 90–140°C range (Fig. 1) were found to exhibit peaks for isotopic clusters corresponding to the binuclear palla-

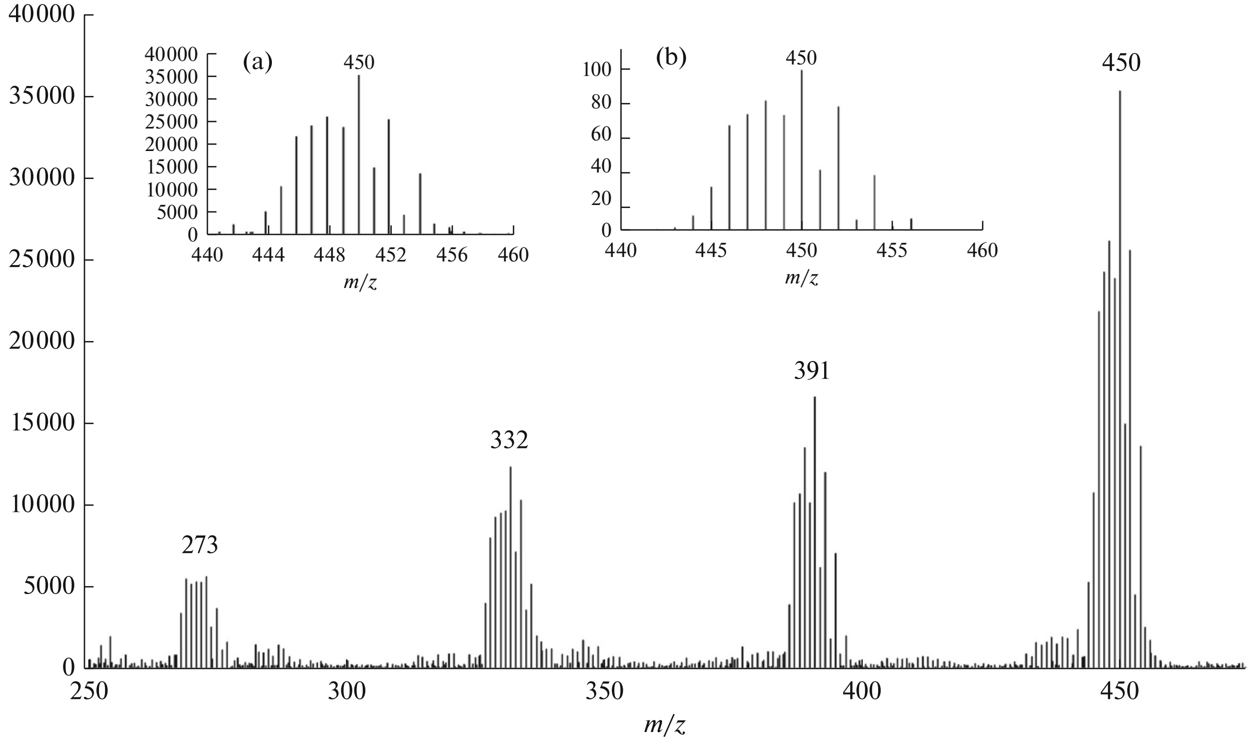

Fig. 1. Mass spectrum of the products of thermal decomposition of *trans*-$Pd(Py)_2(OOCMe)_2$ (**I**) in the range *m/z* 265–460; the inset shows (a) the experimental ionic cluster with the maximum at *m/z* 450 and (b) calculated isotopic distribution for $Pd_2(OOCMe)_4^+$.

dium complex ions (*m/z*): $Pd_2(OOCMe)_4^+$ (**II**) (450); $Pd_2(OOCMe)_3^+$ (391); $Pd_2(OOCMe)_2^+$ (332); and $Pd_2(OOCMe)^+$ (273).

The isotopic distribution of ionic clusters fully coincided with the calculated distribution (Fig. 1, inset).

The geometric and electronic structures of the $Pd_2(\mu\text{-}OOCMe)_4^+$ cation (**II**) and the $Pd_2(OOCMe)_4$ molecule were established by quantum chemical calculations. The calculation showed that for both binuclear complexes, neutral $Pd_2(\mu\text{-}OOCMe)_4$ and cationic $[Pd_2(\mu\text{-}OOCMe)_4]^+$, the low-spin states, singlet and doublet, respectively, are energetically more favorable (table).

The data of the table demonstrate that removal of an electron from the neutral $Pd_2(\mu\text{-}OOCMe)_4$ complex in the ground (singlet) state on going to the ground (doublet) state of the $Pd_2(\mu\text{-}OOCMe)_4^+$ cation is accompanied by a substantial (by 0.16 Å) shortening of the Pd–Pd interatomic distance (Fig. 2). It is of interest that the found Pd–Pd distance in the ground state of neutral $Pd_2(\mu\text{-}OOCMe)_4$ (2.634 Å) is very similar to the distance between the Pd(I) atoms connected by bridging CO groups (2.663 Å) in the crystalline tetranuclear $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OOCMe)_4$ complex [21], which is unusual for palladium(II) complexes with acetate bridging groups [1–5].

In the singlet state of the $Pd_2(\mu\text{-}OOCMe)_4$ complex, the highest occupied highly antibonding MO (Fig. 3a) has two electrons, which determines the long Pd–Pd interatomic distance. The removal of one electron from this orbital results in shortening of the Pd–Pd distance. In the cation, one electron remains in the highly antibonding HOMO. Within the framework of Cotton's metallic MO scheme [22], this means that a metal–metal bond of 0.5 order exists in the $Pd_2(\mu\text{-}OOCMe)_4^+$ cation.

Natural orbital analysis confirmed the possibility of formation of the Pd–Pd bond of the order of 0.5 in $Pd_2(\mu\text{-}OOCMe)_4^+$. The molecular fragment $Pd_2C_8H_{12}O_8$ in both the doublet and quartet states has two natural Pd–Pd bonding orbitals.

The $Pd_2(\mu\text{-}OOCMe)_4^+$ cation and the corresponding $Pd_2(\mu\text{-}OOCMe)_4$ molecule found in this study can be regarded as a virtual "work piece" for the formation of really existing trinuclear $Pd_3(\mu\text{-}OOCMe)_6$ complex. Presumably, the presence of the

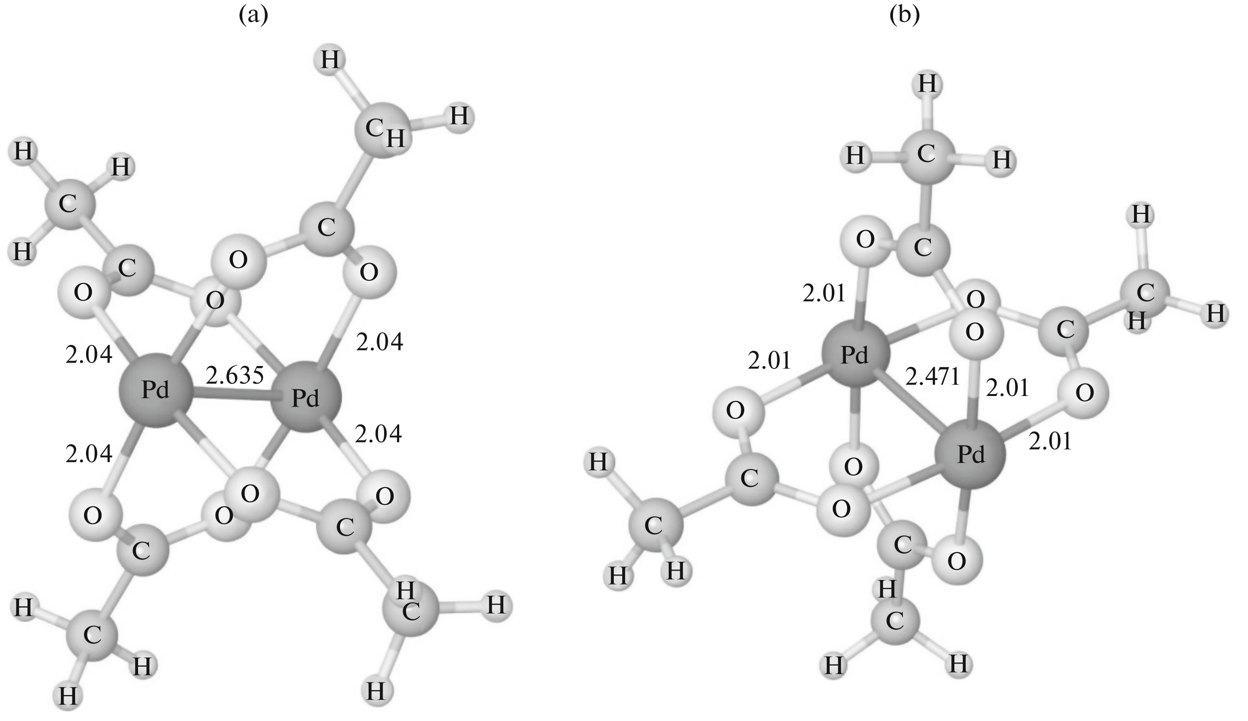

Fig. 2. Optimized geometry of (a) the $[Pd_2(\mu\text{-}OOCMe)_4]$ molecule and (b) $[Pd_2(\mu\text{-}OOCMe)_4]^+$ cation in the low-spin state.

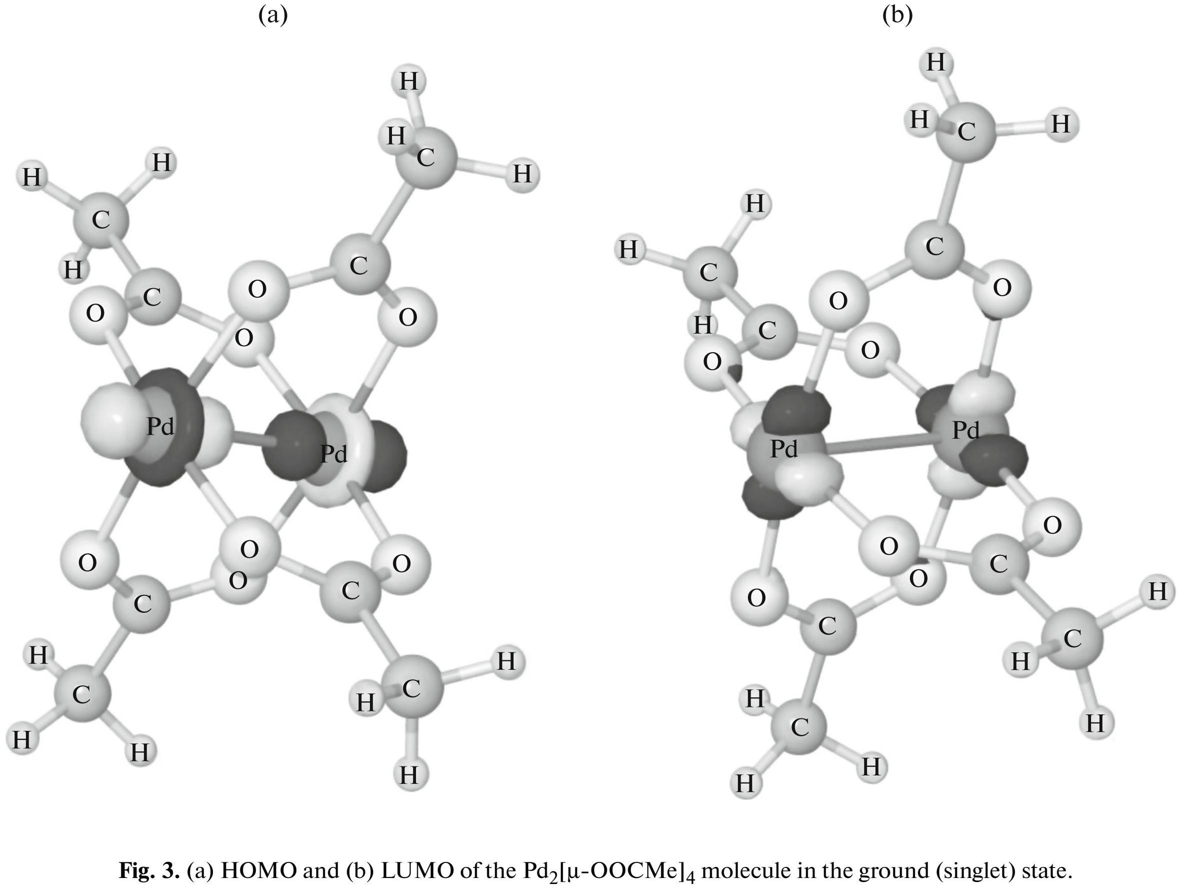

Fig. 3. (a) HOMO and (b) LUMO of the $Pd_2[\mu\text{-}OOCMe]_4$ molecule in the ground (singlet) state.

Equilibrium geometry and energy difference between the low- and high-spin states ($\Delta E_{l\text{-}h}$) of the $Pd_2(\mu\text{-}OOCMe)_4$ complex and the $Pd_2(\mu\text{-}OOCMe)_4^+$ cation

Complex	Spin state	$\Delta E_{l\text{-}h}$, kcal/mol	Pd–Pd, Å	Pd–O, Å
$Pd_2(\mu\text{-}OOCMe)_4$	Singlet Triplet	–9.4	2.634 2.517	2.037 2.011
$Pd_2(\mu\text{-}OOCMe)_4^+$	Doublet Quartet	–34.1	2.471 2.563	2.014 2.012

electron pair in the antibonding orbital of $Pd_2(\mu\text{-}OOCMe)_4$ prevents the molecules from coupling to give the cyclic $Pd_4(\mu\text{-}OOCMe)_8$ tetrtamer.

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