Palladium Clusters Pd₄(SR)₄(OAc)₄ and Pd₆(SR)₁₂ (R = Bu, Ph): Structure and Properties

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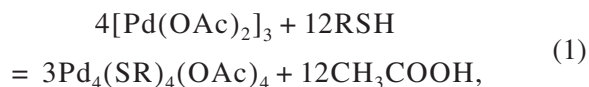*E-mail: akvaxxi@bk.ru*
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Abstract—The structures of the $Pd_4(SBu)_4(OAc)_4$ (**I**) and $Pd_6(SBu)_{12}$ (**II**) palladium clusters are determined by the X-ray diffraction method. For cluster **I**: $a = 8.650(2)$, $b = 12.314(2)$, $c = 17.659(4)$ Å, $\alpha = 78.03(3)°$, $\beta = 86.71(2)°$, $\gamma = 78.13(3)°$, $V = 1800.8(7)$ Å^3, ρcalcd $= 1.878$ g/cm^3, space group $P\bar{1}$, $Z = 4$, $N = 3403$, $R = 0.0468$; for structure **II**: $a = 10.748(2)$, $b = 12.840(3)$, $c = 15.233(3)$ Å, $\alpha = 65.31(3)°$, $\beta = 70.10(3)°$, $\gamma = 72.91(3)°$, $V = 1767.4(6)$ Å^3, ρcalcd $= 1.605$ g/cm^3, space group $P\bar{1}$, $Z = 1$, $N = 3498$, $R = 0.0729$. In cluster **I**, four Pd atoms form a planar cycle. The neighboring Pd atoms are bound by two acetate or two mercaptide bridges (Pd···Pd 2.95–3.23 Å, PdPdPd angles 87.15°–92.85°). In cluster **II**, the Pd atoms form a planar six-membered cycle with Pd···Pd distances of 3.09–3.14 Å, the PdPdPd angles being 118.95°−120.80°. The Pd atoms are linked in pairs by two mercaptide bridges. The formation of clusters **I** and **II** in solution is proved by IR spectroscopy and calorimetry. Analogous clusters are formed in solution upon the reaction of palladium(II) diacetate with thiophenol.

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INTRODUCTION

Palladium(II) diacetate (PDA) with electron donors (D) form complexes of different stoichiometry: the $[Pd(OAc)_2]_3 \cdot D$ (3 : 1), $[Pd(OAc)_2]_3 \cdot 2D$ (3 : 2), and $Pd(OAc)_2 \cdot 2D$ (1 : 2) complexes are formed with tertiary amines and phosphines, whereas the 3 : 2 and 1 : 2 complexes are formed with sulfides and secondary amines [1–5]. A specific feature of the 3 : 2 and 1 : 2 complexes with secondary amines is the formation of the stable N–H···O hydrogen bond between the NH groups of the coordinated amines and the carbonyl groups of the acetate fragments.

However, the following reactions were shown [6] to occur upon the interaction of PDA with ethylmercaptan in solution:

$$4[Pd(OAc)_2]_3 + 12RSH$$
$$= 3Pd_4(SR)_4(OAc)_4 + 12CH_3COOH, \tag{1}$$

$$2[Pd(OAc)_2]_3 + 12RSH = Pd_6(SR)_{12} + 12CH_3COOH. \tag{2}$$

The reactions afford the $Pd_4(SEt)_4(OAc)_4$ and $Pd_6(SEt)_{12}$ palladium clusters, whose crystal structures were determined by X-ray diffraction analysis.

It is known [7] that the values of the induction and steric constants of substituents in both the aliphatic and aromatic series can differ considerably and affect the reactions and structures of the products. To determine the influence of the type of the mercaptan radical on the reactions of PDA with mercaptans, we studied PDA–*n*-butylmercaptan and PDA–thiophenol systems. The results were compared with the data on the earlier studied systems containing other radicals, namely, ethyl and propyl.

The extension of the scope of cyclic palladium clusters with different cavity sizes and various substituents can be of interest for the search for new cyclic metal compounds capable of coordinating anions and electron-donating molecules. For example, the cyclic mercury [8–10] and tin [11] compounds manifest such properties.

In this work, we present the results of X-ray diffraction analyses of the $Pd_4(SBu)_4(OAc)_4$ (**I**) and $Pd_6(SBu)_{12}$ (**II**) clusters and the data on the reactions of PDA with butylmercaptan and thiophenol in solutions obtained by IR spectroscopy and calorimetry.

EXPERIMENTAL

Synthesis. Palladium(II) diacetate was synthesized according to a described procedure [12]. Single crystals of clusters **I** and **II** were prepared by crystallization from the solutions in 1,2-dichloroethane. The latter was doubly distilled over P_2O_5. Benzene was shaken with sulfuric acid and then with an alkali, washed with water, dried over $CaCl_2$, and distilled over sodium. Thiophenol and *n*-butylmercaptan were purified by distillation, and corresponded to the published values.

IR spectra were recorded on a UR-20 spectropho-tometer (BaF$_2$ cells, optical layer 0.005 cm long). The experiments were carried out by the titration method, recording the IR spectra of solutions of the products formed upon the gradual addition of small portions of mercaptan to a solution of palladium diacetate in dichloroethane. The concentration of Pd(OAc)$_2$ was ~0.05 mol/l.

Acetic acid evolved upon the reaction of palla-dium(II) diacetate with *n*-butylmercaptan and thiophe-nol was quantitatively analyzed by GLC (Tsvet 110 chromatograph, columns 2000×3 mm long, Chroma-tion N-AW packing impregnated with 15% PEGA with the 3% H$_3$PO$_4$ additive).

Thermal effects of the reactions were determined in a benzene solution by calorimetric titration [13] using a liquid calorimeter with a piezoquartz resonator as a temperature sensor [14].

X-ray diffraction analysis. An Enraf-Nonius CAD-4 automated diffractometer was used (λMoK_α, β filter, $\sin\theta/\lambda_{max} = 0.6$ Å^{-1}). For cluster **I**: $a = 8.650(2)$, $b = 12.314(2)$, $c = 17.659(4)$ Å, $\alpha = 78.03(3)°$, $\beta = 86.71(2)°$, $\gamma = 78.13(3)°$, $V = 1800.8(7)$ Å^3, ρcalcd = 1.878 g/cm^3, space group $P\bar{1}$, $Z = 4$, $N = 3403$, $R = 0.0468$, crystal size $0.25 \times 0.20 \times 0.15$ mm; for cluster **II**: $a = 10.748(2)$, $b = 12.840(3)$, $c = 15.233(3)$ Å, $\alpha = 65.31(3)°$, $\beta = 70.10(3)°$, $\gamma = 72.91(3)°$, $V = 1767.4(6)$ Å^3, ρcalcd = 1.605 g/cm^3, space group $P\bar{1}$, $Z = 1$, $N = 3498$, $R = 0.0729$, crystal size $0.75 \times 0.12 \times 0.06$ mm.

All calculations were performed using the SHELX-97 program package [15].

Structures **I** and **II** were solved by the heavy atom method, and hydrogen atoms were localized from the difference synthesis. The structures were refined by the least-squares method in the anisotropic approximation of thermal vibration parameters for non-hydrogen atoms. Selected interatomic distances and bond angles in clusters **I** and **II** are given in Table 1.

The coordinates of atoms and other crystallographic parameters for compounds **I** and **II** were deposited with the Cambridge Structural Database (nos. 683 075 and 683 976 for compounds **I** and **II**, respectively).

RESULTS AND DISCUSSION

Reactions (1) and (2) occur successively upon the addition of *n*-butylmercaptan or thiophenol to a solu-tion of PDA in benzene and 1,2-dichloroethane to form the palladium clusters and acetic acid.

The IR spectra of the PDA–ethylmercaptan and PDA–*n*-butylmercaptan systems were obtained earlier and discussed in detail [6]. In the present work, we mention only that the IR spectra of the products formed in these systems due to reactions (1) and (2) contain intense bands at 1760 and 1710 cm^{-1} attributed, accord-ing to [16], to v(C=O) of the acetic acid monomer and
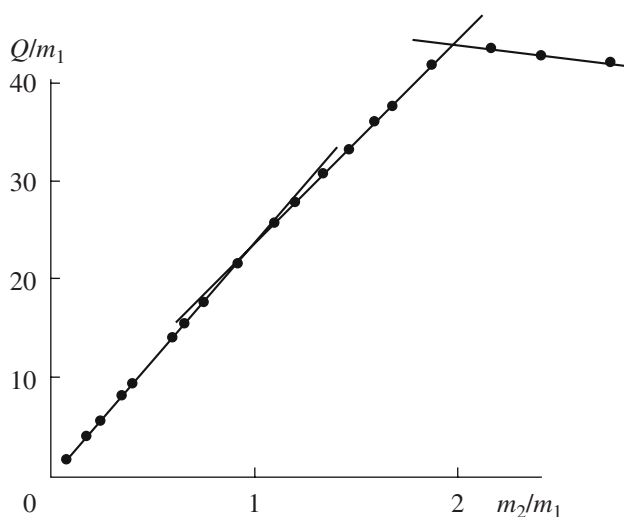
Fig. 1. Curve of calorimetric titration of a solution of PDA in benzene with *n*-butylmercaptan (Q is the quantity of the evolved heat (kJ); m_1 and m_2 are the number of moles of Pd(OAc)$_2$ and C$_4$H$_9$SH in the solution, respectively).

dimer, respectively. The addition of thiophenol to a solution of PDA in 1,2-dichloroethane also results in the appearance of intense bands at 1760 and 1710 cm^{-1} assigned to v(C=O) of the acetic acid monomer and dimer, indicating that the titration with thiophenol is accompanied by reactions (1) and (2). In all cases, the amount of acetic acid found from the GLC data agrees with the stoichiometry of reactions (1) and (2).

The data of calorimetric titration also indicate that PDA interacts with C$_4$H$_9$SH in steps according to reac-tions (1) and (2). The curve of the titration of a benzene solution of PDA with butylmercaptan is shown in Fig. 1. The titration curve exhibits distinct inflections at $m_2/m_1 = 1$ and 2, i.e., in the points corresponding to C$_4$H$_9$SH and Pd(OAc)$_2$ ratios of 1 : 1 and 2 : 1. The regions between these points are rectilinear. The slope of the rectilinear region at the ratio $m_2/m_1 > 2$ corre-sponds to the heat of dissolution of butylmercaptan in benzene. The clusters with R = C$_4$H$_9$ formed according to reactions (1) and (2) were isolated from the solutions and used for the preparation of single crystals.

According to the X-ay diffraction data (Table 1, Fig. 2), in cluster **I** four palladium atoms are arranged in the same plane to form a square and are linked pair-wise by two acetate or two mercaptide bridges (Pd···Pd 2.951–2.983 Å, PdPdPd angles 87.15°–92.85°). The shape of the PdO$_2$S$_2$ fragments is a distorted square pla-nar within ±0.1 Å.

In cluster **II** (Table 1, Fig. 3), six palladium atoms lie in the same plane to form a regular hexagonal struc-ture. The Pd···Pd distances between the neighboring Pd atoms are 3.098–3.139 Å, and those between the most remote atoms are 6.21–6.29 Å, the PdPdPd angles being 118.95°–120.80°. The shape of the PdS$_4$ fragments is a distorted square planar within ±0.07 Å. This shift of the

Table 1. Selected bond lengths and bond angles in clusters **I** and **II***

Bond	d, Å	Bond	d, Å	Bond	d, Å	Bond	d, Å
				I			
Pd(1)–O(1)	2.057(8)	Pd(2)–Pd(1)#1	3.2184(16)	Pd(4)–S(3)#2	2.065(3)	O(1)–C(1)	1.255(13)
Pd(1)–O(3)	2.084(7)	Pd(3)–O(5)	2.054(8)	Pd(4)–Pd(3)#2	3.2296(17)	O(2)–C(1)	1.239(13)
Pd(1)–S(2)#1	2.060(3)	Pd(3)–O(7)	2.060(8)	S(1)–C(9)	1.818(13)	O(3)–C(3)	1.247(12)
Pd(1)–S(1)	2.065(3)	Pd(3)–S(4)#2	2.250(3)	S(1)–Pd(2)#1	2.255(3)	O(4)–C(3)	1.230(13)
Pd(1)–Pd(2)	2.9825(14)	Pd(3)–S(3)	2.255(3)	S(2)–C(13)	1.823(13)	O(5)–C(5)	1.247(13)
Pd(1)–Pd(2)#1	3.2184(16)	Pd(3)–Pd(4)	2.9510(14)	S(2)–Pd(1)#1	2.260(3)	O(6)–C(5)	1.261(14)
Pd(2)–O(4)	2.063(7)	Pd(3)–Pd(4)#2	3.2296(17)	S(3)–C(17)	1.810(12)	O(7)–C(7)	1.235(14)
Pd(2)–O(2)	2.073(8)	Pd(4)–O(8)	2.046(8)	S(3)–Pd(4)#2	2.265(3)	O(8)–C(7)	1.253(14)
Pd(2)–S(2)	2.252(3)	Pd(4)–O(6)	2.051(7)	S(4)–C(21)	1.833(11)		
Pd(2)–S(1)#1	2.255(3)	Pd(4)–S(4)	2.253(3)	S(4)–Pd(3)#2	2.250(3)		
				II			
Pd(1)–S(1)	2.322(4)	Pd(2)–S(3)	2.316(4)	Pd(3)–S(5)	2.328(4)	S(2)–C(9)	1.834(15)
Pd(1)–S(5)#3	2.327(4)	Pd(2)–S(4)	2.318(3)	Pd(3)–S(3)	2.329(4)	S(4)–C(13)	1.819(15)
Pd(1)–S(2)	2.335(4)	Pd(2)–S(2)	2.322(4)	Pd(3)–S(6)	2.331(4)	S(5)–C(17)	1.778(19)
Pd(1)–S(6)#3	2.338(4)	Pd(2)–S(1)	2.326(4)	Pd(3)–Pd(1)#3	3.1168(15)	S(5)–Pd(1)#3	2.327(4)
Pd(1)–Pd(2)	3.0978(19)	Pd(2)–Pd(3)	3.1392(15)	S(1)–C(1)	1.819(15)	S(6)–C(21)	1.818(16)
Pd(1)–Pd(3)#3	3.1168(15)	Pd(3)–S(4)	2.327(4)	S(2)–C(5)	1.836(14)	S(6)–Pd(1)#3	2.338(4)

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
				I			
O(1)Pd(1)O(3)	90.0(3)	O(2)Pd(2)S(2)	93.0(3)	O(8)Pd(4)S(4)	96.0(3)	C(13)S(2)Pd(2)	107.2(4)
O(1)Pd(1)S(2)#1	175.9(2)	O(4)Pd(2)S(1)#1	96.9(2)	O(6)Pd(4)S(4)	168.8(2)	C(13)S(2)Pd(1)#1	104.9(5)
O(3)Pd(1)S(2)#1	94.1(2)	O(2)Pd(2)S(1)#1	168.5(3)	O(8)Pd(4)S(3)#2	175.5(3)	Pd(2)S(2)Pd(1)#1	91.03(12)
O(1)Pd(1)S(1)	96.3(2)	S(2)Pd(2)S(1)#1	79.96(10)	O(6)Pd(4)S(3)#2	94.2(2)	C(17)S(3)Pd(3)	105.0(4)
O(3)Pd(1)S(1)	167.4(2)	Pd(1)Pd(2)Pd(1)#1	87.15(4)	S(4)Pd(4)S(3)#2	79.49(11)	C(17)S(3)Pd(4)#2	104.9(4)
S(2)#1Pd(1)S(1)	79.59(11)	O(5)Pd(3)O(7)	90.4(3)	Pd(3)Pd(4)Pd(3)#2	89.48(4)	Pd(3)S(3)Pd(4)#2	91.22(11)
Pd(2)Pd(1)Pd(2)#1	92.85(4)	O(5)Pd(3)S(4)#2	96.7(2)	C(9)S(1)Pd(2)#1	111.2(4)	C(21)S(4)Pd(3)#2	111.9(5)
O(4)Pd(2)O(2)	90.4(3)	Pd(4)Pd(3)Pd(4)#2	90.52(4)	C(9)S(1)Pd(1)	109.8(4)	C(21)S(4)Pd(4)	110.6(4)
O(4)Pd(2)S(2)	176.4(3)	O(8)Pd(4)O(6)	90.2(3)	Pd(2)#1S(1)Pd(1)	90.81(10)	Pd(3)#2S(4)Pd(4)	91.65(12)
				II			
S(1)Pd(1)S(5)#3	179.43(13)	S(3)Pd(2)S(1)	98.00(13)	Pd(1)#3Pd(3)Pd(2)	120.26(4)	C(13)S(4)Pd(2)	111.2(5)
S(1)Pd(1)S(2)	81.79(13)	S(4)Pd(2)S(1)	179.09(13)	C(1)S(1)Pd(1)	110.6(5)	C(13)S(4)Pd(3)	110.1(5)
S(5)#3Pd(1)S(2)	98.17(14)	S(2)Pd(2)S(1)	81.97(13)	C(1)S(1)Pd(2)	111.9(6)	Pd(2)S(3)Pd(3)	85.04(12)
S(1)Pd(1)S(6)#3	98.36(13)	Pd(1)Pd(2)Pd(3)	118.95(4)	Pd(1)S(1)Pd(2)	83.59(11)	C(17)S(5)Pd(1)#3	111.1(6)
S(5)#3Pd(1)S(6)#3	81.75(14)	S(4)Pd(3)S(5)	179.05(13)	C(5)S(2)Pd(2)	107.1(4)	C(17)S(5)Pd(3)	111.0(6)
S(2)Pd(1)S(6)#3	174.36(12)	S(4)Pd(3)S(3)	81.05(13)	C(5)S(2)Pd(1)	104.3(5)	Pd(1)#3S(5)Pd(3)	84.07(12)
Pd(2)Pd(1)Pd(3)#3	120.80(4)	S(5)Pd(3)S(3)	98.08(14)	Pd(2)S(2)Pd(1)	83.39(13)	C(21)S(6)Pd(3)	106.6(6)
S(3)Pd(2)S(4)	81.51(13)	S(4)Pd(3)S(6)	98.94(13)	C(9)S(3)Pd(2)	106.0(5)	C(21)S(6)Pd(1)#3	103.9(5)
S(3)Pd(2)S(2)	172.13(13)	S(5)Pd(3)S(6)	81.88(13)	C(9)S(3)Pd(3)	105.2(6)	Pd(3)S(6)Pd(1)#3	83.76(12)
S(4)Pd(2)S(2)	98.40(13)	S(3)Pd(3)S(6)	172.76(13)	Pd(2)S(3)Pd(3)	85.04(12)		

* Transformations of the atomic coordinates for I: #1 $-x + 1$, $-y + 1$, $-z$; #2 $-x$, $-y$, $-z + 1$; for II: #3 $-x + 1$, $-y + 1$, $-z + 1$.
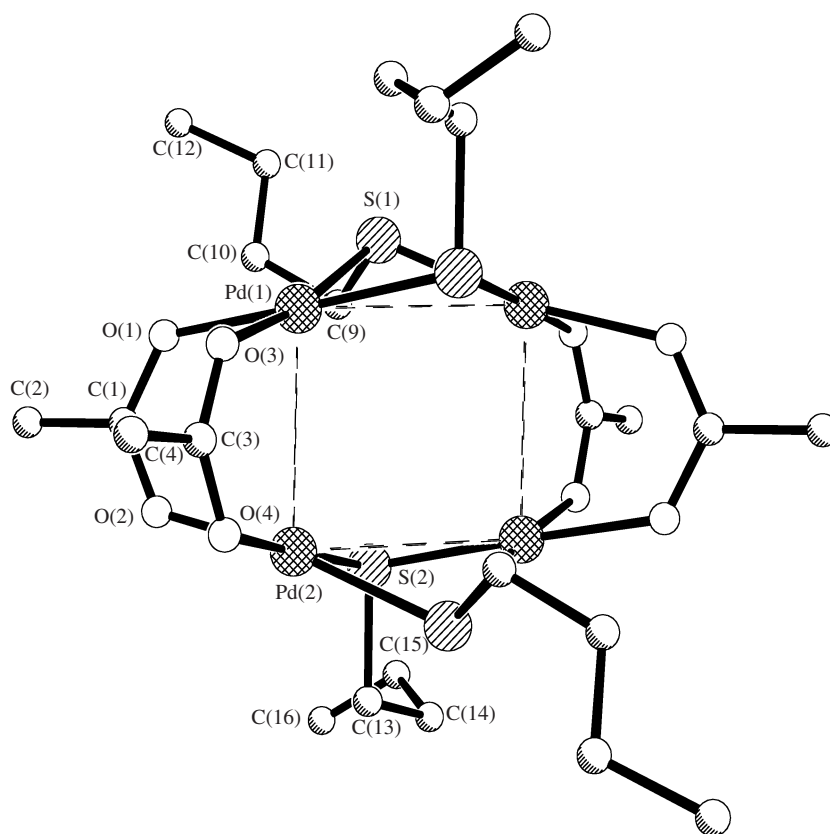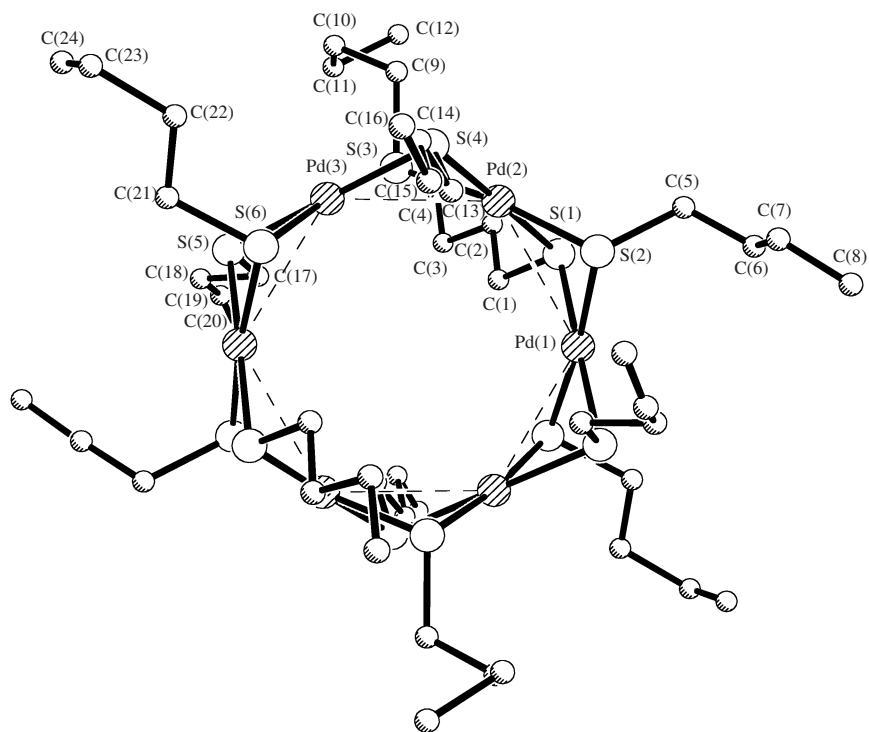
Fig. 2. Structure of the $Pd_4(OAc)_4(C_4H_9S)_4$ cluster (**I**).

Fig. 3. Structure of the $Pd_6(C_4H_9S)_{12}$ cluster (**II**).

Table 2. Bond lengths and bond angles in the palladium clusters

Compound	Pd–Pd, Å	Pd–S, Å	Pd–O, Å	PdSPd, deg	Literature
[Pd(OAc)$_2$(CH$_3$)$_2$SO]$_2$	2.88	2.21	2.03		[17]
[Pd(OAc)$_2$]$_3$	3.14		1.99		[2]
Pd$_4$(OAc)$_4$(C$_2$H$_5$S)$_4$	3.12	2.27	2.07	89.60	[6]
Pd$_4$(OAc)$_4$(C$_4$H$_9$S)$_4$	3.10	2.26	2.06	91.18	This work
Pd$_6$(C$_2$H$_5$S)$_{12}$	3.11	2.33		84.37	[6]
Pd$_6$(C$_3$H$_7$S)$_{12}$	3.14	2.35		83.60	[18]
Pd$_6$(C$_4$H$_9$S)$_{12}$	3.12	2.33		84.00	This work

palladium atoms from the plane of the sulfur atoms to the symmetry axis of the Pd$_6$ fragment in cluster **II** (0.08 Å) is smaller than that in the palladium(II) diacetate trimer (0.233 Å) [2] and resembles the shift in cluster 0.09 Å.

As mentioned above, the character of the R radical in mercaptan can affect the formation reactions and structures of the clusters. The σ* induction constants are –0.100, –0.115, and –0.130; and the E_S^0 steric constants are –0.37, –0.56, and –0.59 for ethyl, propyl, and butyl, respectively. Therefore, both the σ induction effect of the alkyl substituent and steric screening of the sulfur atom increase in the series ethyl < propyl < butyl.

The Pd⋯Pd distances, Pd–O and Pd–S bond lengths, and PdSPd angles in clusters **I** and **II**, which were obtained in the present work, and the bond lengths and angles in the bi-, tri-, tetra-, and hexanuclear clusters [2, 6, 17, 18] are compared in Table 2. The data in Table 2 show that the average Pd⋯Pd distances in the [Pd(OAc)$_2$]$_3$, Pd$_4$(OAc)$_4$(C$_2$H$_5$S)$_4$, Pd$_4$(OAc)$_4$(C$_4$H$_9$S)$_4$, Pd$_6$(C$_2$H$_5$S)$_{12}$, Pd$_6$(C$_3$H$_7$S)$_{12}$, and Pd$_6$(C$_4$H$_9$S)$_{12}$ clusters are similar (3.11–3.14 Å) and much longer than those in the binuclear [Pd(OAc)$_2$ · (CH$_3$)$_2$SO]$_2$ cluster (2.88 Å). The length of the radical of the mercaptide bridge exerts almost no effect on the Pd⋯Pd distance and, hence, on the size of the metallocycle cavity: this size is determined by the number of palladium atoms in the metallocycle.

As for thiophenol, conjugation effects, for instance, the interaction of the lone electron pair of the sulfur atom with the σ* system of the ring ($p\pi$ conjugation), can play an important role along with the induction (σ* = +0.600 for the C$_6$H$_5$ radical) and steric effects. Nevertheless, the mechanism of the reaction of PDA with thiophenol does not differ from that of the interaction with aliphatic mercaptans; i.e., it is consistent with reactions (1) and (2).

The Pd⋯Pd distances presented in Table 2 are longer than the doubled covalent radius of the Pd(II) atom (2.62 Å) [19] but shorter than the doubled van der Waals radius of the Pd atom (Σr_{vwr} = 4.2 Å), if r_{vwr} of the Pd

atom is accepted, according to literature data [19], to be 2.1 Å. Thus, the Pd⋯Pd distances satisfy the correlation

$$\Sigma r_{cov} < r_{Pd–Pd} < \Sigma r_{vwr}. \quad (3)$$

Therefore, we can conclude that the metal atoms directly interact in all the palladium clusters under study. This interaction can be due to the lone electron pair of the 4d sublevel of one of the Pd atoms and the vacant 5p_z or 5d orbitals of another Pd atom.

The correlations analogous to correlation (3) are valid for numerous donor–acceptor complexes and compounds with other metal–metal bonds [13, 20–22]. It is shown [22] that the lengths of the donor–acceptor (DA) bonds (r_{DA}, Å) are related to the enthalpy of formation of sixty molecular complexes (–ΔH, kJ/mol) by the dependence –ΔH = 21.6/Δr, where the characteristic value is Δr = r_{DA} – 0.901(r_D + r_A). When the strength of the complexes enhances, the donor–acceptor bond length approaches to the sum of the covalent radii of the atoms forming this bond (r_D + r_A), and Δr tends to zero. For Δr ≫ 1, the strength of the complexes is determined by weak van der Waals interactions between the components and –ΔH tends to zero. In this case, r_{DA} is shorter than Σr_{vwr} in all systems considered in [22]. The necessary condition for the formation of a donor–acceptor bond is the overlap of the atoms forming the bond [13, 23, 24]; i.e., the length of this bond should be shorter than Σr_{vwr}.

In all the studied clusters containing the acetate bridges, the Pd–O bond lengths (1.99–2.07 Å, Table 2) are close to or slightly longer than the sum of the covalent radii of the Pd and O atoms (1.97 Å) [19, 25]. A different situation is observed in the clusters containing the Pd–S bonds. According to our data, these bond lengths (2.21–2.33 Å) are somewhat shorter than the sum of the covalent radii of the Pd and S atoms (Σr_{cov} = 2.35 Å) [19, 25]. Note that the Pd–S coordination bond length is also shorter than the sum of the covalent radii of the Pd and S atoms. The Pd–S bond shortens, most likely, due to the additional d_π–d_π interaction between the Pd and S atoms. As a result, the Pd–S bond becomes stronger, and the distance between these atoms becomes shorter than the sum of the covalent radii.

Thus, the palladium clusters are formed due to the reactions of PDA with *n*-butylmercaptan and thiophenol. According to the X-ray diffraction data, the Pd_4 and Pd_6 fragments of the $Pd_4(OAc)_4(C_4H_9S)_4$ (**I**) and $Pd_6(C_4H_9S)_{12}$ (**II**) clusters are planar metallocycles. The Pd···Pd distances (~3.1 Å) suggest the existence of a direct chemical bond between the neighboring palladium atoms in clusters **I** and **II**. The type of the mercaptan radical exerts no substantial effect on the cluster structure.

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