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Palladium Complexes of Pyrimidine-2-thiones: Synthesis, Structures, and Properties

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Abstract—Complexes $[PdL_2Cl_2]$ (**I**) and $[PdL_2Br_2]$ (**II**) (L is 5-acetyl-6-methyl-4-(3-nitrophenyl)-1,2,3,4-tetrahydropyrimidine-2-thione) are synthesized and characterized by spectral methods (^1H, ^{13}C NMR and IR spectroscopy). The crystal structure of complex **I** is determined (CIF file CCDC no. 2233053) in which the palladium atom is coordinated by two halide ions and two sulfur atoms of two ligands L in a distorted square planar geometry. The catalytic activity of the synthesized palladium(II) complexes in the model epoxidation of allyl alcohol is estimated in comparison with the catalytic activity of the corresponding palladium halides and titanium-containing zeolite TS-1.

Keywords: Biginelli compounds, pyrimidine-2-thione, palladium, catalysis, epoxidation
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INTRODUCTION

Biginelli compounds and their analogs (among which are pyrimidine-2-thiones and related complexes) attract researchers' attention due to a variety of the manifested properties, primarily biological properties [1–7]. The most popular method for the synthesis of these compounds is the Biginelli reaction that makes it possible to achieve relatively high yields of the target products [8]. The compounds containing the thiocarbamide fragment are known to be capable of acting as calcium-channel blockers [9–11], NO syntase [12, 13] and prostaglandin E syntase [14] inhibitors, and antagonists of adenosine A_{2B} receptors [15] and taking part in many other biological processes. A new tendency in studying the pharmacokinetics of drug accumulation, metabolism, and removal from the organism is the development of metal complexes based on transition metals (Pd, Pt, Rh). The known platinum complexes (cisplatin, carboplatin, and oxaliplatin) are used for the treatment of recurrent glioma (most frequently met form of brain tumor) [16, 17]. However, their application has a series of limitations, including renal toxicity, irreversible neurotoxicity, and internal/acquired resistance [18]. Attempts to prepare new compounds based on metals that surmount restraints related to the use of platinum-based drugs under the modern clinical treatment methods resulted in the complexes containing various transition metals in combination with diverse classes of ligands, and their inhibitory activity against cancer cells was estimated [19–21]. In this context, the palladium(II) derivatives represent a potential alternative for the preparation of new antitumor drugs due to their structural and thermodynamic resemblance with the platinum(II) complexes but with a lower toxicity.

Unsubstituted and substituted thioureas and their derivatives as components of coordination compounds with transition metal ions can act as both hard and soft donors accomplishing numerous coordination modes [22], which provides significant diversity in the design of complexes involving these compounds. In the case of coordination with palladium, it seems reasonable to use ligands containing soft sulfur atoms to which palladium(II) exhibits high affinity [23].

In addition to the preparation of cytotoxic remedies, interest in palladium complexes is also related to their wide use in heterogeneous catalysis, particularly, in olefin arylation [24], cross coupling [25], carbonylation [26], oxidation of aromatic compounds [27], and many other processes. The variation of ligands in the palladium complexes exerts the key effect on their catalytic properties [28]. The catalysis by complexes of the Biginelli compounds remains almost unstudied

[29, 30] and, hence, research in this field can result in the discovery of new catalysts for various processes of organic synthesis.

This work is devoted to the synthesis of new palladium complexes based on 5-acetyl-6-methyl-4-(3-nitrophenyl)-1,2,3,4-tetrahydropyrimidine-2-thione, $[PdL_2Cl_2]$ (**I**) and $[PdL_2Br_2]$ (**II**), and elucidation of their catalytic activity in the epoxidation of allyl alcohol. An analysis of the scientific literature on the topic shows that this is the first work in which the catalytic properties of the palladium complexes of the Biginelli compounds were studied.

EXPERIMENTAL

meta-Nitrobenzaldehyde (Merck, 99%), thiourea (Acros organics, 99%), acetylacetone (Merck, 99%), zinc(II) chloride (Merck, 98%), palladium(II) chloride (Merck, 99%), and palladium(II) bromide (Merck, 99%) were used. Commercial solvents dimethylformamide (DMF), 2-propanol, diethyl ether, ethyl acetate, and acetonitrile (reagent grade) were used as received.

The spectra of all studied compounds were recorded on an INFRALYUM FT-08 FT-IR spectrophotometer in the transmission mode in a frequency range of 4000–400 cm^{-1}. Samples for spectra recording were pressed pellets of a mixture of potassium bromide and target substance in a weight ratio of 400 : 1.

^1H and ^{13}C NMR spectra were recorded at the Laboratory of Novel Physicochemical Problems at the Frumkin Institute of Physical Chemistry and Electrochemistry (Russian Academy of Sciences) at 298 K on a Bruker Avance III 600 spectrometer (600.13 or 150.90 MHz for ^1H and ^{13}C, respectively) in DMSO-d_6 (99%, Deutero GmbH).

The crystal structure of complex $[PdL_2Cl_2]$ (**I**) was determined by powder X-ray diffraction (XRD) [31–33]. The diffraction pattern was measured at room temperature on a Guinier-Huber G670 laboratory powder diffractometer with a bent germanium monochromator ($CuK_{\alpha 1}$ radiation, $\lambda = 1.54059$ Å). The diffraction pattern was indexed in the monoclinic crystal system, and the space group of symmetry $P2_1/c$ was chosen taking into account systematic quenching by the Pawleyrefinement [34]. The structure was solved by the simulated annealing method and refined using the MRIA program [35] according to the known previously described procedure [36–39]. The molecular structure of compound **I** was drawn using the PLATON program [40].

The crystallographic data for the structure of compound **I** was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2233053; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Elemental analysis was carried out on an EA 1112 C,H,N,S analyzer (Thermo Finnigan Italia S.p.A.) at the Center for Collective Use of the Lomonosov Institute of Fine Chemical Technologies of the MIREA — Russian Technological University.

The catalytic properties of the $[PdL_2Cl_2]$ (**I**) and $[PdL_2Br_2]$ (**II**) complexes, as well as $PdCl_2$ and $PdBr_2$, were studied in the heterogeneous epoxidation of allyl alcohol with hydrogen peroxide in a methanol medium at 30°C for 90 min in a temperature-maintained glass reactor with a jet and a reflux condenser on vigorous stirring according to a described procedure [41].

The composition of the reaction mixture was analyzed by gas chromatography on a Tsvet chromatograph using ethyl benzoate as the internal standard (glass packed column 3 m × 3 mm, 3% OV17 chromatographic phase on chromaton-N-super, helium as carrier gas, thermal conductivity detector). The content of H_2O_2 was determined by iodometric titration.

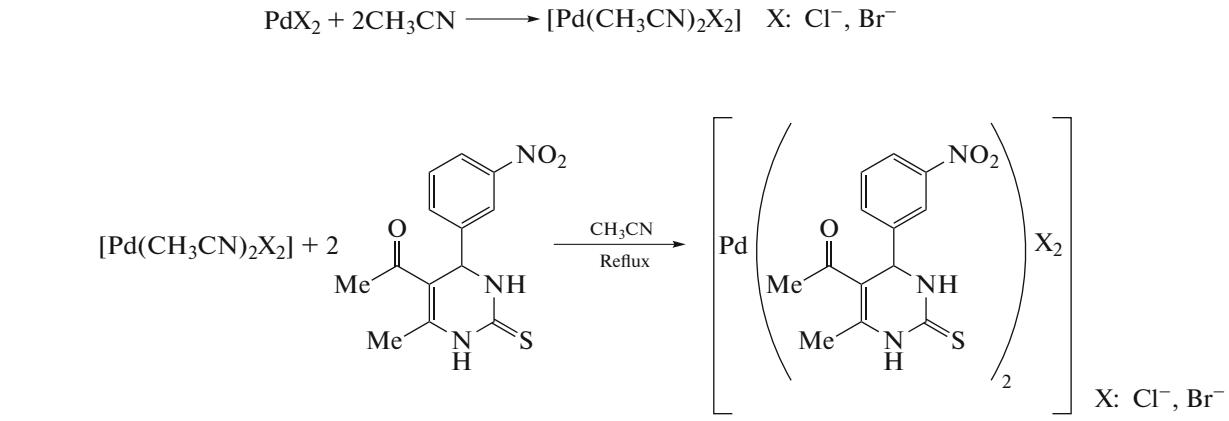
Synthesis of 5-acetyl-6-methyl-4-(3-nitrophenyl)-1,2,3,4-tetrahydropyrimidine-2-thione (L). Weighed samples of thiourea (2.360 g, 0.030 mmol), *m*-nitrobenzaldehyde (4.470 g, 0.030 mmol), and acetylacetone (3.100 mL, 0.030 mmol) were added to DMF (5 mL) in a 50-mL round-bottom flask using a catalytic quantity of $ZnCl_2$ (10 mg). The reaction was carried out with stirring and reflux for 12 h. Isopropyl alcohol (IPA) (5 mL) was poured to the formed deep brick-red solution with a yellow precipitate, and the reaction mixture was refluxed with stirring for 12 h. The formed deep orange suspension was placed in a volumetric beaker with ice, and ethyl acetate (100 mL) was added. The formed three-component emulsion, which represented an orange aqueous layer with a liquid interlayer of the target substance and a dark brown ethyl acetate layer above it, was stirred for 30 min. The organic layer was separated by decantation. The procedure was repeated with ethyl acetate (30 mL). Then IPA (75 mL) was poured to the remained aqueous emulsion, and the liquid interlayer transformed into a light pale yellow precipitate. The mixture was stirred for 30 min. Then the pale yellow precipitate was filtered off and consequently washed with IPA (5 mL × 3 times) and diethyl ether (5 mL × 3 times). The powder was dried under vacuum for 1 h. The yield of L was 54%. $T_m = 271–273$°C.

IR (ν, cm^{-1}): 3300 (ν(N–H)), 3181 (ν(N–H)), 1610 (ν(C=O), ν(C=C)), 1573 (thioamide I δ(N–H) + ν(C–N)), 1532 ($\nu_{as}(NO_2)$ + ν(Ar)), 1346 ($\nu_s(NO_2)$), 1187 (thioamide II ν(C–N) + δ(N–H)), 1023 (thioamide III ν(C–N) + ν(C=S)), 760 (thioamide IV ν(C=S)).

^1H NMR (DMSO-d_6; 600 MHz; δ, ppm): 10.33 (s, 1H, NH), 9.76 (s, 1H, NH), 8.13 (m, 1H, Ph), 8.10 (s, 1H, Ph), 7.66 (m, 2H, Ph), 5.45 (d, 1H, $J = 3.9$ Hz, CH), 2.37 (s, 3H, CH_3CO), 2.24 (s, 3H, CH_3).

^{13}C NMR (DMSO-d_6; 151 MHz; δ, ppm): 194.6 (C=O), 174.6 (C=S), 147.9 (C^6), 145.6 (C, Ph), 144.9 (C, Ph), 133.0 (C, Ph), 130.3 (C, Ph), 122.6 (C, Ph), 121.2 (C, Ph), 110.2 (C^5), 30.7 (CH_3CO), 18.4 (CH_3).

Coordination compounds of palladium(II) $[PdL_2Cl_2]$ (**I**) and $[PdL_2Br_2]$ (**II**) were synthesized by the ligand substitution in the intermediate labile highly soluble acetonitrile palladium(II) complexes, transformation into which occurred via the dissolution of the corresponding palladium(II) salt at room temperature in acetonitrile (CH_3CN). The synthesis of the palladium(II) coordination compounds is shown in Scheme 1.



Scheme 1.

Synthesis of dichlorobis(5-acetyl-6-methyl-4-(3-nitrophenyl)-1,2,3,4-tetrahydropyrimidine-2-thione)palladium(II), $[PdL_2Cl_2]$ (I). $PdCl_2$ (0.0300 g, 0.172 mmol) was added to CH_3CN (10 mL) at room temperature with stirring. A weighed sample of the ligand (0.100 g, 0.343 mmol) was added to the formed solution of the acetonitrile complex $[Pd(CH_3CN)_2Cl_2]$. The reaction was carried out on reflux with vigorous stirring for 8 h in a glycerol bath. The resulting orange solution with a pale orange precipitate was cooled to room temperature, and the precipitate was filtered off and dried in vacuo. The yield of compound **I** was 74%. T_m = 236–238°C.

For $C_{26}H_{26}N_6O_6S_2Cl_2Pd$				
Anal. calcd., %	C, 41.09	H, 3.45	N, 11.06	S, 8.44
Found, %	C, 40.88	H, 3.43	N, 11.12	S, 8.77

IR (ν, cm^{-1}): 3243 (ν(N–H)), 3199 (ν(N–H)), 1628 (ν(C=O), ν(C=C)), 1565 (thioamide I δ(NH) + ν(C–N)), 1530 ($\nu_{as}(NO_2)$ + ν(Ar)), 1349 ($\nu_s(NO_2)$), 1208 (thioamide II ν(C–N) + δ(NH)), 1011 (thioamide III ν(C–N) + ν(C=S)), 730 (thioamide IV (C=S)).

^{1}H NMR (600 MHz, DMSO-d_6; δ, ppm): 11.15 (m, 1H, NH), 9.84 (s, 1H, NH), 8.14 (m, 1H, Ph), 8.09 (m, 1H, Ph), 7.69 (m, 2H, Ph), 5.52 (m, 1H, CH), 2.35 (s, 3H, CH_3CO), 2.25 (m, 3H, CH_3). ^{13}C NMR (151 MHz; DMSO-d_6; δ, ppm): 194.4 (C=O), 167.0 (C=S), 147.8 (C^6), 142.9 (C, Ph), 142.2 (C, Ph), 133.5 (C, Ph), 130.3 (C, Ph), 123.1 (C, Ph), 122.1 (C, Ph), 112.5 (C^5), 30.7 (CH_3CO), 18.2 (CH_3).

Synthesis of dibromobis(5-acetyl-6-methyl-4-(3-nitrophenyl)-1,2,3,4-tetrahydropyrimidine-2-thione)palladium(II), $[PdL_2Br_2]$ (II). $PdBr_2$ (0.0460 g, 0.172 mmol) was added to CH_3CN (10 mL) at room temperature with stirring to form the acetonitrile complex $[Pd(CH_3CN)_2Br_2]$. A weighed sample of ligand L (0.100 g, 0.343 mmol) was added to the formed solution of the acetonitrile complex. The reaction was carried out on reflux with vigorous stirring for 8 h in a glycerol bath. The resulting yellow solution with a large amount of a pale yellow precipitate was cooled to room temperature, and the precipitate was filtered off and dried in vacuo. The yield of compound **II** was 75%, T_m = 240–241°C.

For $C_{26}H_{26}N_6O_6S_2Br_2Pd$				
Anal. calcd., %	C, 36.79	H, 3.09	N, 9.90	S, 7.55
Found, %	C, 36.91	H, 3.05	N, 9.93	S, 7.93

IR (ν, cm^{-1}): 3297 (ν(N–H)), 3233 (ν(N79; H 3.09; N 9.90; S 7.55), 1619 (ν(C=O), ν(C=C)), 1568 (thioamide I δ(N–H) + ν(C–N)), 1530 ($\nu_{as}(NO_2)$ + ν(Ar)), 1350 ($\nu_s(NO_2)$), 1208 (thioamide II ν(C–N) + δ(NH)), 1010 (thioamide III ν(C–N) + ν(C=S)), 723 (thioamide IV ν(C=S)).

^{1}H NMR (600 MHz; DMSO-d_6; δ, ppm): 10.96 (m, 1H, NH), 10.35 (m, 1H, NH), 8.11 (m, 2H, Ph), 7.69 (m, 2H, Ph), 5.60 (m, 1H, CH), 2.36 (s, 3H, CH_3CO), 2.26 (s, 3H, CH_3).

^{13}C NMR (151 MHz; DMSO-d_6; δ, ppm): 195.3 (C=O), 169.5 (C=S), 148.2 (C^6), 144.4 (C, Ph), 143.4 (C, Ph), 134.1 (C, Ph), 130.7 (C, Ph), 123.5 (C, Ph), 122.5 (C, Ph), 112.3 (C^5), 31.3 (CH_3CO), 18.7 (CH_3).

Table 1. Characteristic bands in the IR spectra of compounds **I** and **II**

Compound	Wavenumber of characteristic bands, cm^{-1}			
	thioamide I $\delta(N-H) + \nu(C-N)$	thioamide II $\nu(C-N) + \delta(N-H)$	thioamide III $\nu(C-N) + \nu(C=S)$	thioamide IV $\nu(C=S)$
L	1573	1187	1023	760
$[PdL_2Cl_2]$	1565	1208	1011	730
$[PdL_2Br_2]$	1568	1208	1010	723

RESULTS AND DISCUSSION

In the IR spectra of the Biginelli compounds, the most characteristic bands are those corresponding to vibrations of bonds of the thiocarbamide fragment and the functional groups that are directly conjugated with this fragment, since they are subjected to changes (cleavage, significant shift). Just these bands serve for the conclusion about the formation of a coordination compound and are named thioamide bands (I, II, III, IV). They differ from each other by the bonds that make a high contribution to this or another band. For instance, the bands thioamide I and II are characterized by vibrations of δ(NH) and ν(C–N) bonds, the band thioamide III is characterized by vibrations of ν(C–N) and ν(C=S) bonds, and the band thioamide IV is characterized only by ν(C=S) bond vibrations. The shifts of these characteristic bands are observed in the spectra of complexes $[PdL_2Br_2]$ (**I**) and $[PdL_2Cl_2]$ (**II**) compared to the spectrum of L.

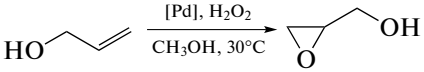
The stretching vibration bands of the N–H bond in the spectra of complexes **I** and **II** underwent considerable shifts from 60 to 100 cm^{-1}. This can be related to sharp changes in hydrogen bonds after coordination. The noticeable shift of the absorption band corresponding to stretching vibrations ν(C=O) of the acetyl group and ν(C=C) of the pyrimidine ring to high frequencies is also observed. This is associated with the formation of new contacts in the structures of the complexes involving the acetyl group in hydrogen bonds of the N–H···O type. In the spectra of both complexes, the bands thioamide I, III, and IV shifted to a low-frequency range, and the band thioamide II shifted to high frequencies. These changes indicate the formation of the complex (Table 1). Moreover, the changes in the spectra of both complexes are nearly identical, which indicates that they are isostructural.

All changes occurred in the ^1H and ^{13}C NMR spectra (strong signal broadening, formation of multiplets) indicate a dramatic influence of the coordination with palladium and competitive binding of palladium with molecules of DMSO used as the solvent for recording NMR spectra. The NMR spectroscopy data show clearly that the protons and carbon atoms of the thiocarbamide fragment and the protons and carbon atoms of other functional groups conjugated with this fragment experience the strongest influence upon coordination.

The crystallographic parameters of the coordination compound $[PdL_2Cl_2]$ (**I**) (Fig. 1) are listed in Table 2. The palladium atom is coordinated by two chlorine ions and two sulfur atoms of two ligands and exists in the distorted planar square configuration. The C=S bond is elongated over an analogous bond of the uncoordinated ligand. The Pd(1)–Cl(1) and Pd(1)–S(1) bond lengths are 2.288(3) and 2.275(3) Å, respectively, and the S(1)Pd(1)Cl(1) angle is 94.8(1)°. All intramolecular bond lengths and their angles are within normal ranges compared to the values for similar compounds found in the Cambridge Structural Database [42]. In each coordinated ligand, the both amino groups (N(1) and N(3)) participate in the formation of intermolecular hydrogen bonds N–H...O and N–H...Cl linking the molecules into chains (Table 3).

A comparison of the diffraction pattern of complex **II** with that of complex **I** shows similar peaks and thus proves the isostructural character of the synthesized complexes (Fig. 2).

The catalytic activity of the synthesized coordination compounds was estimated in the model epoxidation of allyl alcohol with hydrogen peroxide in a methanol medium (Scheme 2).



Scheme 2.

The titanium-containing zeolites are presently used as catalysts for this process [43]. Titanosilicates TS-1 are most popular in practice [44–46]. The results obtained in the epoxidation using the palladium complexes were compared with the results obtained under the same conditions using as catalysts the palladium salts ($PdCl_2$ and $PdBr_2$) and titanosilicate TS-1. During experiment, samples of the solution were taken to determine the concentrations of hydrogen peroxide (HP) (by iodometric titration) and allyl alcohol (AA), glycidol (GD), and by-products (by gas chromatography). The kinetic curves of consumption of the reactants (allyl alcohol, hydrogen peroxide) and formation of the major product (glycidol) for the case of using TS-1 as the catalyst are shown in Fig. 3.

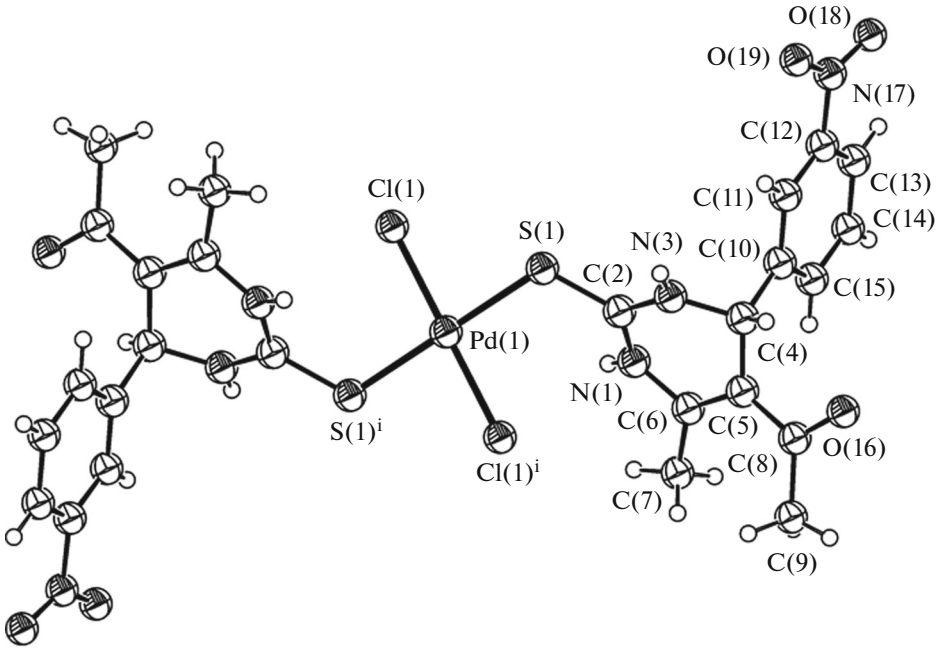


Fig. 1. Molecular structure of complex **I** showing the numeration of non-hydrogen atoms and spheres of atomic shifts of 50% probability. The Pd(1) atom is in the inversion center, and non-numerated atoms are related to the numerated atoms by the symmetry operation ^{i} $-x, 1-y, 2-z$.

The main parameters of the process were determined in the series of experiments: X_{AA} and X_{HP} are the conversions of allyl alcohol and hydrogen peroxide, respectively (%); $\varphi_{GD|AA}$ and $\varphi_{GD|HP}$ are the selectivities of glycidol formation with respect to allyl alcohol and hydrogen peroxide, respectively (%); and TON is the ratio of the number of g-moles of the formed glycidol or allyl alcohol to that of g-moles of the palladium complexes loaded into the reactor or to the number of g-atoms of titanium in the zeolite TS-1 amount loaded into the reactor (Table 4).

Complexes **I** and **II** were found to be catalytically active in the epoxidation of allyl alcohol with hydrogen peroxide. Their catalytic activity is comparable with the catalytic properties of palladium halides. The activity of the palladium compounds in this reaction is inferior to the results obtained under the same conditions using zeolite TS-1. The formation of by-products of allyl alcohol oligomerization and polymerization was detected during epoxidation. The vigorous occurrence of side reactions, the products of which retard the main process, does not yet allow one to consider the palladium-based catalysts as a potential alternative to the titanosilicate catalysts applied in practice.

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Table 2. Crystallographic parameters and structure refinement parameters for compound **I**

Parameter	Value
Empirical formula	$C_{26}H_{26}N_6O_6S_2Cl_2Pd$
FW	759.95
Crystal system	Monoclinic
Space group	$P2_1/c$
Wavelength, Å	1.54059
a, Å	8.6354(7)
b, Å	24.5266(18)
c, Å	7.2853(5)
β, deg	106.732(19)
V, Å^3	1477.68(19)
Z	2
D_x, g cm^{-3}	1.708
μ, mm^{-1}	8.505
$2\theta_{min}$–$2\theta_{max}$; $\Delta 2\theta$, deg	5.00–77.00; 0.01
Number of parameters/restraints	125/75
R_p, R_{wp}, R_{exp}	0.0249, 0.0315, 0.0165

Table 3. Selected bond lengths, bond angles, and geometric parameters of hydrogen bonds in $[PdL_2Cl_2]$*

Bond	*d*, Å	Angle		ω, deg
Pd(1)–Cl(1)	2.288(3)	Cl(1)Pd(1)S(1)		94.8(1)
Pd(1)–S(1)	2.275(3)	S(1)Pd(1)Cl(1)^{i}		85.2(1)
S(1)–C(2)	1.702(11)	Pd(1)S(1)C(2)		115.8(3)
	Distance, Å			
D–H...A	D–H	H...A	D...A	Angle D–H...A, deg
N(3)–H(3)...Cl(1)	0.86	2.42	3.166(7)	146
N(1)–H(1)...O(1)6	0.86	2.07	2.930(8)	174
C(7)–(7C)...O(18)	0.96	2.42	3.260(12)	146

* Symmetry code: ^{i} $-x, 1-y, 2-z$.

Table 4. Main parameters of the epoxidation of allyl alcohol with hydrogen peroxide in methanol

Catalyst	X_{AA}, %	X_{HP}, %	$\varphi_{GD\|AA}$, %	$\varphi_{GD\|HP}$, %	TON (GD)	TON (AA)
I	15.5	12.5	16.6	37.8	1.7	10
$PdCl_2$	30.1	9.6	8.3	26.0	1.2	14
I*	23.0	8.4	20.3	45.2	5.6	20
II	28.2	5.7	8.0	38.4	1.3	16
$PdBr_2$	20.4	5.5	13.1	38.6	1.3	9
II*	28.9	6.3	26.7	22.1	2.0	43
TS-1	46.9	62.6	97.8	95.1	27.0	27

I* and **II*** indicate the samples singly used in the catalytic process, which were filtered, dried, and loaded into the reaction to evaluate a possibility of their repeated use as catalysts. After the single use in the process, the structures of the isolated samples were analyzed by IR spectroscopy: it was proved that the samples underwent no structural changes during the experiment.

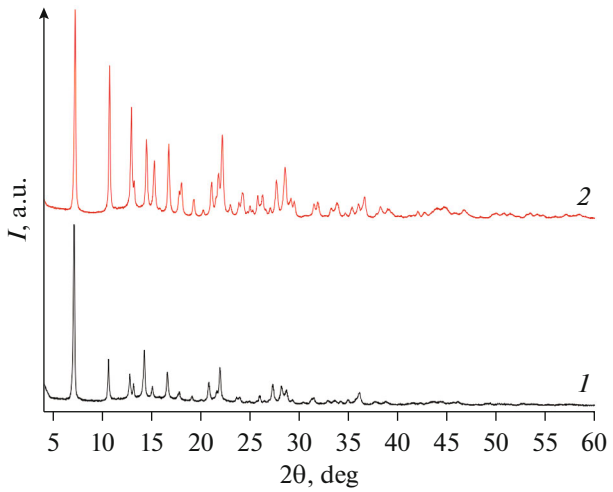

Fig. 2. Experimental diffraction patterns of compounds (curve *1*) **II** and (curve *2*) **I**.

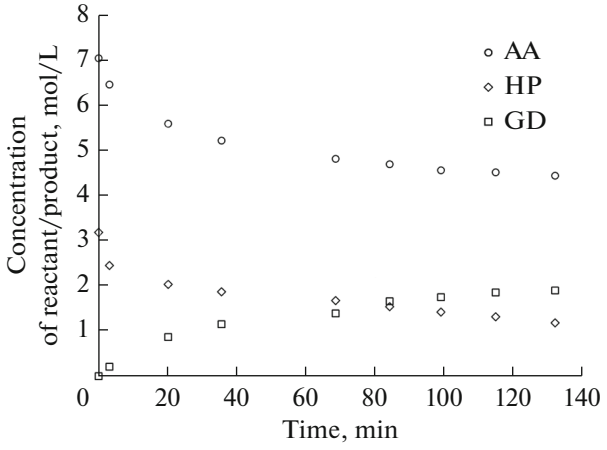

Fig. 3. Kinetic curves of the reactant consumption (AA is allyl alcohol, and HP is hydrogen peroxide) and target product formation (GD is glycidol) during epoxidation using TS-1 as the catalyst.

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CONFLICT OF INTEREST

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

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