Macrocyclic Complexes of Palladium(II) with Benzothiacrown Ethers: Synthesis, Characterization, and Structure of *cis* and *trans* Isomers

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S *Supporting Information*

ABSTRACT: A series of palladium(II) complexes with nitro- and formylbenzothiacrown-ether derivatives was synthesized. The spatial structure of the complexes was studied by NMR, X-ray diffraction analysis, and quantum chemical calculations (density functional theory). The cavity size and the ligand denticity were found to be crucial factors determining the geometric configuration of the thiacrown-ether complexes. Palladium(II) complexes with benzodithia-12(18)-crown-4(6) ethers were demonstrated to have a *cis*-configured S_2PdY_2 fragment (Y = Cl, OAc). In the case of Pd(II) and benzodithia-21-crown-7 ethers, only complexes with a *trans* configuration of the S_2PdY_2 fragment form. In the case of Pd(II) and nitrobenzomonothia-15-crown-5 ether, only 2(ligand):1(Pd) complex with *trans* configuration of the core fragment forms.
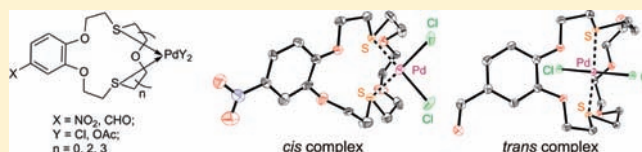
INTRODUCTION

It is known that sulfur-containing macrocyclic compounds show high affinity to transition, heavy, and noble metal cations forming stable complexes with them.[1] These compounds can be used, for example, for efficient and selective determination and recovery of mercury(II), silver(I), and platinum group metals from aqueous solutions;[2] in ion selective electrodes;[3] and so on. The structure of a complex formed upon interaction of thiacrown compounds with the metal cation is determined by the metal nature (oxidation state, typical coordination number, and the preferred geometry of arrangement of donor atoms in the coordination sphere of the metal), the nature of counterions, and structural features of the macroheterocycle.

The inclusion of a noble metal cation inside the thiacrown cavity is rarely observed. In this case, a compliance of the cavity size with the metal ion size is not the crucial factor for the complexation efficiency and selectivity,[2f,4] in contrast to cases of the alkali and alkaline-earth metal cation complexation with classical oxygen crown ethers.[5] For example, known 1:1 complexes formed by palladium(II) salts with oxathiacrown compounds functioning as bidentate ligands have the predominantly *cis* structure (with respect to coordinated S atoms) where Pd(II) is not immersed in the macrocycle cavity.[4,6] Only a few examples of the formation of

similar *trans* complexes, in which Pd(II) is located inside the cavity, have been reported.[4,7] The effect of the macrocycle size of sulfur-containing crown compounds on the formation of either *cis* or *trans* complexes with palladium(II) salts has not been studied previously. This study would be useful for the understanding of complexation features of most promising thiacrown-ether derivatives as regards practical use as efficient and selective complexing agents for platinum group metals. Of particular interest are benzothiacrown-ether derivatives whose structural fragments are used in chromoionophoric compounds—styryl and butadienyl dyes.[8]

Previously, in a brief communication, we presented the synthesis and study of $PdCl_2$ complexes with bidentate ligands, namely, nitro- and formylbenzodithia-18(21)-crown-6(7)-ether derivatives.[9] This article presents the synthesis and comprehensive structure study for a series of palladium(II) complexes with nitro- and formylbenzothiacrown-ether derivatives 1—9 having different sizes and ligand denticities (Chart 1). The study was carried out by means of NMR, X-ray diffraction, and density functional theory.

Chart 1

1-8
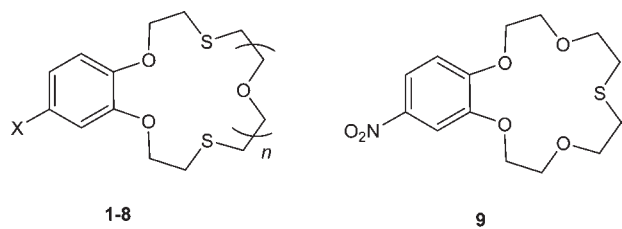
X = NO$_2$ (**1-4**), CHO (**5-8**); n = 0 (**1, 5**), 1 (**2, 6**), 2 (**3, 7**), 3 (**4, 8**)

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■ EXPERIMENTAL SECTION

General Procedures. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX500 spectrometer (operating at 500.13 and 125.76 MHz, respectively). The solvents were CDCl$_3$, DMSO-d$_6$, and MeCN-d$_3$; the solvent served as the internal standard (δ 7.27, 2.50, 1.96 ppm for ^{1}H and 77.00, 39.43, 118.10 ppm for ^{13}C, respectively). The chemical shifts were measured to an accuracy of 0.01 ppm, and the spin−spin coupling constants were determined to within 0.1 Hz. The proton and carbon signals were assigned by means of 2D homonuclear ^{1}H−^{1}H COSY and NOESY and ^{1}H−^{13}C heteronuclear COSY techniques (HSQC and HMBC). Two-dimensional experiments were carried out using the standard parameters included in the Bruker software. The mixing time in the NOESY experiment was 300 μs; the HMBC experiment was optimized to $J_{H,C}$ = 8 Hz. IR spectra were measured on a Shimadzu IR-435 spectrophotometer in KBr pellets. MALDI-TOF mass spectra were obtained on a UltraFlex Bruker spectrometer with a nitrogen laser (337 nm, pulse energy 80−110 μJ, pulse repetition rate 50 Hz). α-Cyano-4-hydroxycinnamic acid (CCA) (Bruker) was used as the matrix. High resolution ESI mass spectra were measured on a Bruker Daltonics MicrOTOF instrument in the range of m/z = 50−3000 for positive ions (MeCN solution inlet, nitrogen gas flow, 4500 V capillary voltage). Elemental analysis was performed at the Shared Use Centre of M. V. Lomonosov Moscow State Academy of Fine Chemical Technology. The melting points of compounds were determined on a MEL-Temp II instrument in a capillary. Ligands **1**−**9** were prepared following literature procedures.[10]

Preparation of Palladium(II) Chloride Complexes with Benzodithiacrown Ethers 1−8 (General Procedure): Method A. A solution of nitro- or formylbenzodithiacrown ether **1**−**4** or **5**−**8** (0.21 mmol) in dry MeCN (3 mL) was added dropwise at room temperature to a stirred solution of [PdCl$_2$(MeCN)$_2$] (83 mg, 0.32 mmol) in dry MeCN (5 mL). The reaction mixture was cooled to −10 °C (in the case of compounds **1**, **2**, **5**−**8**) or allowed to stand at room temperature for 2 days (compound **3**) or 3 days (compound **4**). The yellow precipitate thus formed was filtered off, washed with dry MeCN, and dried in the air.

*cis-[Pd(**1**)Cl$_2$].* Yield: 68 mg (68%). Mp: 282−284 °C (decomp.). C$_{12}$H$_{15}$Cl$_2$NO$_4$PdS$_2$ (478.70), calcd.: C, 30.11; H, 3.16; N, 2.93; Cl, 14.81. Found: C, 30.28; H, 3.19; N, 3.00; Cl, 14.80. IR (KBr pellets): ν 1520 (NO$_2$) cm^{-1}. MS (ESI), exact mass calcd.: 499.8752 for C$_{12}$H$_{15}$-Cl$_2$NO$_4$PdS$_2$·Na$^+$ (with ^{106}Pd and ^{35}Cl). Found: 499.8760. ^{1}H NMR (DMSO-d$_6$): δ 3.21 (m, 1 H, CHH'S), 3.32 (m, 3 H, CHH'S, 2 CH-H'S), 3.43 (br.d, ^{2}J = 15.0 Hz, 1 H, CHH'S), 3.58 (br.d, 1 H, ^{2}J = 14.5 Hz, CHH'S), 3.63 (m, 1 H, CHH'S), 3.90 (m, 1 H, CHH'S), 4.56 (m, 2 H, 2 CHH'OAr), 4.86 (br.d, ^{2}J = 10.4 Hz, 1 H, CHH'OAr), 4.91 (br.d, ^{2}J = 10.5 Hz, 1 H, CHH'OAr), 7.47 (d, ^{3}J = 8.9 Hz, 1 H, 6-H), 8.06 (dd, ^{3}J = 8.9 Hz, ^{4}J = 2.6 Hz, 1 H, 5-H), 8.11 (d, ^{4}J = 2.6 Hz, 1 H, 3-H) ppm.

*[Pd(**2**)Cl$_2$].* Yield: 74 mg (68%). Mp: 230 °C (decomp.). C$_{14}$H$_{19}$Cl$_2$-NO$_5$PdS$_2$ (522.76), calcd.: C, 32.17; H, 3.66; N, 2.68; Cl, 13.56. Found: C, 32.30; H, 3.71; N, 2.80; Cl, 13.81. IR (KBr pellets): ν 1515 (NO$_2$) cm^{-1}. MS (MALDI-TOF): m/z 485 [M − HCl]$^+$ (with ^{106}Pd and ^{35}Cl). The

^{1}H NMR spectrum of [Pd(**2**)Cl$_2$] is of unsatisfactory quality due to low solubility in CDCl$_3$ and MeCN-d$_3$.

*cis-[Pd(**3**)Cl$_2$].* Yield: 71 mg (59%). Mp: 248−250 °C (decomp.). C$_{16}$H$_{23}$Cl$_2$NO$_6$PdS$_2$ (566.81), calcd.: C, 33.90; H, 4.09; N, 2.47; Cl, 12.51. Found: C, 34.06; H, 4.16; N, 2.46; Cl, 12.88. IR (KBr pellets): ν 1511 (NO$_2$) cm^{-1}. MS (MALDI-TOF): m/z 529 [M − HCl]$^+$ (with ^{106}Pd and ^{35}Cl). ^{1}H NMR (CDCl$_3$): δ 2.85 (m, 4 H, 2 CHH'S, 2 CH-H'S), 3.75 (m, 4 H, 2 CHH'S, CH$_2$O), 3.80 (m, 4 H, 2 CHH'O, CH$_2$O), 4.17 (br.s, 3 H, 2 CHH'OAr, CHH'S), 4.26 (m, 1 H, CHH'S), 4.36 (m, 2 H, 2 CHH'O), 4.86 (br.s, 2 H, 2 CHH'OAr), 7.07 (d, ^{3}J = 8.5 Hz, 1 H, 6-H), 7.89 (br.s, 1 H, 3-H), 8.00 (br.d, ^{3}J = 8.5 Hz, 1 H, 5-H) ppm. ^{1}H NMR (MeCN-d$_3$): δ 2.90 (m, 4 H, 2 CHH'S, 2 CHH'S), 3.56 (m, 2 H, 2 CHH'S), 3.71 (s, 4 H, 2 CH$_2$O), 3.73 (m, 2 H, 2 CHH'O), 3.97 (m, 1 H, CHH'S), 4.10 (m, 1 H, CHH'S), 4.19 (m, 4 H, 2 CH-H'OAr, 2 CHH'O), 4.79 (br.s, 2 H, 2 CHH'OAr), 7.20 (d, ^{3}J = 8.6 Hz, 1 H, 6-H), 7.93 (d, ^{4}J = 1.8 Hz, 1 H, 3-H), 8.00 (br.d, ^{3}J = 8.6 Hz, 1 H, 5-H) ppm.

*trans-[Pd(**4**)Cl$_2$].* Yield: 65 mg (51%). Mp: 226−227 °C (decomp.). C$_{18}$H$_{27}$Cl$_2$NO$_7$PdS$_2$ (610.86), calcd.: C, 35.39; H, 4.46; N, 2.29. Found: C, 35.42; H, 4.58; N, 2.23. IR (KBr pellets): ν 1521 (NO$_2$) cm^{-1}. MS (MALDI-TOF): m/z 573 [M − HCl]$^+$ (with ^{106}Pd and ^{35}Cl). ^{1}H NMR (CDCl$_3$): δ 2.58 (br.s, 2 H, 2 CHH'S), 2.77 (br.s, 2 H, 2 CHH'S), 3.53 (m, 2 H, CH$_2$O), 3.70 (m, 2 H, 2 CHH'S), 3.78 (br.m, 4 H, 2 CH$_2$O), 3.84 (br.m, 2 H, 2 CHH'S), 3.98 (br.m, 4 H, CH$_2$O, 2 CHH'O), 4.27 (br.m, 2 H, 2 CHH'OAr), 4.63 (br.m, 4 H, 2 CHH'OAr, 2 CHH'O), 6.85 (d, ^{3}J = 8.8 Hz, 1 H, 6-H), 7.69 (br.s, 1 H, 3-H), 7.95 (dd, ^{3}J = 8.8 Hz, ^{4}J = 2.5 Hz, 1 H, 5-H) ppm. ^{1}H NMR (MeCN-d$_3$): δ 2.58 (br.d, 2 H, 2 CHH'S), 2.89 (br.s, 2 H, 2 CHH'S), 3.54 (br.m, 6 H, 2 CHH'S, 2 CHH'S, CH$_2$O), 3.70 (br.m, 4 H, 2 CH$_2$O), 3.79 (br.s, 2 H, CH$_2$O), 3.88 (br.s, 2 H, 2 CHH'O), 4.21 (br.s, 2 H, 2 CHH'OAr), 4.44 (br.s, 2 H, 2 CHH'O), 4.64 (br.s, 2 H, 2 CHH'OAr), 7.03 (d, ^{3}J = 8.9 Hz, 1 H, 6-H), 7.74 (d, ^{4}J = 2.4 Hz, 1 H, 3-H), 7.94 (dd, ^{3}J = 8.9 Hz, ^{4}J = 2.4 Hz, 1 H, 5-H) ppm.

*cis-[Pd(**5**)Cl$_2$].* Yield: 53 mg (54%). Mp: 255−256 °C (decomp.). C$_{13}$H$_{16}$Cl$_2$O$_3$PdS$_2$ (461.72), calcd.: C, 33.82; H, 3.49. found: C, 33.80; H, 3.45. IR (KBr pellets): ν 1685 (C=O) cm^{-1}. MS (MALDI-TOF): m/z 424 [M − HCl]$^+$ (with ^{106}Pd and ^{35}Cl). ^{1}H NMR (DMSO-d$_6$): δ 3.22 (m, 1 H, CHH'S), 3.33 (m, 3 H, CHH'S, 2 CHH'S), 3.41 (br.d, ^{2}J = 15.0 Hz, 1 H, CHH'S), 3.56 (br.d, ^{2}J = 15.0 Hz, 1 H, CHH'S), 3.67 (dt, ^{2}J = 13.2 Hz, ^{3}J = 5.9 Hz, 1 H, CHH'S), 3.95 (m, 1H, CHH'S), 4.51 (m, 2 H, 2 CHH'OAr), 4.83 (m, 2 H, 2 CHH'OAr), 7.47 (d, ^{3}J = 8.6 Hz, 1 H, 6-H), 7.72 (dd, ^{3}J = 8.6 Hz, ^{4}J = 1.8 Hz, 1 H, 5-H), 7.73 (d, ^{4}J = 1.8 Hz, 1 H, 3-H), 9.90 (s, 1 H, CHO). ^{13}C NMR (DMSO-d$_6$): δ 36.33 (CH$_2$S), 36.94 (CH$_2$S), 40.16 (CH$_2$S), 41.24 (CH$_2$S), 68.20 (CH$_2$-OAr), 71.65 (CH$_2$OAr), 116.36 (6-C), 117.88 (3-C), 128.25 (5-C), 131.21 (4-C), 149.24 (2-C), 154.68 (1-C), 191.32 (CHO) ppm.

*[Pd(**6**)Cl$_2$].* Yield: 64 mg (60%). Mp: 150 °C (decomp.). C$_{15}$H$_{20}$Cl$_2$-O$_4$PdS$_2$ (505.77), calcd.: C, 35.62; H, 3.99; Cl, 14.02. Found: C, 35.71; H, 3.98; Cl, 13.67. IR (KBr pellets): ν 1679 (C=O) cm^{-1}. MS (MALDI-TOF): m/z 469 [M − Cl]$^+$ (with ^{106}Pd and ^{35}Cl). The ^{1}H NMR spectrum of [Pd(**6**)Cl$_2$] is of unsatisfactory quality due to low solubility in CDCl$_3$ and MeCN-d$_3$.

*cis-[Pd(**7**)Cl$_2$].* Yield: 67 mg (58%). Mp: 182−184 °C (decomp.). C$_{17}$H$_{24}$Cl$_2$O$_5$PdS$_2$ (549.82), calcd.: C, 37.14; H, 4.40; Cl, 12.90. Found: C, 37.35; H, 4.60; Cl, 12.48. IR (KBr pellets): ν 1696 (C=O) cm^{-1}. MS (MALDI-TOF): m/z 512 [M − HCl]$^+$ (with ^{106}Pd and ^{35}Cl). ^{1}H NMR (CDCl$_3$): δ 2.83 (m, 4 H, 2 CHH'S, 2 CHH'S), 3.72 (m, 4 H, 2 CHH'S, CH$_2$O), 3.79 (m, 4 H, 2 CHH'O, CH$_2$O), 4.12 (m, 3 H, 2 CHH'OAr, CHH'S), 4.22 (m, 1 H, CHH'S), 4.32 (m, 2 H, 2 CHH'O), 4.79 (m, 2 H, 2 CHH'OAr), 7.10 (d, ^{3}J = 7.9 Hz, 1 H, 6-H), 7.50 (br.s, 1 H, 3-H), 7.56 (br.d, ^{3}J = 7.9 Hz, 1 H, 5-H), 9.88 (s, 1 H, CHO) ppm. ^{13}C NMR (CDCl$_3$): 39.51 (CH$_2$S), 39.77 (CH$_2$S), 40.18 (CH$_2$S), 40.39 (CH$_2$S), 66.90 (2 CH$_2$O), 67.29 (CH$_2$OAr), 67.88 (2 CH$_2$O), 67.97 (CH$_2$OAr), 116.59 (6-C), 117.39 (3-C), 127.53 (5-C), 131.88 (4-C), 149.09 (2-C),

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dx.doi.org/10.1021/ic2003063 |*Inorg. Chem.* 2011, 50, 7500−7510

154.39 (1-C), 190.51 (CHO) ppm. ^{1}H NMR (MeCN-d_3): δ 2.88 (m, 4 H, 2 CHH'S, 2 CHH'S), 3.53 (m, 2 H, 2 CHH'S), 3.71 (s, 4 H, 2 CH$_2$O), 3.80 (m, 2 H, 2 CHH'O), 3.95 (m, 1 H, CHH'S), 4.06 (m, 1 H, CHH'S), 4.19 (m, 4 H, 2 CHH'OAr, 2 CHH'O), 4.76 (br.s, 2 H, 2 CHH'OAr), 7.23 (d, ^3J = 8.3 Hz, 1 H, 6-H), 7.58 (br.s, 1 H, 3-H), 7.64 (br.d, ^3J = 8.3 Hz, 1 H, 5-H), 9.88 (s, 1 H, CHO) ppm. ^{13}C NMR (MeCN-d_3): δ 38.56 (CH$_2$S), 38.80 (CH$_2$S), 39.63 (CH$_2$S), 39.86 (CH$_2$S), 66.18 (2 CH$_2$O), 67.29 (CH$_2$OAr), 67.88 (2 CH$_2$O), 67.87 (CH$_2$OAr), 115.48 (6-C), 116.42 (3-C), 126.59 (5-C), 131.88 (4-C), 149.09 (2-C), 154.39 (1-C), 190.40 (CHO) ppm.

trans-[Pd(**8**)Cl$_2$]. Yield: 65 mg (48%). Mp: 219−221 °C (decomp.). C$_{19}$H$_{28}$Cl$_2$O$_6$PdS$_2$·MeCN·0.3H$_2$O (640.34), calcd.: C, 39.39; H, 4.97; Cl, 11.07. Found: C, 39.21; H, 5.23; Cl, 11.10. IR (KBr pellets): ν 1689 (C=O) cm^{-1}. MS (MALDI-TOF): m/z 557 [M − Cl]$^+$ (with ^{106}Pd and ^{35}Cl). ^{1}H NMR (MeCN-d_3): δ 2.57 (br.s, 2 H, 2 CHH'S), 2.88 (br.s, 2 H, 2 CHH'S), 3.53 (br.m, 6 H, 2 CHH'S, 2 CHH'S, CH$_2$O), 3.68 (br.m, 4 H, 2 CH$_2$O), 3.78 (br.s, 2 H, CH$_2$O), 3.88 (br.s, 2 H, 2 CHH'O), 4.17 (br.s, 2 H, 2 CHH'OAr), 4.44 (br.s, 2 H, 2 CHH'O), 4.61 (br.s, 2 H, 2 CHH'OAr), 7.07 (d, ^3J = 7.9 Hz, 1 H, 6-H), 7.38 (br.s, 1 H, 3-H), 7.55 (dd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1 H, 5-H), 9.86 (s, 1 H, CHO) ppm. ^{1}H NMR (CDCl$_3$): δ 2.57 (br.s, 2 H, 2 CHH'S), 2.74 (br.d, ^2J = 12.3 Hz, 2 H, 2 CHH'S), 3.51 (br.m, 2 H, CH$_2$O), 3.68 (br.m, 2 H, 2 CHH'S), 3.77 (br.m, 4 H, CH$_2$O), 3.83 (br.m, 2 H, CHH'O), 3.98 (br.m, 4 H, CH$_2$O, 2 CHH'O), 4.25 (br.m, 2 H, CHH'OAr), 4.59 (br.m, 2 H, CHH'OAr), 4.64 (br.m, 2 H, CHH'O), 6.90 (d, ^3J = 8.0 Hz, 1 H, 6-H), 7.34 (br.s, 1 H, 3-H), 7.46 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1 H, 5-H), 9.84 (s, 1 H, CHO) ppm. ^{13}C NMR (CDCl$_3$): δ 36.99 (CH$_2$S), 37.18 (CH$_2$S), 38.86 (2 CH$_2$S), 64.28 (CH$_2$OAr), 64.54 (CH$_2$OAr), 68.70 (2 CH$_2$O), 70.59 (2 CH$_2$O), 73.37 (2 CH$_2$O), 108.51 (3-C), 110.24 (6-C), 127.36 (5-C), 130.32 (4-C), 148.30 (2-C), 152.98 (1-C), 190.83 (CHO) ppm.

cis-[Pd(**1**)Cl$_2$]: **Method B.** A solution of compound **1** (18 mg, 0.06 mmol) in MeOH (5 mL) was added dropwise to a stirred solution of K$_2$[PdCl$_4$] (20 mg, 0.06 mmol) in water (5 mL) at room temperature. Then, the reaction mixture was cooled for 24 h. The precipitate was filtered off, washed with benzene, and dried in the air to give 11 mg (38%) of *cis*-[Pd(**1**)Cl$_2$]. Mp: 282−284 °C (decomp.).

[Pd(**1**)$_2$]Cl$_2$: **Method C.** A solution of K$_2$[PdCl$_4$] (17 mg, 0.05 mmol) in a MeOH−water mixture (1:1, v/v; 10 mL) was added dropwise at room temperature to a stirred suspension of **1** (31 mg, 0.1 mmol) in a MeOH−water mixture (1:1, v/v) (10 mL). Then, the reaction mixture was cooled. The resulting dark-green precipitate was filtered off, washed with distilled water and Et$_2$O, and dried in the air to give 22 mg (54%) of [Pd(**1**)$_2$]Cl$_2$. C$_{24}$H$_{30}$Cl$_2$N$_2$O$_8$PdS$_4$·0.5H$_2$O (789.10), calcd.: C, 36.53; H, 3.96; N, 3.55. Found: C, 36.52; H, 4.04; N, 3.55. IR (KBr pellets): ν 1516 (NO$_2$) cm^{-1}. MS (MALDI-TOF): m/z 742 [M − HCl]$^+$ (with ^{106}Pd and ^{35}Cl). Complex [Pd(**1**)$_2$]Cl$_2$ was soluble only in DMSO-d_6. The ^{1}H NMR spectrum of complex [Pd(**1**)$_2$]Cl$_2$ in DMSO-d_6 indicated that the complex completely decomposed to [Pd(**1**)Cl$_2$] and ligand **1**.

cis-[Pd(**1**)(OAc)$_2$]. Pd(OAc)$_2$ (25 mg, 0.11 mmol) and a solution of **1** (35 mg, 0.12 mmol) in benzene (4 mL) were mixed at room temperature, and a precipitate was filtered off, washed with benzene, and dried in the air to give 30 mg (48%) of *cis*-[Pd(**1**)(OAc)$_2$]. Mp: 120−122 °C (decomp.). C$_{16}$H$_{21}$NO$_8$PdS$_2$·2.5H$_2$O (570.93), calcd.: C, 33.66; H, 4.59; N, 2.45. Found: C, 33.85; H, 4.59; N, 2.76. IR (KBr pellets): ν 1602 (C=O), 1519 (NO$_2$) cm^{-1}. MS (MALDI-TOF): m/z 465 [M − AcOH]$^+$ (with ^{106}Pd and ^{35}Cl). ^{1}H NMR (CDCl$_3$): δ 1.97 (s, 3 H, Me), 1.98 (s, 3 H, Me), 2.84 (m, 2 H, 2 CHH'S), 2.94 (m, 2 H, 2 CHH'S), 3.34 (dt, ^2J = 14.1 Hz, ^3J = 5.2 Hz, 1 H, CHH'S), 3.44 (br.d, ^2J = 14.6 Hz, 1 H, CHH'S), 3.70 (br.d, ^2J = 14.1 Hz, 1 H, CHH'S), 3.81 (m, 1 H, CHH'S), 4.46 (m, 1 H, CHH'OAr), 4.50 (m, 1 H, CHH'OAr), 4.76 (m, 2 H, 2 CHH'OAr), 7.13 (d, ^3J = 9.0 Hz, 1 H, 6-H), 7.98 (d, ^4J = 2.7 Hz, 1 H, 3-H), 8.06 (dd, ^3J = 9.0 Hz, ^4J = 2.7 Hz, 1 H, 5-H) ppm. ^{13}C NMR (CDCl$_3$): δ 22.43 (2 *Me*CO$_2$), 39.02 (CH$_2$S), 40.42 (CH$_2$S), 40.56 (CH$_2$S), 40.89 (CH$_2$S), 69.34 (CH$_2$OAr), 72.57 (CH$_2$OAr), 114.46 (3-C), 115.39

(6-C), 120.49 (5-C), 142.78 (4-C), 148.72 (2-C), 155.06 (1-C), 176.99 (2 *Me*CO$_2$) ppm.

trans-[Pd(**9**)$_2$Cl$_2$]. A solution of compound **9** (103 mg, 0.31 mmol) in MeCN (2 mL) was added dropwise at room temperature to a stirred solution of [PdCl$_2$(MeCN)$_2$] (41 mg, 0.16 mmol) in MeCN (6 mL). Then, the reaction mixture was cooled to −10 °C. The bright-yellow finely dispersed precipitate thus formed was filtered off, washed with MeCN, and dried in the air to give 100 mg (76%) of *trans*-[Pd(**9**)$_2$Cl$_2$]. Mp 200 °C (decomp.). C$_{28}$H$_{38}$Cl$_2$N$_2$O$_{12}$PdS$_2$ (836.06), calcd.: C, 40.22; H, 4.58; N, 3.35. Found: C, 40.53; H, 4.83; N, 3.42. IR (KBr pellets): ν 1511 (NO$_2$) cm^{-1}. The MALDI-TOF and ESI mass spectra of *trans*-[Pd(**9**)$_2$Cl$_2$] do not show peaks of palladium−ligand complexes, because the latter are decomposed under these conditions. In the ESI mass spectrum, we found only an intensive peak corresponding to the **9**·Na$^+$ complex. MS (ESI), exact mass calcd.: 352.0831 for C$_{14}$H$_{19}$NO$_6$S·Na$^+$. Found: 352.0815. ^{1}H NMR (CDCl$_3$): 3.33 (m, 8 H, 4 CH$_2$S), 3.98 (m, 8 H, 4 CH$_2$CH$_2$OAr), 4.06 (t, ^3J = 6.1 Hz, 8 H, 4 CH$_2$O), 4.19 (m, 8 H, 4 CH_2OAr), 6.87 (d, ^3J = 8.9 Hz, 2 H, 6-H), 7.72 (d, ^4J = 2.3 Hz, 2 H, 3-H), 7.91 (dd, ^3J = 8.9 Hz, ^4J = 2.3 Hz, 2 H, 5-H) ppm.

Quantum Chemical Calculations. The structures of benzodithia-12(15,18,21)-crown-4(5,6,7) ethers, their nitro and formyl derivatives **1**−**8**, and the corresponding complexes with PdCl$_2$ were calculated by DFT using the PBE functional[11] and original all-electron relativistic Λ2 basis set[12] by means of the PRIRODA program.[13] All of the calculations were carried out for a gas phase, i.e., without solvent. Only structures corresponding to the local minima (i.e., lacking imaginary vibrational frequencies) were considered. A substituent in the benzene ring (CHO or NO$_2$ group) has little influence on the structures and relative energies of the conformers of these compounds; however, it affects the chemical shifts of the aromatic protons. The proton chemical shifts for the free ligands and their complexes in the ^{1}H NMR spectra were calculated using the PRIRODA program.[13] The GIAO approximation,[14] PBE functional, and nonrelativistic 3z basis set were used.[13a]

X-Ray Structural Determination. Yellow single crystals of the complex *cis*-[Pd(**5**)Cl$_2$] were prepared by slow evaporation of the solution of ligand mixture with [PdCl$_2$(MeCN)$_2$] (1:1.5 molar ratio) in MeCN at room temperature. An X-ray diffraction experiment was carried out on a Bruker SMART−CCD diffractometer [Mo Kα radiation (λ = 0.71073 Å), graphite monochromator, ω-scan mode; T = 120.0(2) K]. The obtained reflections were processed using Bruker SAINT software.[15] The absorption corrections were applied on the basis of equivalent reflection intensity by SADABS software. The structure was solved by the direct method, and the non-hydrogen atoms were refined anisotropically by the least-squares method on F^2. The positions of all hydrogen atoms were calculated geometrically and then refined using the riding model and isotropic approximation. All of the calculations were carried out using SHELXTL-Plus software.[16] CCDC-796961 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
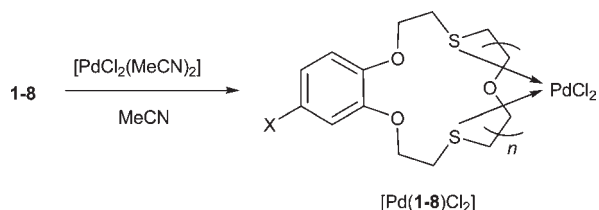
■ RESULTS AND DISCUSSION

Synthesis of Complexes. The synthesis of benzothiacrown ethers **1**−**9** was described in our previous works.[10] Upon reactions of [PdCl$_2$(MeCN)$_2$] with ligands **1**−**8** in acetonitrile, the complexes [Pd(**L**)Cl$_2$], where **L** is the ligand, were isolated in 48−68% yields (Scheme 1).
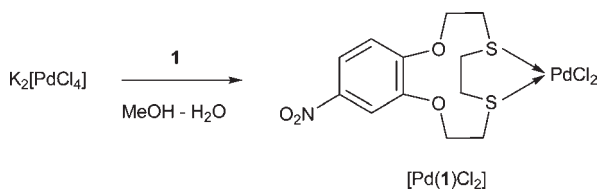
It was shown in relation to benzodithiacrown ether **1** that complex [Pd(**1**)Cl$_2$] can be prepared in 38% yield under alternative conditions by the gradual addition of ligand **1** to a water−methanol solution of K$_2$[PdCl$_4$] (Scheme 2).

The reverse order of mixing the reactants, namely, the addition of a solution of K$_2$[PdCl$_4$] to a 2-fold excess of **1**, gave a complex
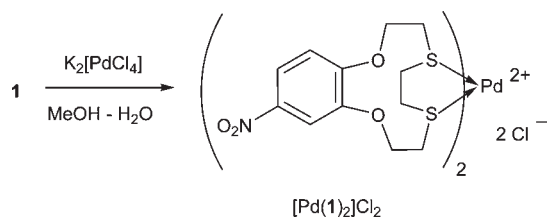
Scheme 1

$$[Pd(\mathbf{1\text{-}8})Cl_2]$$

Scheme 2

$$[Pd(\mathbf{1})Cl_2]$$

Scheme 3

$$[Pd(\mathbf{1})_2]Cl_2$$

Scheme 4

$$[Pd(\mathbf{1})(OAc)_2]$$

Scheme 5

$$[Pd(\mathbf{9})_2Cl_2]$$

with the hypothetical composition $[Pd(\mathbf{1})_2]Cl_2$ in 54% yield, where Pd(II) is likely to bind two molecules of ligand **1** (Scheme 3); complexes of similar composition were previously described in the literature.[17] No analogous changes in the composition of the complex upon the addition of $[PdCl_2(MeCN)_2]$ to a 2-fold excess of ligand **1** were observed.

The reaction of Pd(OAc)₂ with **1** in benzene produced complex $[Pd(\mathbf{1})(OAc)_2]$, which is an analogue of $[Pd(\mathbf{1})Cl_2]$, differing only by the fact that, apart from the thiacrown-ether sulfur atoms, the Pd(II) coordination environment includes acetate groups rather than chlorine atoms (Scheme 4).

The reaction of $[PdCl_2(MeCN)_2]$ with a 2-fold excess of ligand **9** in acetonitrile furnished complex $[Pd(\mathbf{9})_2]Cl_2$ in 76% yield, wherein the Pd(II) atom was bound to two benzomonothia-crown-ether molecules (Scheme 5).

The structure of the obtained complexes was determined by ^{1}H and ^{13}C NMR, MALDI, and ESI mass spectrometries and IR spectroscopy and confirmed by elemental analysis data.

NMR Spectroscopy Studies. We investigated the structures of obtained palladium(II) complexes with benzothiacrown-ether derivatives in detail using NMR spectroscopy. The investigations were carried out in different deuterated solvents due to different solubilities and stabilities of the complexes in different solvents. For Pd(II) complexes with 12-membered crown ethers, DMSO-d_6 was the most suitable solvent, as these complexes were poorly soluble in other solvents. Upon replacement of palladium chloride by palladium acetate, the solubility of the complexes became much higher, thus permitting recording of the spectra in CDCl₃.
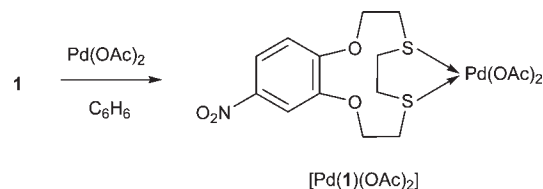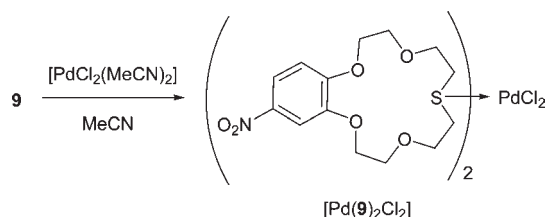
The solubility of Pd(II) complexes with 15-membered dithia-crown ethers was low in CDCl₃ and MeCN-d_3, while in DMSO-d_6, these complexes decomposed to give free ligands **2**, **6**, and, probably, PdCl₂ coordinated with the solvent molecules.[18] This behavior can be explained by the formation of linear polymeric structures like $[-PdCl_2-\mathbf{2(6)}-PdCl_2-\mathbf{2(6)}-]_k$, which have formal $1(PdCl_2):1(\mathbf{2,6})$ stoichiometry, but the Pd atoms in them are coordinated by two sulfur atoms of two ligands. As a result, we were unable to record spectra of $[Pd(\mathbf{2})Cl_2]$ and $[Pd(\mathbf{6})Cl_2]$ of a satisfactory quality. Complexes $[Pd(\mathbf{3,4})Cl_2]$ and $[Pd(\mathbf{7,8})Cl_2]$ also partly decomposed in DMSO-d_6, which leads to the appearance of the signals from free ligands **3**, **4**, **7**, and **8**. These signals significantly overlapped with broadened signals of the complexes. In the latter case, DMSO-d_6 molecules could be incorporated in the inner coordination sphere of Pd(II).[19] Fortunately, complexes $[Pd(\mathbf{3,4})Cl_2]$ and $[Pd(\mathbf{7,8})Cl_2]$ were markedly soluble in CDCl₃ or MeCN-d_3; moreover, in the case of Pd complexes with compounds **4** and **8** containing a 21-membered ring, the spectra recorded in CDCl₃ were of better quality than in MeCN-d_3. The structures of the Pd(II) complexes with 18-membered rings **3** and **7** were interpreted using the spectra recorded both in CDCl₃ and MeCN-d_3, because the spectra of these complexes showed considerable broadening and overlap of proton signals; therefore, the use of different solvents enabled accurate assignment of all signals. Complex $[Pd(\mathbf{1})_2]Cl_2$ was soluble only in DMSO-d_6 with complete decomposition to $[Pd(\mathbf{1})Cl_2]$ and ligand **1**.

The formation of complexes from benzothiacrown ethers with Pd(II) salts is accompanied by considerable complication of the ^{1}H NMR spectral pattern (e.g., Figure 1). For elucidating the structures of complexes, COSY, NOESY, HSQC, and HMBC 2D procedures were used in addition to one-dimensional ^{1}H and ^{13}C NMR spectra.

The obtained complexes proved to be individual compounds, as their ^{1}H NMR spectra showed only a single set of signals. The fact that the spectra of $[Pd(\mathbf{1})Cl_2]$ and $[Pd(\mathbf{5})Cl_2]$, $[Pd(\mathbf{3})Cl_2]$ and $[Pd(\mathbf{7})Cl_2]$, and $[Pd(\mathbf{4})Cl_2]$ and $[Pd(\mathbf{8})Cl_2]$ are almost identical in the aliphatic region attests to similar structures of complexes having the same macrocycle size and different functional groups in the benzene ring. That is, the most distant from Pd(II) peripheral groups do not affect the geometry of thiacrown-ether
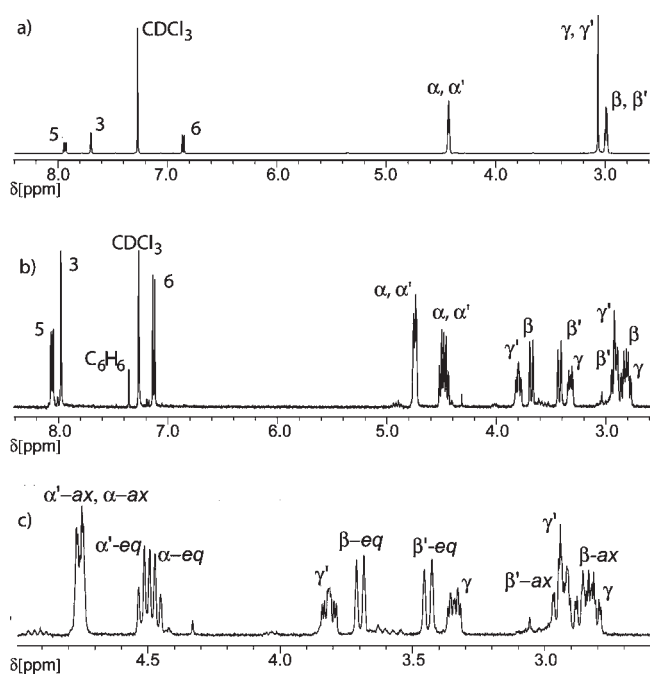
Figure 1. ^{1}H NMR spectra (500 MHz, CDCl$_3$) of (a) crown ether **1** and (b, c) complex [Pd(**1**)(OAc)$_2$].

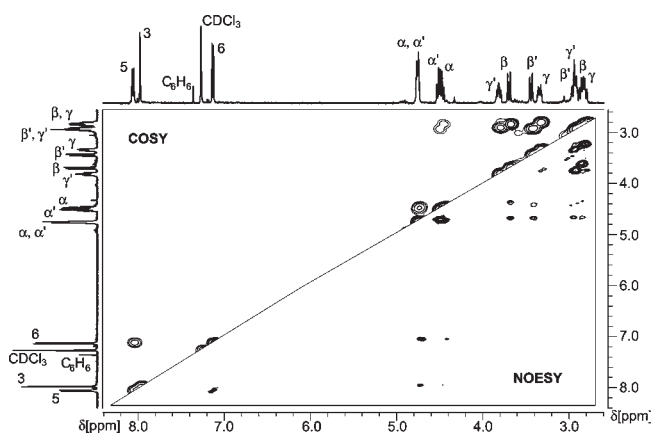**Figure 2.** Fragments of the COSY and NOESY spectra of the complex [Pd(**1**)(OAc)$_2$] (CDCl$_3$).

complexes. The considerable complication of the spectral pattern in the aliphatic region is obviously related to the formation of strong coordination bonds between sulfur and palladium(II) atoms, restricting the mobility of crown-ether units in the rigid spatial structure of the complexes. This results in splitting of the signals of the geminal protons of the crown-ether methylene groups. We suggested that, in the structures formed upon complexation, the environments of the two methylene-group protons, which are magnetically equivalent in the free compound, would be markedly different due to substantial retardation of the exchange processes in the complexes on the ^{1}H NMR time scale (500 MHz). Quantum-chemical calculation (see below) also confirmed the presence of a rigid structure of the complex with magnetically nonequivalent geminal protons.

Figure 2 shows fragments of the COSY and NOESY spectra of the palladium(II) acetate complex with compound **1** where one can clearly see the cross-peaks corresponding to coupling of the methylene-group geminal protons. For PdCl$_2$ complexes with compounds **1** and **5**, the same spectral pattern is observed.

The NMR spectra of the complexes of 18- and 21-membered dithiacrown ethers with palladium(II) chloride are similar, which is indicative of the conformational rigidity of the structure of complexes.

It is known that a palladium(II) coordination polyhedron is a planar square with the palladium atom at the center and the ligands in the corners. Therefore, we assume that, in the case of 12- and 18-membered macrocycles, there exists a square planar configuration of palladium in the *cis* complex where two chlorine atoms are located in two adjacent square corners and the other two corners are occupied by sulfur atoms. Apparently, a similar structure can also be formed in the case of 15-membered macrocycles, although the considerable decrease in the solubility of complexes of **2** and **6** with Pd(II) salts indicates indirectly the possibility of their polymeric structure, as noted above.

Using quantum chemical calculations (see below), we were able to completely interpret the spectra of Pd(II) salt complexes

with 12-membered dithiamacrocycles **1** and **5** (the designations are as follows: "*ax*" are axial and "*eq*" are equatorial protons in Figure 1c).

Palladium(II) complexes with 21-membered thiacrown ethers **4** and **8** deserve special consideration. The spectra of these complexes also show signal splitting for the geminal methylene protons of the macrocycle. This could suggest that a structure similar to those described above, i.e., that with a *cis*-configured S$_2$PdY$_2$ fragment, is also formed in this case. However, quantum chemical and X-ray diffraction data[9] attest to a *trans* complex with the sulfur atoms being located in the diametrically opposite corners of the Pd(II) coordination square. Probably, the *trans* complex can also be formed as a rigidly fixed structure with hampered conformational transitions.

As follows from analysis of the ^{1}H NMR spectra, the formation of complexes is accompanied by shifts ($\Delta\delta_H$) of the signals of all types of ligand protons (see Table 1 and Chart 2 for atom numbering that differs from the IUPAC rules). This is due to both the electron-withdrawing effect of the Pd(II) atom and the change in the crown-ether conformation upon complexation. In the case of complex [Pd(**1**)(OAc)$_2$], $\Delta\delta_H$ can be affected by the acetate groups, which exhibit a pronounced anisotropic effect, while in the case of [Pd(**9**)$_2$]Cl$_2$, the mutual influence of the two benzene rings in the complex can play a role.

To estimate the changes that take place in the spectra of the thiacrown ethers upon complexation, we employed two values, $\Delta\delta_{H,max}$ and $\Delta\delta_{H,min}$, which are the differences between the maximum and minimum, respectively, chemical shifts of the crown-ether protons in the complex and in the free state (Table 1). Positive or negative $\Delta\delta_H$ values attest to downfield or upfield shifts, respectively. Note that the use of different deuterated solvents does not affect the trends in the variation of the proton chemical shifts of the ligands upon complexation.

The position of the proton signal of the formyl group is affected by complexation to the least extent; $\Delta\delta_H$ is up to 0.06 ppm for Pd(II) complexes with **5**, **7**, and **8**. It is evident that upon complex formation involving only sulfur atoms, the effect of complexation on the groups located far from the binding site is minor.
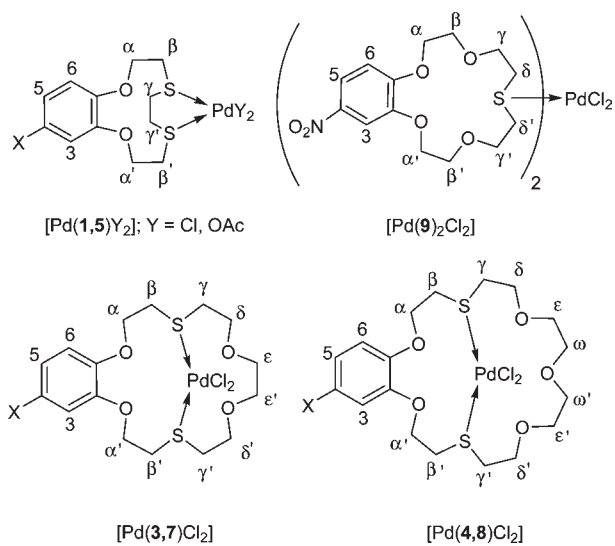
In the case of Pd(II) complex formation with 12- and 18-membered benzodithiacrown ethers, in the aromatic region, the greatest downfield shift ($\Delta\delta_H$ up to 0.37 ppm) was observed for the signals of the 3-H and 6-H protons located in the *ortho* position relative to the macrocycle. This attests to considerable

Table 1. Changes in the Proton Chemical Shifts of Benzothiacrown Ethers 1, 3−5, 7−9 upon Complex Formation with Pd(II)

complex	solvent	CHO	3-H	5-H	6-H	α,α'	β,β'	γ,γ'	δ,δ'	ε,ε'	ω,ω'
							$\Delta\delta_{H,max}/\Delta\delta_{H,min}$, ppm[a]				
[Pd(**1**)Cl$_2$]	DMSO-d$_6$		0.37	0.15	0.32	0.51/0.16	0.65/0.39	0.97/0.28			
[Pd(**1**)(OAc)$_2$]	CDCl$_3$		0.29	0.13	0.28	0.33/0.07	0.64/ −0.22	0.82/ −0.15			
[Pd(**5**)Cl$_2$]	DMSO-d$_6$	0.06	0.35	0.16	0.31	0.46/0.14	0.62/0.39	1.01/0.26			
[Pd(**3**)Cl$_2$]	MeCN-d$_3$		0.18	0.10	0.14	0.50/ −0.10	0.99/ −0.21	0.63 −0.03	0.49/0.03	0.14	
	CDCl$_3$		0.18	0.09	0.20	0.69/ −0.10	1.09/ −0.32	0.77/ −0.13	0.61/0.05	0.18/0.13	
[Pd(**7**)Cl$_2$]	MeCN-d$_3$	0.04	0.18	0.13	0.13	0.49/ −0.08	0.96/ −0.22	0.60/ −0.05	0.49/0.10	0.14	
	CDCl$_3$	0.03	0.12	0.12	0.15	0.52/ −0.15	1.07/ −0.32	0.74/ −0.15	0.53/0.04	0.17/0.12	
[Pd(**4**)Cl$_2$]	MeCN-d$_3$		−0.03	0.03	−0.04	0.34/ −0.09	0.51/ −0.14	0.64/ −0.32	0.73/0.17	0.20/ −0.05	0.11
	CDCl$_3$		−0.05	0.04	−0.05	0.35/ −0.01	0.77/ −0.30	0.75/ −0.37	0.84/0.19	0.31/ −0.14	0.11
[Pd(**8**)Cl$_2$]	MeCN-d$_3$	0.01	−0.04	0.03	−0.04	0.33/ −0.11	0.51/ −0.14	0.63/ −0.33	0.73/0.17	0.20/ −0.05	0.10
	CDCl$_3$	0.00	−0.05	0.01	−0.06	0.32/ −0.02	0.78/ −0.31	0.73/ −0.38	0.86/0.20	0.32/ −0.15	0.11
[Pd(**9**)$_2$]Cl$_2$	CDCl$_3$		−0.01	−0.02	−0.02	−0.02	0.03	0.19	0.47		

[a] $\Delta\delta_{H,max} = \delta_{H,max,compl} - \delta_{H,free}$. $\Delta\delta_{H,min} = \delta_{H,min,compl} - \delta_{H,free}$.

Chart 2

[Pd(**1,5**)Y$_2$]; Y = Cl, OAc　　　　　　　[Pd(**9**)$_2$Cl$_2$]

[Pd(**3,7**)Cl$_2$]　　　　　　　　　　[Pd(**4,8**)Cl$_2$]

**Chart 3**

trans-[Pd(**9**)$_2$Cl$_2$]

conformational rearrangement of the crown-ether fragment up-on complex formation, leading to violation of the conjugation of an oxygen lone electron pair with the aromatic system in the CH$_2$OAr group. The quantum chemical and X-ray diffraction data for complexes [Pd(**3**)Cl$_2$] and [Pd(**5**)Cl$_2$] confirm this assumption (see below).

The greatest complexation-induced shift of the ^{1}H NMR signals takes place for the methylene groups attached to sulfur atoms, the most pronounced downfield shift being as large as 1.09 ppm. This fact implies that the sulfur atoms mainly participate in the complex formation. The splitting of the geminal proton signals for these groups may reach 1.41 ppm, the signal of one proton being shifted upfield and the signal of the other proton being shifted downfield.

The most significant distinction of complexes of 21-mem-bered crown-ethers **4** and **8** from complexes of other ligands is relatively small change in the position of δ_H for benzene ring protons where the signals of 3-H and 6-H protons are shifted
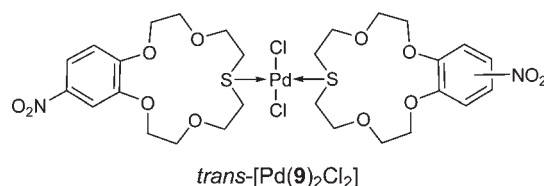
upfield. This difference in the spectral characteristics may be a consequence of different structures of the complexes.

A different spectral pattern is observed upon the formation of complex [Pd(**9**)$_2$]Cl$_2$, in which the macrocycle contains one sulfur atom located as far as possible from the aromatic ring. Upon complex formation, the positions of the signals of α,α'-methylene group protons and benzene ring protons do not change, whereas the proton signals of the δ,δ'-methylene groups directly bound to the sulfur atom undergo the largest downfield shift ($\Delta\delta_{H,max}$ up to 0.47 ppm). The proton signals of the γ,γ'-methylene groups next but one to the sulfur atom shift to a markedly lesser extent ($\Delta\delta_{H,max}$ up to 0.19 ppm). This type of behavior points to the formation of a *trans*-configured exclusion complex, which rules out the mutual effect of the two benzene rings within the complex, and the Pd(II) atom is coordinated only by the sulfur atoms of two macrocycles (Chart 3). The similar structure of the benzomonothia-15-crown-5-ether complex with PdCl$_2$ was es-tablished previously by X-ray diffraction analysis.[20]

Thus, the NMR studies demonstrated that thiacrown ethers and palladium(II) salts form stable complexes with a rigid spatial structure. The spectral properties of the complexes are affected by the macrocycle size and denticity.

Quantum Chemical Calculations. The calculated structures of free nitro derivatives of benzodithiacrown ethers **1**−**4** are shown in Figure 3. Compounds **3** and **4**, which have a flexible large-size macrocyclic fragment, exhibit a large number of conformers with-in a narrow energy range. The presence of several low-lying ($E_{conf} \leq 3$ kcal·mol^{-1})[21] conformers of free crown ethers indicates that any of them or several of them can exist at room temperature in solution or in the solid phase. The structures and
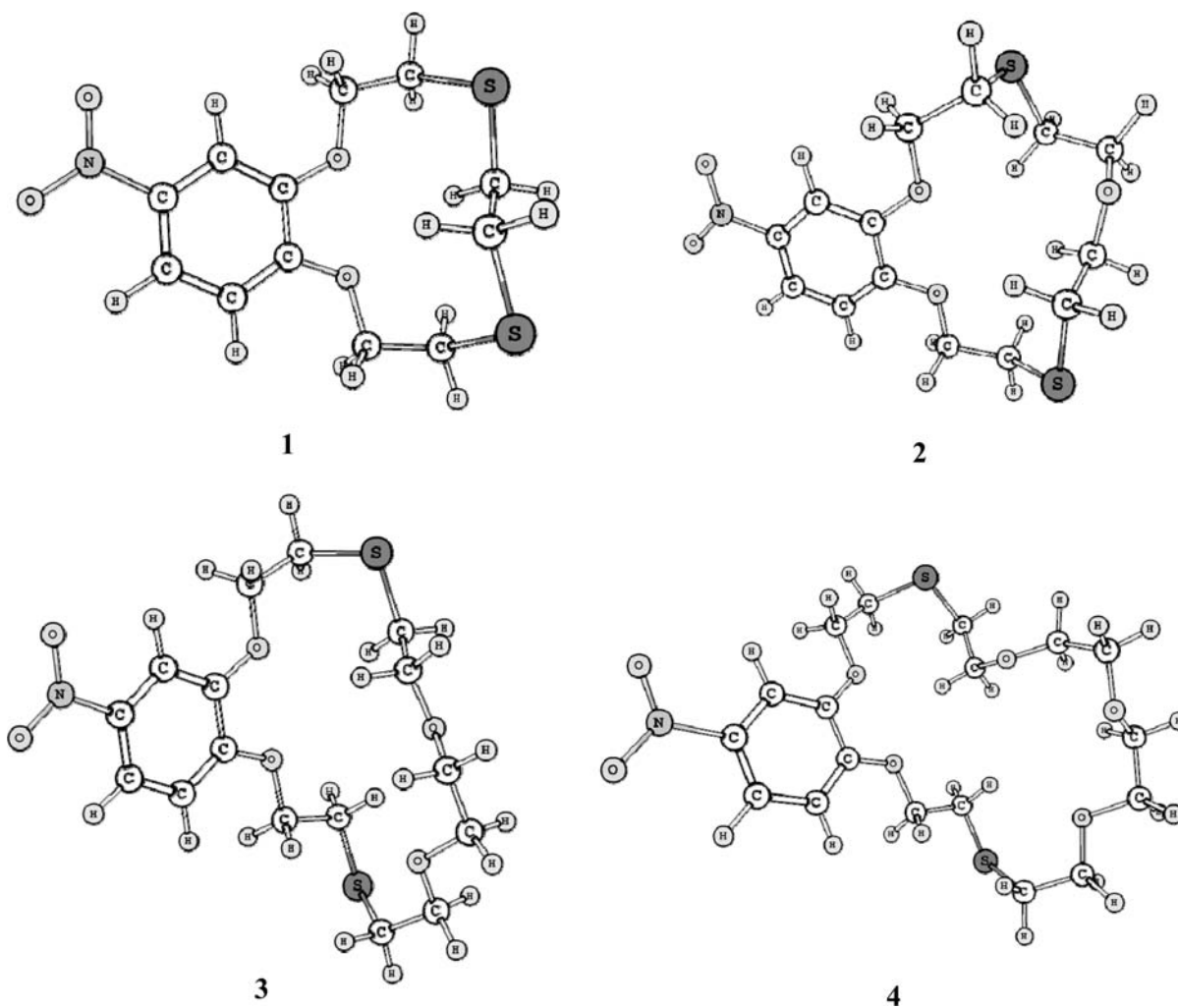
Figure 3. Calculated structures of the most stable conformers of nitrobenzodithiacrown ethers **1**–**4**.

electronic energies of the lowest-energy conformers of **1**–**4** are given in the Supporting Information (SI).
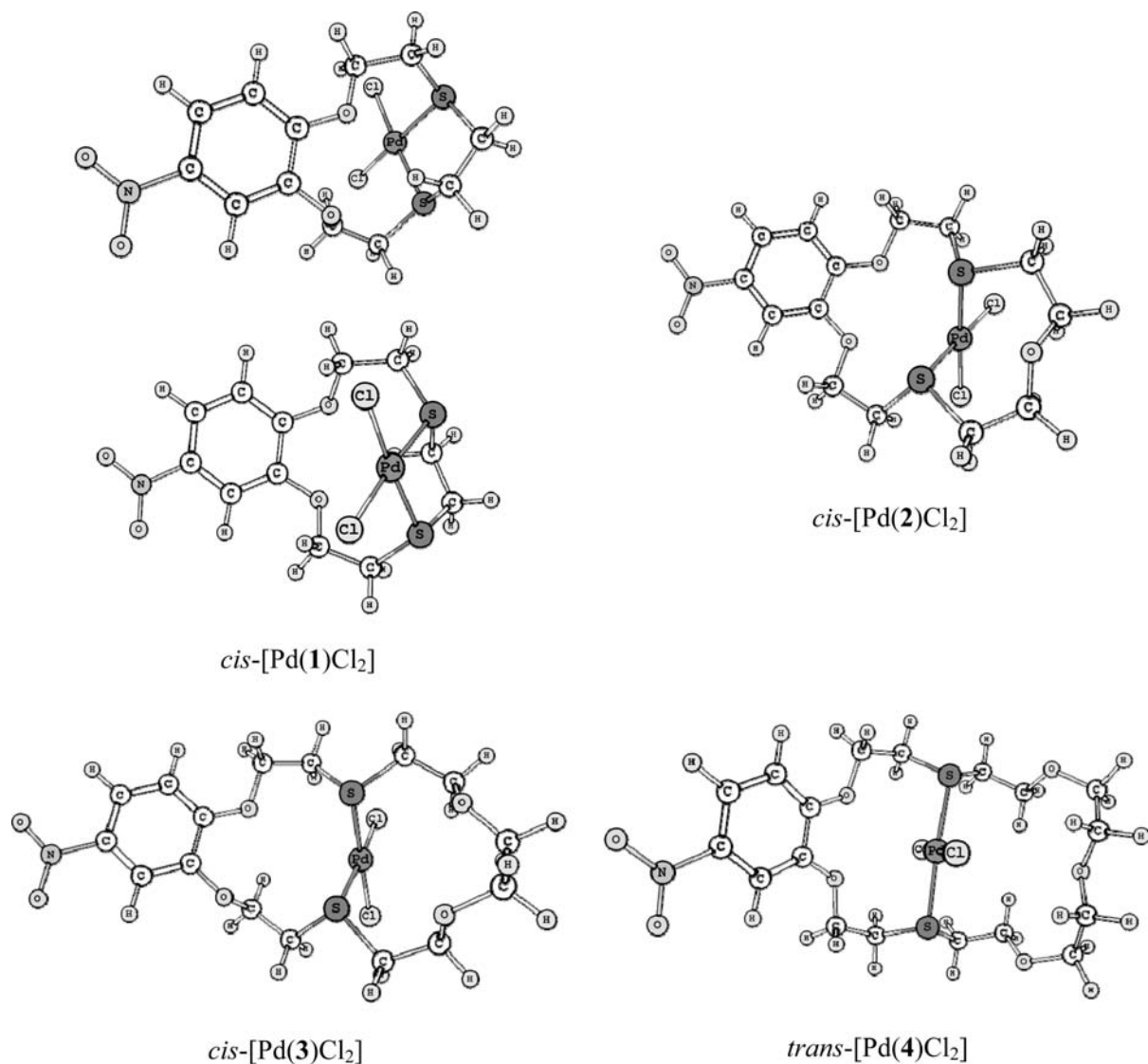
The structures of most stable conformers of benzodithiacrown ethers and their derivatives are in good agreement with the available X-ray diffraction data.[1c,8c,10b] An additional structure stabilization of free crown ethers is provided by intramolecular C–H···O contacts.

For PdCl₂ complexes with benzodithiacrown ethers and their nitro and formyl derivatives, we considered the structures with *cis*- and *trans*-arranged sulfur atoms in the S₂PdCl₂ fragment. The most stable conformers of complexes [Pd(**1**–**4**)Cl₂] are shown in Figure 4; their structures together with the electronic energies are given in the SI. It was found that Pd(II) complexes with benzo-dithia-12-crown-4-ether derivatives cannot exist in the *trans* form for geometrical reasons, and the Pd(II) complex with benzo-dithia-15-crown-5 ether in the *trans* configuration has a rather high conformational energy, which precludes its presence in solution. Complexes of 12-membered benzodithiacrown-ether derivatives in the *cis* configuration have two low-energy conformers (Figure 4), which only slightly differ in energy. One of these such conformers was found in the [Pd(**5**)Cl₂] crystal (see below). The *cis* isomers of PdCl₂ complexes of benzodithia-15-crown-5 ethers have several low-energy conformers differing in the position of the PdCl₂ fragment relative to the root-mean-square macrocycle

plane. When the benzene ring is unsubstituted, each conformer has a symmetry plane; substitution breaks the symmetry and gives rise to mirror-symmetric pairs of conformers of each type. The *cis* isomers of PdCl₂ complexes of benzodithia-18-crown-6 ethers have only one low-energy conformer without symmetry elements. In principle (provided that the barrier is sufficiently low), this conformer can transform to its mirror-symmetric counterpart. This was manifested in the X-ray diffraction pattern of [Pd(**3**)Cl₂] as a disordered structure.[9] A relatively low-lying (E_{conf} = 3.2 kcal·mol^{-1}) *trans* iso-mer was found for the PdCl₂ complex with benzodithia-18-crown-6 ether; its structure and electronic energy are given in the SI. One cannot rule out the possibility that this isomer occurs in equilibrium mixture with *cis* isomers (although in trace amounts).

The PdCl₂ complexes with benzodithia-21-crown-7 ethers, unlike the complexes with smaller crown ethers, exist only as the *trans* isomers (e.g., Figure 4), while the corresponding *cis* isomer (see the SI) has a much higher energy (E_{conf} = 5.5 kcal·mol^{-1}). The *trans* isomer of the PdCl₂ complex with unsubstituted benzodithia-21-crown-7 ether has a symmetry plane, like the *cis* isomer of the PdCl₂ complex with benzodithia-15-crown-5 ether, while the presence of a substituent in the benzene ring gives rise to a pair of mirror-symmetric conformers.

The calculated binding energies, E_{bind}, of the PdCl₂ with ligands **1**–**4** can be arranged in the sequence **2** < **1** ≈ **3** < **4**.

Figure 4. Calculated structures of the most stable conformers of nitrobenzodithiacrown ether **1**−**4** complexes with PdCl$_2$.

This correlates with the deviation of the S$_2$PdCl$_2$ fragment from the planar square, which is characterized by the S−Pd−S angle (Table 2). This deviation is largest in the case of *cis*-[Pd(**2**)Cl$_2$]; that is, this complex is more strained than small-size *cis*-[Pd-(**1**)Cl$_2$] and flexible *cis*-[Pd(**3**)Cl$_2$] and *trans*-[Pd(**4**)Cl$_2$]. The correlation between the complex stability and the S−Pd−S angle is most pronounced in the lowest-energy conformers, where other factors, such as distortion of the macrocycle itself, are negligible; in higher-energy conformers, the distortion of the macrocycle may be the key factor in complex destabilization. That is, complexation of Pd(II) with nitrobenzodithia-15-crown-5 ethers to form complexes of 1:1 stoichiometry is less favorable than with other ligands. The formation of such complexes is associated with considerable rearrangement of the macrocycle and overcoming the conformational barriers.
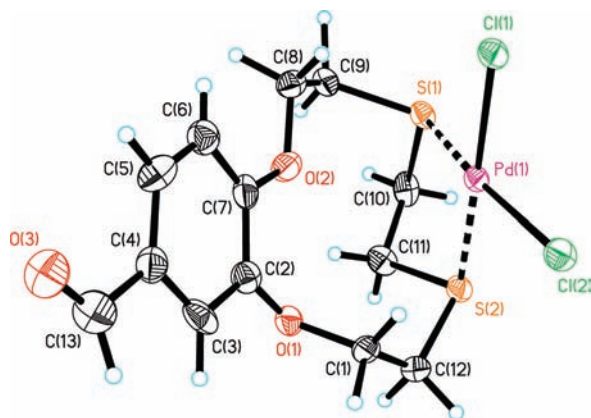
The proton chemical shifts for the free ligands **1**−**4** and their complexes were calculated for the optimized molecular geometries (see the SI). It is important that the calculations qualitatively reflect the relative positions of the signals of almost all types of protons, although the errors with respect to the

Table 2. Binding Energy, E_{bind}, of PdCl$_2$ Fragment in the Most Stable Conformer of the Complex and S−Pd−S Angle

complex	E_{bind}, kcal·mol^{-1}	S−Pd−S, deg
cis-[Pd(**1**)Cl$_2$]	65.4	89.8
cis-[Pd(**2**)Cl$_2$]	61.5	83.3
cis-[Pd(**3**)Cl$_2$]	66.2	89.0
trans-[Pd(**4**)Cl$_2$]	76.6	174.1

experimental spectra may reach 0.5−1 ppm. This might be caused by the fact that the calculations were done for isolated molecules without a solvent. The protons involved in the intramolecular C−H···O contacts exhibit downfield shifted signals as compared to similar protons that do not contact with O atoms. However, solvation can break these contacts. In the complexes, large downfield shifts (at δ 5−6 ppm) are observed for the protons in the vicinity of Cl atoms. Similarly, solvation can shield this H···Cl interaction. Indeed, the experimental chemical shifts of these protons are at δ 4−5 ppm, which,

Figure 5. Structure of complex *cis*-[Pd(5)Cl$_2$] in thermal ellipsoids at the 50% probability level.

Table 3. Selected Bond Lengths and Angles for *cis*-[Pd(5)Cl$_2$]

	cis-[Pd(5)Cl$_2$]
Pd(1)−Cl(1)	2.3354(17)
Pd(1)−Cl(2)	2.3172(17)
Pd(1)−S(1)	2.2807(17)
Pd(1)−S(2)	2.2527(17)
O(1)−C(1)	1.425(8)
O(1)−C(2)	1.393(8)
O(2)−C(7)	1.357(8)
O(2)−C(8)	1.435(8)
O(1)···O(2)	2.59
Cl(1)−Pd(1)−Cl(2)	94.58(6)
S(1)−Pd(1)−S(2)	89.09(6)
C(1)−O(1)−C(2)	110.8(5)
C(7)−O(2)−C(8)	119.9(5)
O(1)−C(2)−C(3)	122.4(6)
O(1)−C(2)−C(7)	117.1(6)
O(2)−C(7)−C(2)	115.0(6)
O(2)−C(7)−C(6)	124.5(6)

nevertheless, is larger than the shifts of the neighboring protons that do not contact with Cl atoms.

The agreement between the calculated and experimental proton chemical shifts in the [Pd(**1,3,4**)Cl$_2$] complexes is better for the low-energy structures (see the SI, Figure S1). The plots of δ_{exp} vs δ_{calcd} were fitted with straight lines. The slope of the line (0.92−0.96) indicates a good agreement on average for all of the studied conformers, but the scatter (characterized by the R^2 value) shows that some conformers fit the line better than others do. One can see from the plots that the R^2 value is closer to unity (which shows better fit) for the lowest-energy conformers.

Therefore, it is possible to identify the *cis* and *trans* isomers of the complexes by simulation of the ^{1}H NMR spectra. For example, the simulated spectra of the *cis* isomers of [Pd(**1−4**)Cl$_2$] contain two closely spaced signals (3-H and 5-H) and a slightly upfield shifted signal of 6-H in the aromatic region. In the simulated spectra of the corresponding *trans* isomers, the 3-H and 5-H signals are separated by a larger distance. A similar pattern is observed in the experimental spectra (see Table 1). For complexes of compounds **1** and **3**, the 3-H and 5-H signals are close to each other, indicating the *cis* configuration of the S$_2$PdCl$_2$ fragment, while for the complex of **4**, they are separated, which may be indicative of the *trans* configuration of this complex.

Since no signals corresponding to the *trans* isomer of the PdCl$_2$ complex with **3** and **7** or signals for *cis* isomers of the PdCl$_2$ complex with **4** and **8** derivatives are observed in the experimental spectra, these isomers can be present in the equilibrium mixture only in trace amounts, if at all.

X-Ray Diffraction Studies. Previously,[1c,10b] the spatial structures of nitrobenzodithiacrown ethers **1**, **3**, and **4** and formylbenzodithiacrown ethers **6** and **7** were studied by X-ray diffraction. It was found that both sulfur atoms in these compounds are located beyond the macrocycle cavity, which is a typical structural feature of benzothiacrown ethers in single crystals.[1c,8c] Evidently, these conformations of the dithiacrown-ether fragments are unfavorable for the formation of inclusion complexes with metal ions in all compounds. Hence, the coordination of palladium(II) salts to benzodithiacrown ethers requires a considerable conformational rearrangement of the macrocycle. Earlier, we found examples of such macrocycle rearrangement for the crystalline complexes *cis*-[Pd(**3**)Cl$_2$] and *trans*-[Pd(**8**)Cl$_2$].[9] The crystalline complex *cis*-[Pd(**5**)Cl$_2$] was also studied by X-ray diffraction. It is unlikely that a replacement of the peripheral nitro group by the formyl group has a considerable effect on the conformational characteristics of

macroheterocycles; therefore, a comparison of the crystal structures of the complexes of these compounds is well-posed.

Figure 5 shows the structure of complex *cis*-[Pd(**5**)Cl$_2$]. The selected bond lengths and angles, crystallographic data, and X-ray experimental details are summarized in Tables 3 and 4. For comparison, the data on complexes *cis*-[Pd(**3**)Cl$_2$] and *trans*-[Pd(**8**)Cl$_2$] are given in the SI (Tables S2 and S3).

In complex *cis*-[Pd(**5**)Cl$_2$], two sulfur atoms of the ligand and chlorine atoms form covalent bonds with the palladium(II) atom. The sulfur atoms have the *cis* arrangement in the coordination sphere of the Pd atom with the S(1)−Pd(1)−S(2) angle of 89.09(6)°, which is undoubtedly caused by the small size of the macrocycle. The deviation of the palladium(II) atom from the mean coordination plane through the chlorine and sulfur atoms is 0.109 Å, which definitely points to a strain of the S$_2$PdCl$_2$ fragment (cf. the Pd deviation of only 0.003 Å in *cis*-[Pd(**3**)Cl$_2$]). The same is indicated by the wider range of Pd(1)−S and Pd(1)−Cl distances [2.253(2)−2.335(2) Å] compared to that in *cis*-[Pd(**3**)Cl$_2$] [2.287(3)−2.317(2) Å]. Palladium(II) deviates from the mean plane through all heteroatoms of macrocycle **5** by a distance of 1.58 Å. The O(1) and O(2) atoms of macrocycle **5** are considerably remote from Pd(1); the Pd(1)···O distances are 3.95 and 3.20 Å, respectively, which is much greater than the sum of the palladium(II) ion radius and the van der Waals radius of the O atom (∼2.4 Å). This implies the absence of the coordination interaction between the "hard" oxygen atoms and "soft" palladium(II) atom, which is typical of this metal.[9]

In complex *cis*-[Pd(**5**)Cl$_2$], the geometric parameters of the 12-membered ring change as compared to the corresponding geometric parameters in related structure **1**.[10b] It can be seen in Figure 6a that the conformation of the benzodithia-12-crown-4-ether fragment considerably changes in order to enable the S(1) and S(2) atoms to approach each other to a distance of 3.18 Å upon *cis* coordination to Pd(1) (cf. 4.43 Å in free **1**). Simultaneously, the conformation of the S(1)−C(10)−C(11)−S(2) bridge changes from transoid (in both conformers of free **1**) to the *gauche* conformation in *cis*-[Pd(**5**)Cl$_2$]. As the sulfur atoms approach each other, the size of the macrocycle cavity apparently

**Table 4. Crystallographic Data and Structure Refinement for cis-[Pd(5)Cl$_2$]**

	cis-[Pd(5)Cl$_2$]
empirical formula	C$_{13}$H$_{16}$Cl$_2$O$_3$PdS$_2$
fw	461.68
cryst syst	orthorhombic
space group	Pna2$_1$
a, Å	7.8827(4)
b, Å	22.5032(11)
c, Å	8.8948(5)
V, Å^3	1577.81(14)
Z	4
ρ_{calcd}, g·cm^{-3}	1.944
μ(Mo−K$_\alpha$), mm^{-1}	1.784
no. of collected reflns	10103
no. of unique reflns	4140 (R_{int} = 0.0615)
no. of reflns with $I > 2\sigma(I)$	3210
no. of parameters	230
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0478, wR_2 = 0.0953
R indices (all data)	R_1 = 0.0683, wR_2 = 0.1022
GOF	1.038
residual electron density, min/max, e Å^{-3}	−1.776/1.142

decreases, resulting in the loss of conjugation of the p-electron lone pair of O(1) with the benzene ring: the C(1)−O(1)−C-(2)−C(3) torsion angle in complex cis-[Pd(5)Cl$_2$] is −77.9° (cf. −14.2° for this torsion angle in free **1**). The C(8)−O-(2)−C(7)−C(6) torsion angle is 0.0°, which is indicative of retention of effective conjugation of the O(2) atom with the benzene ring (cf. 9.2° in **1**). A comparison of the bond angles at the O(1) and O(2) atoms and the O(1)/O(2)−C$_{(Ar)}$ distances in cis-[Pd(5)Cl$_2$] attests to the sp^3 and sp^2 hybrid states of these oxygen atoms, respectively (see Table 3).

Figure 6b shows the change in conformation of ligand **3** upon the complex formation with Pd(II). It can be readily seen that palladium has a "contracting" effect at the middle of the macrocycle, as the S(1) and S(2) atoms in the cis complex approach each other to a distance of 3.18 Å (vs 7.64 Å in free **3**[10b]). This approach seems to give rise to considerable steric hindrance in the macroheterocycle, which is manifested as the loss of conjugation of the lone p-electron pairs of the O(1) atom with the benzene ring. Indeed, the torsion angle C(1)−O(1)−C(2)−C(3) is 106°, which differs fundamentally from 0 or 180°, characteristic of the ideal case of the conjugation. The C(8)−O(2)−C(7)−C(6) torsion angle equal to 17° corresponds to a retention of quite effective conjugation of the O(2) atom with the benzene ring in cis-[Pd(3)Cl$_2$] compared to that in free **3**. It should be emphasized that, in the complexes cis-[Pd(3)Cl$_2$] and cis-[Pd(5)Cl$_2$], it is the O(2) atom located in the para position relative to the nitro or formyl group in the benzene ring that remains conjugated, thus pointing to the existence of conjugation between these substituents and O(2).

Unlike the previous two complexes, trans-[Pd(8)Cl$_2$]·MeCN has a trans arrangement of two ring sulfur atoms in the S$_2$PdCl$_2$ fragment: the S(1)−Pd(1)−S(2) angle is, here, 172.82(2)°. The trans arrangement of sulfur atoms, which is a rare case for palladium-(II) complexes with bidentate ligands,[7] is probably due to the large size of the cavity of benzodithia-21-crown-7 ether **8**, which allows the formation of an inclusive complex with palladium(II). It can be seen in Figure 6c that the formation of trans-[Pd(8)Cl$_2$]
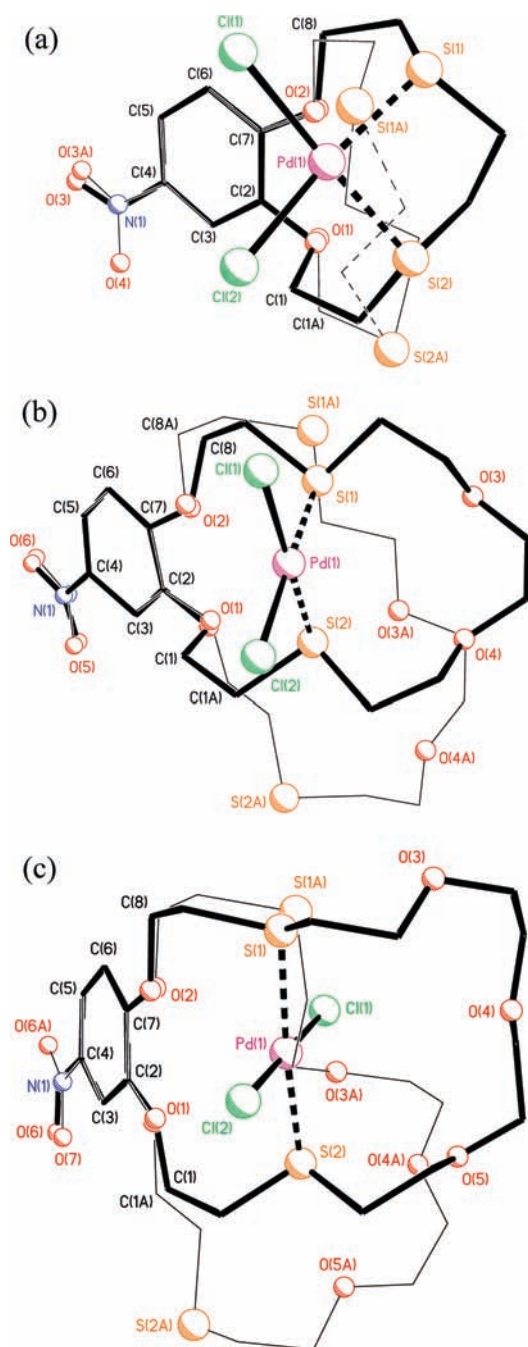
Figure 6. Superposition over the benzene rings: (a) complex cis-[Pd-(5)Cl$_2$] and free dithiacrown ether **1**, (b) complex cis-[Pd(3)Cl$_2$] and free **3** (for the predominant conformer of cis-[Pd(3)Cl$_2$]), (c) complex trans-[Pd(8)Cl$_2$]·MeCN and free **4**.

changes the macrocycle conformation in such a way that the formation of the trans complex with two sulfur atoms requires displacement of only one of them, S(2): the S(1)···S(2) distance in the complex is 4.64 Å vs 8.01 Å in free **4**. The formation of the complex trans-[Pd(8)Cl$_2$] does not apparently induce considerable strain in the 21-membered dithiamacrocycle, as indicated by the absence of noticeable changes in the bond angles at O(1) and O(2) atoms and maintenance of small torsion angles, C(1)−O(1)−C(2)−C(3) and C(8)−O(2)−C(7)−C(6) (−9.3 and −0.4°, respectively), compared with those in **4** (−2.0 and

0.8°). The set of obtained data attests to a rather high conformational flexibility of the benzodithia-21-crown-7-ether macrocycle; this allows the ring rearrangement for the formation of the inclusive *trans* complex with palladium(II) chloride without inducing considerable steric strain.

CONCLUSIONS

Thus, we synthesized previously unknown 1:1 and 1:2 Pd(II) complexes with nitro- and formylbenzothiacrown-ether derivatives. The configuration of benzodithiacrown-ether complexes was found to depend on the macrocycle size. An increase in the ring size in the benzodithiacrown ether from a 12- to 18- to 21-membered ring resulted in transition from the *cis* to *trans* arrangement of two S atoms in the palladium(II) coordination plane, giving rise to inclusive complexes with the Pd(II) atom located approximately at the center of the macroheterocycle cavity. The results allow one to forecast the possibility of using benzothiacrown ethers as efficient and selective macrocyclic ligands for the extraction of palladium(II) and as structural fragments in chromoionophore compounds for palladium(II) determination by optical methods.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Calculated proton chemical shifts for crown ethers **1**−**4** and their complexes with PdCl$_2$ compared with the experimental data (Table S1), Cartesian coordinates of their optimized structures, correlation between the calculated and experimental proton chemical shifts of the complexes (Figure S1), selected bond lengths and angles (Table S2) and crystallographic data and structure refinement (Table S3) for crystalline complexes, and X-ray crystallographic data for *cis*-[Pd(**5**)Cl$_2$] in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

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(21) Conformation energy, E_{conf}, is the energy of a given conformer with respect to the lowest-energy conformer.