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Synthesis and crystal structure of *cis* and *trans* complexes of benzodithia-18(21)-crown-6(7) ethers with $PdCl_2$

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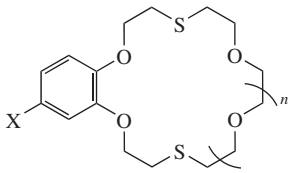
The *cis* and *trans* complexes of nitro- and formylbenzodithia-18(21)-crown-6(7) ethers with $PdCl_2$ are synthesized and studied by X-ray diffraction and ^{1}H NMR spectroscopy.

Sulfur-containing macrocyclic compounds exhibit high affinity to transition, heavy and noble metal cations and form stable complexes.[1–3] These compounds can be used, for example, for efficient and selective determination and extraction of Hg^{2+}, Ag^+, and platinum group metals from aqueous solutions, in ion-selective electrodes, *etc*. The structure of the complex formed through the interaction of a thiacrown compound with a metal cation is governed by the nature of the metal (its oxidation degree, typical coordination number, and preferred geometry of the donor atoms in its coordination sphere), the nature of the counterions, and the structure of the macroheterocycle.

Inclusion of a noble metal cation in a cavity of a thiacrown compound is rarely observed, and the match between the macrocycle cavity size and the ionic radius of the metal cation is not the factor governing the efficiency and selectivity of complexation,[4,5] as it happens with the complexation of conventional oxygen-containing crown ethers with alkali and alkaline-earth cations.[6] Thus, 1:1 complexes between palladium(II) salts and oxathiacrown compounds known from literature, where the crown ether acts as a bidentate ligand, exhibit mainly *cis* structure, in which Pd^{II} is not included in the macrocycle cavity. Formation of similar *trans* complexes, in which Pd^{II} is located in the macrocycle cavity, is only sporadic.[5] The effect of the cavity size of the sulfur-containing crown compounds on formation of *cis* or *trans* complexes with palladium(II) salts was not studied before. This study is necessary to understand the peculiarities of the complexation of the most promising thiacrown ethers that can be used as efficient and selective complexing agents for platinum group metals. Benzodithia-crown ethers, whose structure fragments are used in chromo-ionophores, namely, styryl and butadienyl dyes,[7,8] are of special interest.

Here we report a synthesis and NMR and X-ray diffraction study of the structure of $PdCl_2$ complexes with bidentate ligands, namely, nitro- and formylbenzodithia-18(21)-crown-6(7) ethers **1**–**4**.

The synthesis of dithiacrown ethers **1**–**4** was described earlier.[9,10] The complexes were produced by interaction of the ligands with $[PdCl_2(MeCN)_2]$ in acetonitrile.† According to ^{1}H NMR spectroscopy data, all the complexes in solution exist as one isomer, because their spectra exhibit only one set of signals. The fact that ^{1}H NMR spectra of [Pd(**1**)Cl_2] and [Pd(**3**)Cl_2], as well as [Pd(**2**)Cl_2] and [Pd(**4**)Cl_2], are identical in the crown ether region indicates that the macrocycles of the same size containing different functional groups in the benzene ring give similar complex structures. That is, the functional groups located far from Pd^{II} atom have no effect on the complex geometry. This is obviously true for crystalline complexes as well; therefore, comparing the crystal structures of [Pd(**1**)Cl_2] and [Pd(**4**)Cl_2] complexes found by X-ray diffraction is correct (see below). Additionally, one may expect that the complexes with dithia-crown ethers of the same size have similar configuration both in solution and in crystal.



1 X = NO_2, n = 1
2 X = NO_2, n = 2
3 X = CHO, n = 1
4 X = CHO, n = 2

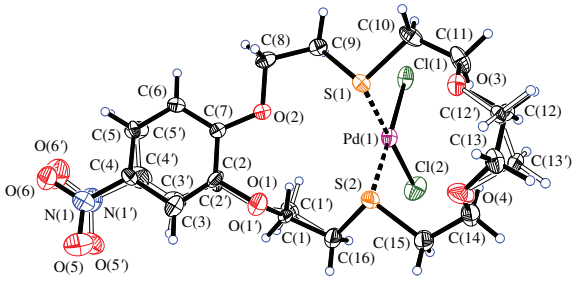


Figure 1 Complex structure of *cis*-[Pd(**1**)Cl_2] shown in the displacement ellipsoids at the 30% probability level. The minor components of the disordered fragments are shown by open lines.

The structure of dithiacrown ether **1** and **4** complexes with $PdCl_2$ was found by X-ray diffraction.‡ Figure 1 shows the structure of *cis*-[Pd(**1**)Cl_2] complex, in which the two sulfur atoms of the ligand and chlorine anions form covalent bonds with Pd(1) atom; Pd(1)–S and Pd(1)–Cl distances are close, 2.287(3)–2.317(2) Å. Palladium exhibits a typical square planar coordination[5] with the *cis* arrangement of sulfur atoms in the S_2PdCl_2 fragment; the S(1)–Pd(1)–S(2) angle is 87.7(1)°; the deviation of the central Pd(1) atom from the average plane of its coordinating atoms is only 0.003 Å. Here, Pd(1) atom substantially deviates from the average plane passing through all the heteroatoms of macrocycle **1** (by 2.17 Å), which obviously results from the *cis* arrangement of the sulfur atoms in the coordination plane of palladium. Oxygen atoms of macrocycle **1** in this complex are rather far from Pd(1); Pd(1)···O distances are within 3.70–4.34 Å, which is much greater than the sum of the ionic radius of Pd^{2+} and van der Waals radius of O (2.36 Å). This means lack of coordination of the 'hard' oxygen atoms with 'soft' Pd^{II}, which is typical of this metal.[5] A substantial disorder of the crown ether links at the periphery of the coordination site found in *cis*-[Pd(**1**)Cl_2] results from the lack of Pd(1)···O contacts that could have fixed the conformation of a rather flexible 18-membered macrocycle.

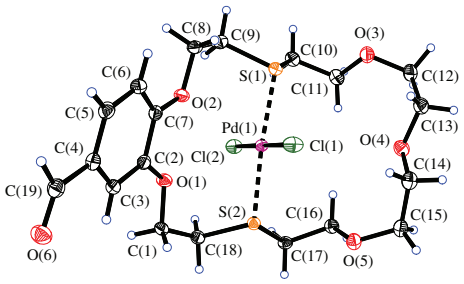


Figure 2 Complex structure of *trans*-[Pd(**4**)Cl_2]·MeCN shown in the displacement ellipsoids at the 50% probability level. The solvate MeCN molecule is omitted.

Figure 2 shows the structure of *trans*-[Pd(**4**)Cl_2]·MeCN complex. Pd(1) atom in this complex also exhibits a square planar coordination with Pd(1)–S and Pd(1)–Cl distances within 2.2953(7)–2.3244(7) Å and deviation of Pd(1) from the average plane of its coordinating atoms being 0.029 Å. The difference from the previous complex is in the *trans* arrangement of the two sulfur atoms of the macrocycle in the S_2PdCl_2 fragment; S(1)–Pd(1)–S(2) angle is 172.82(2)°. The *trans* arrangement of the sulfur atoms rarely observed in palladium(II) complexes with bidentate ligands[5,13] obviously results from the large cavity size of benzodithia-21-crown-7 ether **4**, which facilitates the

† NMR spectra were recorded on a Bruker DRX500 spectrometer at 30 °C. IR spectra were measured on a Shimadzu IR-435 instrument in KBr pellets. Mass spectra (MALDI) were recorded on a Bruker UltraFlex spectrometer.

General procedure for the synthesis of the complexes. A solution of benzothiacrown ether **1**–**4** (0.21 mmol) in dry MeCN (3 ml) was added dropwise with stirring to a solution of [$PdCl_2$(MeCN)$_2$] (Fluka) (83 mg, 0.32 mmol) in dry MeCN (5 ml) at room temperature. The reaction mixture was cooled to –10 °C (for compounds **1** and **2**) or left at room temperature for 1–3 days (for compounds **3** and **4**). The resulting yellow precipitate was filtered off, washed with dry MeCN, and dried in air.

cis-[Pd(**1**)Cl_2]: yield 59%; mp 248–250 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ: 2.85 (m, 4H, 2C*H*H′S, 2CH*H*′S), 3.75 (m, 4H, 2C*H*H′S, CH_2O), 3.80 (m, 4H, 2C*H*H′O, CH_2O), 4.17 (br. m, 3H, 2C*H*H′OAr, CH*H*′S), 4.26 (m, 1H, CH*H*′S), 4.36 (m, 2H, 2CH*H*′O), 4.86 (br. m, 2H, 2CH*H*′OAr), 7.07 (d, 1H, H^{20}, *J* 8.5 Hz), 7.89 (br. s, 1H, H^{17}), 8.00 (br. d, 1H, H^{19}, *J* 8.5 Hz). IR (ν/cm^{-1}): 1511 (NO_2). MS, *m*/*z*: 529 [M – HCl]$^+$ (with ^{106}Pd and ^{35}Cl). Found (%): C, 34.06; H, 4.16; N, 2.46; Cl, 12.88. Calc. for $C_{16}H_{23}Cl_2NO_6PdS_2$ (566.81) (%): C, 33.90; H, 4.09; N, 2.47; Cl, 12.51.

trans-[Pd(**2**)Cl_2]: yield 51%; mp 226–227 °C (decomp.). ^{1}H NMR ([$^2H_3$]MeCN) δ: 2.58 (br. m, 2H, 2C*H*H′S), 2.89 (br. m, 2H, 2CH*H*′S), 3.54 (br. m, 6H, 2C*H*H′S, 2CH*H*′S, CH_2O), 3.70 (br. m, 4H, 2CH_2O), 3.79 (br. m, 2H, CH_2O), 3.88 (br. m, 2H, 2C*H*H′O), 4.21 (br. m, 2H, 2C*H*H′OAr), 4.44 (br. m, 2H, 2CH*H*′O), 4.64 (br. m, 2H, 2CH*H*′OAr), 7.03 (d, 1H, H^{23}, *J* 8.9 Hz), 7.74 (d, 1H, H^{20}, *J* 2.4 Hz), 7.94 (dd, 1H, H^{22}, *J* 8.9 Hz, *J* 2.4 Hz). IR (ν/cm^{-1}): 1521 (NO_2). MS, *m*/*z* 573 [M – HCl]$^+$ (with ^{106}Pd and ^{35}Cl). Found (%): C, 35.42; H, 4.58, N, 2.23. Calc. for $C_{18}H_{27}Cl_2NO_7PdS_2$ (610.86) (%): C, 35.39; H, 4.46, N, 2.29.

cis-[Pd(**3**)Cl_2]: yield 58%; mp 182–184 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ: 2.83 (m, 4H, 2C*H*H′S, 2CH*H*′S), 3.72 (m, 4H, 2C*H*H′S, CH_2O), 3.79 (m, 4H, 2C*H*H′O, CH_2O), 4.12 (m, 3H, 2C*H*H′OAr, CH*H*′S), 4.22 (m, 1H, CH*H*′S), 4.32 (m, 2H, 2CH*H*′O), 4.79 (m, 2H, 2CH*H*′OAr), 7.10 (d, 1H, H^{20}, *J* 7.9 Hz), 7.50 (br. s, 1H, H^{17}), 7.56 (br. d, 1H, H^{19}, *J* 7.9 Hz), 9.88 (s, 1H, CH=O). ^{13}C NMR ($CDCl_3$) δ: 39.51 (CH_2S), 39.77 (CH_2S), 40.18 (CH_2S), 40.39 (CH_2S), 66.90 (2CH_2O), 67.29 (CH_2OAr), 67.88 (2CH_2O), 67.97 (*C*H_2OAr), 116.59 (C^{20}), 117.39 (C^{17}), 127.53 (C^{19}), 131.88 (C^{18}), 149.09 (C^{16a}), 154.39 (C^{20a}), 190.51 (CH=O). IR (ν/cm^{-1}): 1696 (C=O). MS, *m*/*z*: 512 [M – HCl]$^+$ (with ^{106}Pd and ^{35}Cl). Found (%): C, 37.35; H, 4.60; Cl, 12.48. Calc. for $C_{17}H_{24}Cl_2O_5PdS_2$ (549.82) (%): C, 37.14; H, 4.40; Cl, 12.90.

trans-[Pd(**4**)Cl_2]: yield 48%; mp 219–221 °C (decomp.). ^{1}H NMR ([$^2H_3$]MeCN) δ: 2.58 (br. m, 2H, 2C*H*H′S), 2.88 (br. m, 2H, 2CH*H*′S), 3.53 (br. m, 6H, 2C*H*H′S, 2CH*H*′S, CH_2O), 3.69 (br. m, 4H, 2CH_2O), 3.78 (br. m, 2H, CH_2O), 3.88 (br. m, 2H, 2C*H*H′O), 4.17 (br. m, 2H, 2C*H*H′OAr), 4.46 (br. m, 2H, 2CH*H*′O), 4.62 (br. m, 2H, 2CH*H*′OAr), 7.07 (d, 1H, H^{23}, *J* 8.2 Hz), 7.37 (br. d, 1H, H^{20}, *J* 1.8 Hz), 7.54 (dd, 1H, H^{22}, *J* 8.2 Hz, *J* 1.8 Hz), 9.85 (s, 1H, CH=O). IR (ν/cm^{-1}): 1689 (C=O). MS, *m*/*z*: 557 [M – Cl]$^+$ (with ^{106}Pd and ^{35}Cl). Found (%): C, 39.21; H, 5.23; Cl, 11.10. Calc. for $C_{19}H_{28}Cl_2O_6PdS_2$·MeCN·0.3H_2O (640.34) (%): C, 39.39; H, 4.97; Cl, 11.07.

‡ Yellow single crystals of [Pd(**1**)Cl_2] and [Pd(**4**)Cl_2]·MeCN complexes were grown by slow evaporation of MeCN solutions of ligands mixed with [$PdCl_2$(MeCN)$_2$] (at a 1:1.5 molar ratio) at room temperature. The X-ray diffraction experiments were carried out on a Bruker SMART-CCD diffractometer [MoKα radiation (λ = 0.71073 Å), graphite monochromator, ω-scanning; *T* = 120.0(2) K]. The X-ray intensity data were processed using the Bruker SAINT software.[11] The absorption corrections were applied using the SADABS method.

The structures were solved by a direct method and refined anisotropically by the full-matrix least-squares method against F^2. In [Pd(**1**)Cl_2] crystal, the nitrobenzene fragment and the fragment of the polyether chain between O(3) and O(4) atoms are disordered over two positions with site occupation ratios of 0.53:0.47 and 0.60:0.40, respectively. The unit cell of the $PdCl_2$ complex with **4** was found to contain a solvate acetonitrile molecule. The positions of hydrogen atoms (excluding the hydrogens of the solvate acetonitrile molecule) were calculated geometrically and then refined using a riding model for [Pd(**1**)Cl_2] or isotropically for [Pd(**4**)Cl_2]·MeCN. The hydrogen atoms of the solvate acetonitrile molecule corresponding to the two rotational positions are found from difference electron density synthesis. The site occupation ratio for these positions is 0.58:0.42. All calculations were carried out with the use of the SHELXTL-Plus program package.[12]

For [Pd(**1**)Cl_2]: $C_{16}H_{23}Cl_2NO_6PdS_2$, *M* = 566.77, tetragonal, space group $P\bar{4}2_1c$, *a* = *b* = 21.8342(8) and *c* = 9.2074(5) Å, *V* = 4389.5(3) Å^3, *Z* = 8, d_{calc} = 1.715 g cm^{-3}, μ(MoKα) = 1.311 mm^{-1}, goodness-of-fit on F^2 0.981, 44565 collected reflections including 5821 independent ones (R_{int} = 0.1690), *R* indices for 3336 reflections with $I > 2\sigma(I)$ in the θ range of 1.87–28.99°, R_1 = 0.0604 and wR_2 = 0.1429, for all reflections R_1 = 0.1371 and wR_2 = = 0.1736, residual electron density (min/max) is –0.896/0.955 eÅ^{-3}.

For [Pd(**4**)Cl_2]·MeCN: $C_{21}H_{31}Cl_2NO_6PdS_2$, *M* = 634.89, triclinic, space group $P\bar{1}$, *a* = 9.4358(19), *b* = 9.845(2) and *c* = 14.186(3) Å, α = 104.09(3)°, β = 97.14(3)° and γ = 94.61(3)°, *V* = 1259.9(4) Å^3, *Z* = 2, d_{calc} = 1.674 g cm^{-3}, μ(MoKα) = 1.152 mm^{-1}, goodness-of-fit on F^2 1.081, 23454 collected reflections including 6690 independent ones (R_{int} = 0.0477), *R* indices for 6416 reflections with $I > 2\sigma(I)$ in the θ range of 2.15–28.99°, R^1 = 0.0261 and wR_2 = 0.0638, for all reflections R_1 = 0.0275 and wR_2 = 0.0646, residual electron density (min/max) is –0.646/0.563 eÅ^{-3}.

CCDC 713081 and 713082 contain 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. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2009.

formation of its inclusion complex with $PdCl_2$. Indeed, the deviation of Pd(1) from the average plane passing through all the heteroatoms of the macrocycle is only 0.36 Å. However, as in *cis*-[Pd(**1**)Cl2] complex, large Pd(1)···O distances (2.98–4.38 Å) indicate the lack of coordination of the oxygen atoms with palladium(II) atom.

Therefore, we synthesized previously unreported complexes of nitro- and formylbenzodithiacrown ethers with $PdCl_2$ and found that their configuration depends on the macrocycle size of the ligand. As the macrocycle of a benzodithiacrown ether increases from 18- to 21-membered ring, *cis* arrangement of the two S atoms in the coordination plane of palladium(II) changes to *trans* arrangement, and inclusion complexes are formed with Pd^{II} atom located approximately in the cavity center of the macroheterocycle.

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