Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 74 (4) 389–400 (2009)
JSCS–3840

UDC 546.982–386:548.7:535.441
Original scientific paper

Palladium(II) complexes with R_2edda derived ligands. Part I. Reaction of diisopropyl (*S*,*S*)-2,2'-(1,2-ethanediyldiimino)-dipropanoate with $K_2[PdCl_4]$

BOJANA B. KRAJČINOVIĆ[1#], GORAN N. KALUĐEROVIĆ[1,2*#], DIRK STEINBORN[2], HARRY SCHMIDT[2], CHRISTOPH WAGNER[2], KURT MERZWEILER[2], SREĆKO R. TRIFUNOVIĆ[3] and TIBOR J. SABO[4#]

[1]*Department of Chemistry, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Studentski trg 14, 11000 Belgrade, Serbia,* [2]*Institut für Chemie, Martin-Luther--Universität Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle, Germany,* [3]*Department of Chemistry Faculty of Science, University of Kragujevac, 34000 Kragujevac and* [4]*Faculty of Chemistry, University of Belgrade, P.O. Box 158, 11001 Belgrade, Serbia*

(Received 24 June, revised 6 October 2008)

Abstract: The reaction of $K_2[PdCl_4]$ with (*S*,*S*)-(*i*-Pr)$_2$eddip diester (diisopropyl (*S*,*S*)-2,2'-(1,2-ethanediyldiimino)dipropanoate) resulted in {$PdCl_2$[(*S*,*S*)-(*i*--Pr)$_2$eddip-κ^2*N*,*N*']} (**1**) and {PdCl[(*S*,*S*)-(*i*-Pr)eddip-κ^2*N*,*N*',κ*O*]} (**2**) with one hydrolyzed ester group. The compounds were characterized by spectroscopic methods and it was proved that the reaction is diastereoselective (^{1}H- and ^{13}C-NMR) in the case of **2** (one diastereoisomer of four possible). The structure of **2** was determined by X-ray diffraction analysis, indicating that the product is the (*R*,*R*)-*N*,*N*' configured isomer. In contrast, the reaction yielding **1** produced two of three possible diastereoisomers. DFT calculations support the formation of two diastereoisomers of **1** and of one diastereoisomer of **2**.

Keywords: palladium complexes; crystal structure; EDDP ligands; DFT calculations.

INTRODUCTION

In a previous study, platinum(IV) complexes with R_2edda (esters of ethylenediamine-*N*,*N*'-diacetic acid) ligands were prepared (R = Me, Et or *n*-Pr; Fig. 1, **I**).[1] In contrast, reactions between homologous propionate ligands (R_2eddp = = ROOCCH_2CH_2NHCH_2CH_2NHCH_2CH_2COOR; R = Me, Et, *n*-Pr, *n*-Bu or *n*-Pe), and potassium hexachloroplatinates(IV) gave different products depending on the R moiety (Fig. 1, **II** and **III**)[2,3]. For R = Me, Et or *n*-Pr, these reactions

* Corresponding author. E-mail: goran@chem.bg.ac.yu
# Serbian Chemical Society member.
doi: 10.2298/JSC0904389K

proceeded with the hydrolysis of the ester groups yielding [$PtCl_2$(eddp-κ^2*N*,*N*',κ^2*O*,*O*')] (Fig. 1, **II**). Structural analysis gave proof of the *trans*-dichloro arrangement. When R was *n*-butyl or *n*-pentyl, the isolated platinum(IV) complexes [$PtCl_4$(R_2eddp-κ^2*N*,*N*')] maintained the ester functions of the ligand intact, see **III** in Fig. 1.[2]

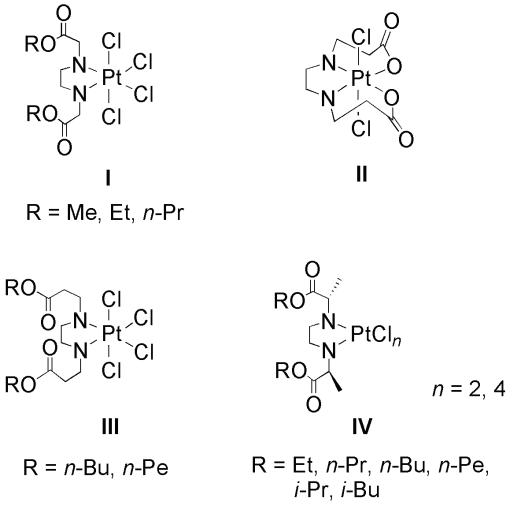


Fig. 1. Platinum complexes containing R_2edda derived ligands.

Furthermore, the work was extended by synthesizing chiral branched-chain esters, (*S*,*S*)-R_2eddip = ROOC$C^{(S)}$H(CH_3)NHCH_2CH_2NH$C^{(S)}$H(CH_3)COOR (R = = Et, *n*-Pr, *n*-Bu, *n*-Pe, *i*-Pr or *i*-Bu), and the corresponding platinum(II/IV) complexes, {$PtCl_n$[(*S*,*S*)-R_2eddip]} (*n* = 2 or 4; Fig. 1, **IV**).[4] Also here, as in the reaction of R_2edda and hexachloroplatinate(IV), the ligands maintained their ester functional groups without hydrolyzing in the obtained complexes. Studies on the antitumoral activity of some Pt(IV) complexes with R_2edda derived ligands showed higher cytotoxicity than cisplatin and the kinetics of the tumor cell death process induced by these complexes was considerably faster in comparison to that induced by cisplatin.[5,6]

The coordination mode of palladium(II) and platinum(II) is analogous, but the palladium(II) complexes are kinetically less stable than the platinum(II) complexes.[7,8] Due to the similar coordination modes and chemical properties of palladium(II) and platinum(II) compounds, it was also decided to synthesize and characterize complexes of palladium(II) with edta tetraalkyl esters and ethylene-diammonium-*N*,*N*'-di-3-propanoic acid.[9,10] In the light of the increasing interest in the biological activity of palladium(II) complexes, their antiproliferative activity is also of interest.[11–13]

The complexes {$PdCl_2$[(*S*,*S*)-(*i*-Pr)$_2$eddip]} (**1**) and {PdCl[(*S*,*S*)-(*i*-Pr)eddip]} (**2**) were prepared and spectroscopically and structurally characterized. In addition, DFT calculations were conducted on the diastereoisomers of **1** and **2**.

EXPERIMENTAL

General

[(*S*,*S*)-H_3eddip]Cl and [(*S*,*S*)-H_2(*i*-Pr)$_2$eddip]$Cl_2 \cdot H_2O$ were prepared as previously reported.[4,14-16] $K_2[PdCl_4]$ was obtained from Merck and used as received. The infrared spectra were recorded on a Perkin-Elmer FTIR 31725-X spectrophotometer using the KBr pellet technique (4000–400 cm^{-1}). The ^1H- and ^{13}C-NMR spectra were recorded on Varian Gemini 200 (200 MHz) (**1**) and Varian Unity 500 (500 MHz) spectrometers (**2**) in $CDCl_3$ and DMF-d_7, respectively. Elemental analyses for C, H and N were performed on a Vario III CHNOS Elemental Analyzer, Elementar Analysensysteme GmbH.

Synthesis of complexes

$K_2[PdCl_4]$ (0.158 g, 0.512 mmol) was dissolved in water (20 ml) at 40 °C and [(*S*,*S*)-H_2(*i*-Pr)$_2$eddip]$Cl_2 \cdot H_2O$ (0.194 g, 0.512 mmol) was added. During 2 h of stirring, 10 ml of 0.10 M LiOH was added in small portions to the reaction solution. On cooling to room temperature, a yellow precipitate of **1** was obtained. The precipitate was filtered off and the filtrate was left for several days at room temperature. The mother liquor produced crystals of **2** suitable for X-ray measurement.

*X-ray crystallography of **2***

Intensity data were collected on a STOE IPDS diffractometer at 220(2) K using graphite monochromatized Mo–K_α radiation (λ = 0.71073 Å). A summary of the crystallographic data, the data collection parameters and the refinement parameters are given in Table I. The structure was solved by direct methods with SHELXS-96 and refined using full-matrix least-squa-

TABLE I. Crystallographic data for **2**

Empirical formula	$C_{11}H_{21}ClN_2O_4Pd$
M_r	387.17 g mol^{-1}
Crystal system	monoclinic
Space group	$P\,2_1$
a / Å	5.877(1)
b / Å	9.672(2)
c / Å	14.424(3)
β / °	100.78(2)
V / Å^3	805.5(3)
Z	2
D_{calc} / g cm^{-3}	1.584
μ(Mo–K_α) / mm^{-1}	1.328
F(000)	392
θ Range / °	2.55–25.80
Refln. collected	1637
Refln. observed ($I > 2\sigma(I)$)	1543
Refln. independent	1637
Data/restraints/parameters	1637/1/177
Goodness-of-fit on F^2	1.079
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0316, 0.0789
$R1$, $wR2$ (all data)	0.0338, 0.0797
Largest diff. peak and hole / e Å^{-3}	1.02/–1.64

res routines against F^2 with SHELXS-97.[17,18] Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically. They were placed in the calculated positions with fixed displacement parameters (riding model), except for H12 atom, which was found in the electron density map. The large displacement parameters of atoms C5, C6 and O1 are explained by oscillation in the crystal structure and because these atoms are far away from the palladium atom. The Diamond program was used for the representation of the structure.[19]

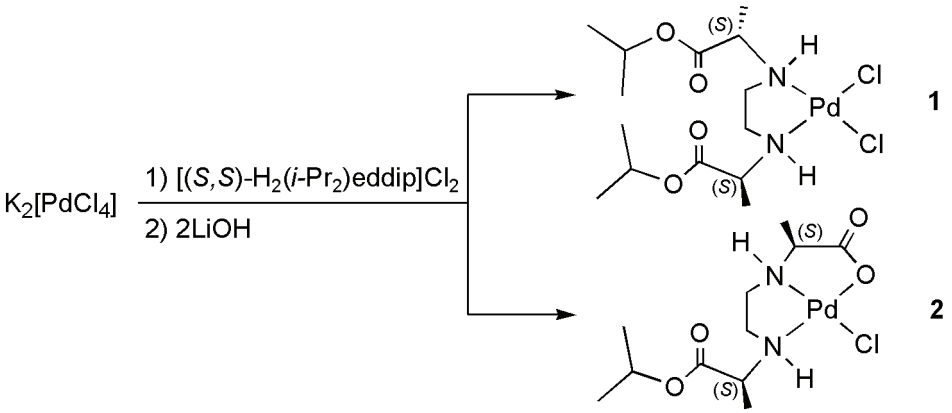
The Cambridge Crystallographic Data Centre, CCDC No. 681419, contains supplementary crystallographic data for this paper.*

Computational details

Geometry optimizations were performed with the Gaussian 03 package.[20] All structures were optimized using the MPW1PW91 functional.[21] The SDD basis set for all atoms was employed in the calculations.[22,23] All systems were optimized without symmetry restrictions. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of normal vibrations. Supplementary data associated with the quantum chemical calculations can be obtained from the authors upon request.

RESULTS AND DISCUSSION

The addition of an aqueous solution containing the ligand precursor [(*S*,*S*)-H_2(*i*-Pr)$_2$eddip]Cl_2 to a solution of $K_2[PdCl_4]$ followed by the addition of the stoichiometric amount of base (molar ratio 1:1:2) results in the formation of a yellow precipitate of **1** (56 % yield). The mother liquor was left for several days at room temperature and crystals of **2** (20 % yield) suitable for X-ray analysis were obtained (Scheme 1). The $\kappa^2N,N',\kappa O$ coordination mode of the [(*S*,*S*)-(*i*-Pr)-eddip]$^-$ ligand in complex **2** arises from the hydrolysis of one of the two ester groups of the original (*S*,*S*)-(*i*-Pr)$_2$eddip ligand.



Scheme 1. Reaction of $K_2[PdCl_4]$ with [(*S*,*S*)-H_2(*i*-Pr)$_2$eddip]Cl_2.

*These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccfdc/cam.ac.uk).

Characterization of the complexes

*{PdCl$_2$[(*S,S*)-(i-*Pr*)$_2$eddip]} (**1**)*. Yield: 0.13 g (56 %). Anal. Calcd. for $C_{14}H_{28}Cl_2N_2O_4Pd$: C, 36.11; H, 6.06; N, 6.02. Found: C, 35.79; H, 6.33; N, 5.77 %. IR (KBr, cm^{-1}): 3448, 3153, 2983, 1734, 1380, 1224, 1187, 1143, 1105, 918, 830, 754, 430. ^{1}H-NMR* (200 MHz, $CDCl_3$, δ / ppm): 1.25/1.32 (*d*/*d*, 12H, $^3J_{H,H}$ = 6.60/7.80 Hz, $C_{5,6}H_3$), 1.61/2.00 (*d*/*d*, 6H, $^3J_{H,H}$ = 7.00/7.60 Hz, $C_{3,9}H_3$), 2.44/3.21 and 2.81/3.68 (*m*/*m*, 4H, AA'BB', $C_{10,11}H_2$), 4.09/4.52 (*m*/*m*, 2H, $C_{2,8}H$), 5.03/5.15 (*m*/*m*, 2H, C_4H), 6.12–6.26/6.31–6.42 (*m*/*m*, 2H, NH). ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 14.6/16.0 (*s*/*s*, $\mathbf{C}_{3,9}$), 21.7/21.7 (*s*/*s*, $\mathbf{C}_{5,6}$), 48.7/51.9 (*s*/*s*, $\mathbf{C}_{10,11}$), 57.4/59.0 (*s*/*s*, $\mathbf{C}_{2,8}$), 69.3/69.9 (*s*/*s*, $\mathbf{C}_4$), 169.4/170.9 (*s*/*s*, $\mathbf{C}_{1,7}$).

*{PdCl$_2$[(*S,S*)-(i-*Pr*)eddip]} (**2**)*. Yield: 0.04 g (20 %). IR (KBr, cm^{-1}): 3441, 3357, 3127, 2985, 1737, 1644, 1389, 1219, 1104, 944, 833, 590, 430. ^{1}H-NMR (500 MHz, DMF-d_7, δ / ppm): 1.23 (*d*, 6H, $^3J_{H,H}$ = 6.95 Hz, $C_{5,6}H_3$), 1.75 (*d*, 3H, $^3J_{H,H}$ = 7.21 Hz, C_3H_3), 1.76 (*d*, 3H, $^3J_{H,H}$ = 7.21 Hz, C_9H_3), 2.73 and 2.90 (*m*, 4H, $C_{10,11}H_2$), 3.69 (*m*, 1H, C_8H), 4.05 (*m*, 1H, C_2H), 4.96 (*m*, 1H, C_4H), 6.55–6.65 (*m*, 1H, N_1H), 6.68–6.77 (*m*, 1H, N_2H). ^{13}C-NMR (125 MHz, DMF-d_7, δ, ppm): 14.8 (*s*, $\mathbf{C}_3$), 15.6 (*s*, $\mathbf{C}_9$), 21.0 (*s*, $\mathbf{C}_{5,6}$), 49.4 (*s*, $\mathbf{C}_{11}$), 52.5 (*s*, $\mathbf{C}_{10}$), 56.4 (*s*, $\mathbf{C}_2$), 62.2 (*s*, $\mathbf{C}_8$), 68.9 (*s*, $\mathbf{C}_4$), 169.6 (*s*, $\mathbf{C}_1$), 181.1 (*s*, $\mathbf{C}_7$).

Spectroscopic properties

The IR spectrum of **1** shows specific absorption bands: ν(C=O) at 1734 cm^{-1} (strong), (typical absorption for aliphatic esters), ν(C–O) at 1236 cm^{-1} (strong) and ν(CH_3) at 2983 cm^{-1} (medium). For comparison [(*S*,*S*)-H_2(i-Pr)$_2$eddip]Cl_2 exhibited the corresponding bands at 1734, 1239 and 2982 cm^{-1}, respectively.[4] The band for the C=O group is at the same position as in the spectrum of the free ligand, meaning that the oxygen atoms of the COOR moieties are not coordinated. In the IR spectrum of **2**, there are two absorption bands for ν(C=O) at 1737 and 1644 cm^{-1}, indicating two different C=O groups, which is in correspondence with the hydrolysis of one of the isopropyl groups and the coordination of the residual oxygen atom. The ν(N–H) absorption bands at 3153 (for **1**) and 3127 cm^{-1} (for **2**) (both typical absorptions for secondary amino groups) may indicate that the coordination occurred *via* the nitrogen atoms.[2–4]

For both complexes **1** and **2**, the NMR spectroscopic measurements gave proof for their constitution. Selected data are given in Table II. The coordination of the N atoms gives rise to the formation of chiral centers, thus in principle, three diastereoisomers can be formed for [$PdCl_2${(*S*,*S*)-(*i*-Pr)$_2$eddip}] (**1**) ((*R*,*R*), (*R*,*S* ≡ *S*,*R*) and (*S*,*S*), Fig. 2). Two sets of signals of about the same intensity (for each diastereoisomer one set of signals) were found (Table II). Two of these

*The values for the two diastereoisomers are separated by a slash. The assignment was verified by COSY experiments.

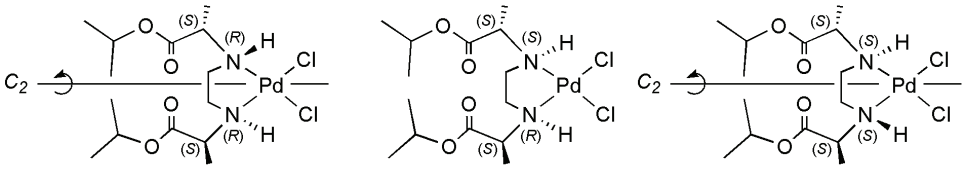
three possible diastereoisomers (*S*,*S*)- and (*R*,*R*)-*anti*-**1**, will give rise (due to C_2 symmetry) to one set of resonances each for their ester branches. The third diastereoisomer, (*R*,*S*)-*syn*-**1**, is expected to give rise to two sets of signals, since the ester branches are non-equivalent in symmetry, although these two sets may coincide by chance.

TABLE II. Selected ^{1}H- and ^{13}C-NMR data (δ / ppm)[a] of {$PdCl_2$[(*S*,*S*)-(*i*-Pr)$_2$eddip]} (**1**) and {PdCl[(*S*,*S*)-(*i*-Pr)eddip]} (**2**)

Complexes	$C^{3,9}\mathbf{H}_3$	$C^4\mathbf{H}$	$C^{5,6}\mathbf{H}_3$	$\mathbf{C}^{3,9}$	$\mathbf{C}^4$	$\mathbf{C}^{1,7}$OO	$\mathbf{C}^{5,6}H_3$
1[b]	1.61	5.03	1.25	14.6	69.3	169.4	21.7
	2.00	5.15	1.32	16.0	69.9	170.9	21.7
2	1.75	4.96	1.23	14.8	68.9	169.6	21.0
	1.76			15.6		181.1	

[a]Numbering as in Fig. 3 and analogous for {$PdCl_2$[(*S*,*S*)-(*i*-Pr)$_2$eddip]}; [b]diastereoisomers of **1**

In the ^{1}H-NMR spectrum, the signals of the methylene hydrogen atoms from the ethylenediamine moiety show coordination induced shifts of up to 0.9 ppm, which indicates that the coordination occurred *via* the nitrogen atoms. Chemical shifts arising from ester carbon atoms are found at the expected position for this class of compounds.[1,3,4]



(*R*,*R*)-*anti*-**1** (*R*,*S*)-*syn*-**1** (*S*,*S*)-*anti*-**1**

Fig. 2. Diastereoisomers of {$PdCl_2$[(*S*,*S*)-(*i*-Pr)$_2$eddip]} (**1**).

In contrast, four diastereoisomers are possible in **2**: (*S*,*S*)- and (*R*,*R*)-*anti*-**2** and (*S*,*R*)- and (*R*,*S*)-*syn*-**2**, but only one set of signals was found in both the ^{1}H- and ^{13}C-NMR spectra (Table II). In the ^{13}C-NMR spectrum, it can be seen that two signals assigned to carbon atoms from the COO moieties are at very different shift values. Comparison with [(*S*,*S*)-H_2(*i*-Pr)$_2$eddip]Cl_2 gave proof that the signal at 169.6 ppm belongs to the ester carbon atom and the signal at 181.1 ppm belongs to the carbon atom of the carboxyl group that participates in the coordination *via* its oxygen atom.

*Solid state structure of **2***

{PdCl[(*S*,*S*)-(*i*-Pr)eddip]} was found to crystallize in the monoclinic crystal system in the chiral space group $P2_1$. The molecular structure is shown in Fig. 3, and selected bond lengths and angles are listed in Table III.

The Pd atom was found in square–planar coordination geometry with one [(*S*,*S*)-(*i*-Pr)eddip]$^-$ ligand coordinated through one carboxylic oxygen and two

nitrogen atoms (κ^2*N*,*N*',κ*O* coordination mode). The remaining coordination site is occupied by the chloro ligand. The crystal structure represents the (*R*,*R*)–*N*,*N*' configured isomer.

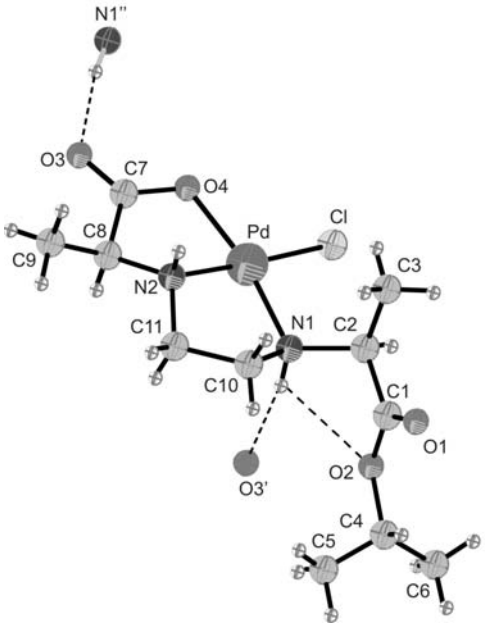


Fig. 3. Molecular structure of {PdCl[(*S*,*S*)-(*i*-Pr)eddip]} (**2**). The dashed lines represent H-bonds.

TABLE III. Selected experimentally found bond lengths (Å) and angles (°) in the molecular structure of **2** and the calculated values (2**c**) for the diastereoisomers of **2**

Bond	Compound				
	2	(*R*,*R*)-*anti*-**2c**	(*R*,*S*)-*anti*-**2c**	(*S*,*R*)-*anti*-**2c**	(*S*,*S*)-*anti*-**2c**
Pd–N2	1.995(5)	2.039	2.045	2.032	2.034
Pd–O4	2.019(5)	2.003	2.012	2.002	2.006
Pd–N1	2.047(6)	2.078	2.077	2.079	2.055
Pd–Cl	2.325(1)	2.344	2.340	2.350	2.353
C1–O1	1.190(1)	1.234	1.234	1.241	1.243
C1–O2	1.314(1)	1.374	1.376	1.353	1.351
C4–O2	1.441(1)	1.495	1.500	1.495	1.497
C7–O3	1.216(8)	1.242	1.242	1.242	1.243
C7–O4	1.316(8)	1.334	1.337	1.336	1.337
C10–N2	1.476(8)	1.494	1.502	1.494	1.504
C11–N1	1.508(8)	1.502	1.500	1.515	1.508
N2–Pd–N1	86.3(2)	86.5	85.5	87.2	86.5
N2–Pd–Cl	177.1(1)	177.2	178.3	176.8	175.2
O4–Pd–N1	167.7(2)	168.9	166.2	169.8	169.1
O4–Pd–Cl	95.2(1)	98.2	97.8	98.6	101.6
N1–Pd–Cl	96.6(1)	92.2	95.4	91.5	88.8
N2–C10–C11	108.2(6)	108.4	110.6	109.6	111.5

TABLE III. Continued

Bond	Compound				
	2	(*R*,*R*)-*anti*-**2c**	(*R*,*S*)-*anti*-**2c**	(*S*,*R*)-*anti*-**2c**	(*S*,*S*)-*anti*-**2c**
N1–C11–C10	108.9(5)	109.9	109.8	112.3	113.1
C3–C2–N1	112.0(6)	114.1	114.1	113.3	113.8
N2–C8–C9	113.0(5)	113.2	113.3	113.2	112.8
C11–N1–Pd	106.9(4)	106.1	102.6	106.2	103.3
C7–O4–Pd	113.7(4)	114.6	113.2	114.3	113.5

The Pd–N bond lengths (1.995(5)–2.047(6) Å) are shorter than those found in palladium complexes with edta tetra-alkyl ester ligands (2.098(4)–2.106(7) Å).[9,24–26] The Pd–N1 bond length is in the range for Pd(II) complexes with ethylenediamine ligands (2.03–2.09 Å).[14,27] The Pd–O bond length of 2.019(5) Å in **2** is consistent with the range of values (1.999(6)–2.105(3) Å) reported for five- and six-membered chelates containing Pd–O bonds.[28,29] The Pd–Cl bond length (2.325(1) Å) is in the same range as those in $[PdCl_2(R_4edta)]$ and $[PdCl_2(H_4edta)]\cdot xH_2O$ (R = Me or Et; x = 5 or 6; 2.287(2)–2.298(2) and 2.30(1) Å, respectively).[9,25,26]

In the structure of **2**, intramolecular hydrogen bonds N1–H···O2 (N1···O2 = = 2.838(9) Å, N1–H···O2 = 102°) and intermolecular N1–H···O3 hydrogen bonds (N1···O3 = 2.997(8) Å, N1–H···O3 = 170°, Fig. 3), which fulfill the geometric parameters given in the literature,[30–33] were found. As the H atoms could not be located in the electron density map, the discussion of these hydrogen bonds is restricted to the heavy atoms. It may be possible that the hydrogen on the N1 atom participates in a bifurcated hydrogen bond, giving rise to the formation of one-dimensional chains in the crystals of **2**.

Quantum chemical calculations

To investigate the selectivity of the formation of only one of the four possible isomers of **2** and to presume which two isomers were formed in the case of **1**, quantum chemical calculations were employed. DFT calculations were conducted for the isomers arising from the coordination of [(*S*,*S*)-(*i*-Pr)$_2$eddip] and its partly hydrolyzed derivative [(*S*,*S*)-(*i*-Pr)eddip]$^-$ to palladium(II). The optimized structures of the {$PdCl_2$[(*S*,*S*)-(*i*-Pr)$_2$eddip]} (**1c**) and {PdCl[(*S*,*S*)-(*i*-Pr)eddip]} (**2c**) complexes are represented in Figs. 4 and 5, respectively. The structures were fully optimized without any symmetry constraints and were found to represent equilibria structures.

In the case of complex **1c**, the results showed that (*R*,*R*)-*anti*-**1c** and (*R*,*S*)-*syn*-**1c** diastereoisomers appear to be structurally and synthetically feasible (Fig. 4). Namely, the energy difference between the (*R*,*R*)-*anti*-**1c** and (*R*,*S*)-*syn*-**1c** isomers amounts to 0.7 kcal/mol (2.9 kJ/mol), which is within the error of DFT calculations, so that these isomers are of the same energy. The third diastereoisomer (*S*,*S*)-

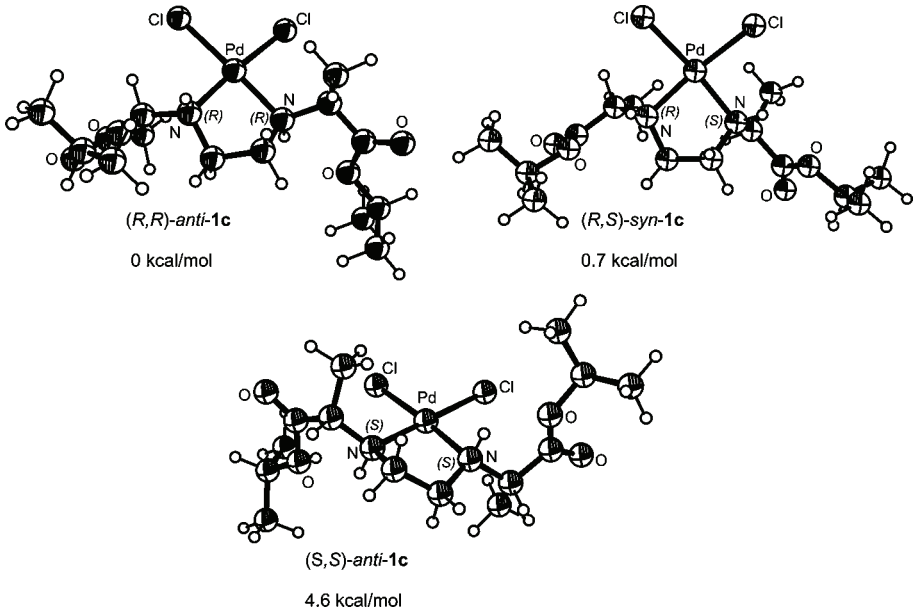


Fig. 4. Calculated structures of {$PdCl_2${(*S*,*S*)-(*i*-Pr)$_2$eddip]} (**1c**) (the energies are relative to the most stable isomer (*R*,*R*)-*anti*-**1c**).

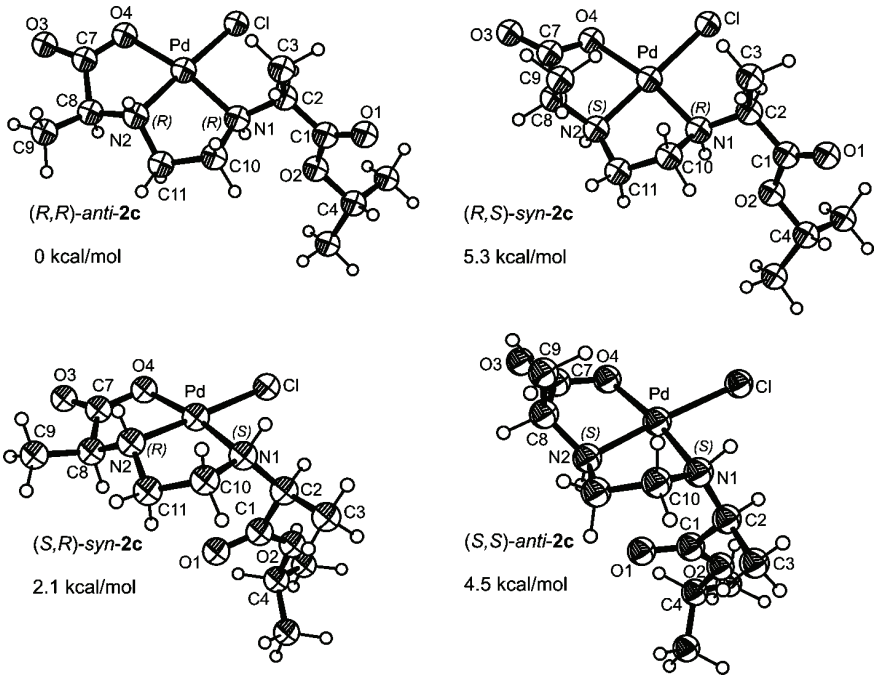


Fig. 5. Calculated structures of {PdCl[(*S*,*S*)-(*i*-Pr)eddip]} (**2c**) (the energies are relative to the most stable isomer (*R*,*R*)-*anti*-**2c**).

-*anti*-**1c** is 4.6 kcal/mol (19.2 kJ/mol) higher in energy than (*R*,*R*)-*anti*-**1c** and the formation of this isomer is not to be expected. This indicates that the obtained two isomers of **1**, proved by NMR spectroscopy (within the sensitivity limits of NMR spectroscopy), could be assigned as (*R*,*R*)-*anti*-**1c** and (*R*,*S*)-*syn*-**1c**. This is consistent with a recently reported study on DFT calculations of platinum(II) complexes with the Et_2edda ligand.[1]

Furthermore, from the quantum chemical calculations, it is apparent that three of the four isomers of **2c** have more strain and that they are higher in energy than (*R*,*R*)-*anti*-**2c** by 2.1–5.3 kcal/mol (8.8–22.2 kJ/mol) (Fig. 5). Thus, this indicates that the (*R*,*R*)-*anti*-**2c** isomer is thermodynamically more stable than the other isomers and that the energy differences correlate well with the results from X-ray crystallography and NMR spectroscopic investigations. As can be seen from a comparison of the calculated and experimental bond lengths and angles shown in Table III, the calculated values for (*R*,*R*)-*anti*-**2c** are in good agreement with the results obtained from X-ray structural analysis.

CONCLUSIONS

The present investigation shows that the [(*S*,*S*)-H_2(*i*-Pr)$_2$eddip]Cl_2 ligand precursor reacts with $K_2[PdCl_4]$ yielding the corresponding {$PdCl_2$[(*S*,*S*)-(*i*-Pr)$_2$eddip]} complex (**1**) and the palladium(II) complex with a partly hydrolyzed ester {PdCl[(*S*,*S*)-(*i*-Pr)eddip]} (**2**). In case of **1**, two from the three possible isomers were detected (^{1}H- and ^{13}C-NMR spectroscopy). In contrast, the reaction yielding **2** is diastereoselective, only one from the four possible diastereoisomers was formed, (*R*,*R*)-*anti*-**2** (^{1}H- and ^{13}C-NMR spectroscopy, X-ray structural analysis). Quantum chemical calculations for **1** proposed the formation of the (*R*,*R*)-*anti*-**1** and (*S*,*R*)-*anti*-**1** diastereoisomers and confirmed the formation of the (*R*,*R*)-*anti*-**2** diastereoisomer for **2**.

Acknowledgement. G. N. Kaluđerović gratefully acknowledges the financial support from the Alexander von Humboldt Foundation. The authors are grateful to the Ministry of Science and Technological Deveplopment of the Republic of Serbia for financial support (Grants No. 142010 and 142008). We thank Sebastian Schwieger (Universität Halle) for helpful discussions.

ИЗВОД

КОМПЛЕКСИ ПАЛАДИЈУМА(II) СА ЛИГАНДИМА R_2EDDA ТИПА. ДЕО I. РЕАКЦИЈА ДИИЗОПРОПИЛ-(*S*,*S*)-2,2'-(1,2-ЕТАНДИИЛДИИМИНО)ДИПРОПАНОАТА СА $K_2[PdCl_4]$

БОЈАНА Б. КРАЈЧИНОВИЋ[1], ГОРАН Н. КАЛУЂЕРОВИЋ[1,2], DIRK STEINBORN[2], HARRY SCHMIDT[2], CHRISTOPH WAGNER[2], KURT MERZWEILER[2], СРЕЋКО Р. ТРИФУНОВИЋ[3] и ТИБОР Ј. САБО[4]

[1]*Институт за хемију, технологију и металургију – Центар за хемију,Универзитет у Београду, Студентски трг 14, 11000 Београд,* [2]*Institut für Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle, Germany,* [3]*Департман за хемију, ПМФ, Универзитет у Крагујевцу, 34000 Крагујевац и* [4]*Хемијски факултет, Универзитет у Београду, п.пр. 158, 11001 Београд*

У реакцији $K_2[PdCl_4]$ са (*S*,*S*)-(*i*-Pr)$_2$eddip диестром [диизопропил-(*S*,*S*)-2,2'-(1,2-етандиилдиимино)дипропаноат] добијају се {$PdCl_2$[(*S*,*S*)-(*i*-Pr)$_2$eddip-κ^2*N*,*N*']} (**1**) и {PdCl[(*S*,*S*)-(*i*-

-Pr)eddip-κ^2*N*,*N*',κ*O*]} (**2**) са једном хидролизованом естарском групом. Једињења су окарактерисана спектроскопским методама и доказано је да је ова реакција дијастереоселективна (^{1}H- и ^{13}C-NMR) у случају **2** (један дијастереоизомер од могућа четири). Структура једињења **2** је одређена рендгенском структурном анализом и нађено је да је добијени производ (*R*,*R*)–*N*,*N*' изомер. Супротно томе, у случају једињења **1** добијени производ је смеша два од три могућа дијастереоизомера. DFT прорачуни потврђују формирање два дијастереоизомера једињења **1** и једног дијастереоизомера једињења **2**.

(Примљено 24. јуна, ревидирано 6. октобра 2008)

REFERENCES

1. G. N. Kaluđerović, H. Schmidt, S. Schwieger, Ch. Wagner, R. Paschke, A. Dietrich, T. Müller, D. Steinborn, *Inorg. Chim. Acta* **361** (2008) 1395
2. T. J. Sabo, G. N. Kaluđerović, S. R. Grgurić-Šipka F. W. Heinemann, S. R. Trifunović, *Inorg. Chem. Commun.* **7** (2004) 241
3. G. N. Kaluđerović, V. M. Đinović, Z. D. Juranić, T. P. Stanojković, T. J. Sabo, *J. Inorg. Biochem.* **99** (2005) 488
4. B. B. Krajčinović, G. N. Kaluđerović, D. Steinborn, H. Schmidt, Ch. Wagner, Ž. Žižak, Z. D. Juranić, S. R. Trifunović, T. J. Sabo, *J. Inorg. Biochem.* **102** (2008) 892
5. G. N. Kaluđerović, D. Miljković, M. Momčilović, V. M. Đinović, M. Mostarica-Stojković, T. J. Sabo, V. Trajković, *Int. J. Cancer* **116** (2005) 479
6. S. Mijatović, D. Maksimović-Ivanić, J. Radovica, D. Miljković, G. N. Kaluđerović, T. J. Sabo, V. Trajković, *Cell. Mol. Life Sci.* **62** (2005) 1275
7. J. Ruiz, J. Lorenzo, L. Sanglas, N. Cutillas, C. Vicente, M. D. Villa, F. X. Avilés, G. López, V. Moreno, J. Pérez, D. Bautista, *Inorg. Chem.* **45** (2006) 6347
8. E. R. Jamieson, S. J. Lippard, *Chem. Rev.* **99** (1999) 2467
9. G. N. Kaluđerović, H. Schmidt, Ch. Wagner, K. Merzweiler, D. Steinborn, *Collect. Czech. Chem. Commun.* **72** (2007) 560
10. G. N. Kaluđerović, F. W. Heinemann, N. Ž. Knežević, S. R. Trifunović, T. J. Sabo, *J. Chem. Crystallogr.* **34** (2004) 185
11. I. Brudzińska, Y. Mikata, M. Obata, Ch. Ohtsuki, Sh. Yano, *Bioorg. Med. Chem. Lett.* **14** (2004) 2533
12. B. T. Khan, J. Bhatt, K. Najmuddin, S. Shamsuddin, K. Annapoorna, *J. Inorg. Biochem.* **44** (1991) 55
13. C. Navarro-Ranninger, J. M. Pérez, F. Zamora, V. M. González, J. R. Masaguer, C. Alonso, *J. Inorg. Biochem.* **52** (1993) 37
14. S. Baggio, L. M. Amzel, L. N. Becka, *Acta Crystallogr. B* **26** (1970) 1698
15. G. N. Kaluđerović, T. J. Sabo, *Polyhedron* **21** (2002) 2277
16. D. B. Haydock, T. P. C. Mulholland, *J. Chem. Soc. C* (1971) 2389
17. G. M. Sheldrick, *SHELXS-96, Programs for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1997
18. G. M. Sheldrick, *SHELXS-97, Programs for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997
19. K. Branderburg, *Diamond, Release 2*, Crystal Impact GbR, Bonn, 1997
20. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H.

Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, *GAUSSIAN 03, Revision C.02*, Gaussian, J.A. Pople, Inc., Wallingford, CT, 2004

21. C. Adamo, V. Barone, *Chem. Phys. Lett.* **274** (1997) 242
22. T. H. Dunning Jr., P. J. Hay, *Modern Theoretical Chemistry*, 3rd Ed., Vol. 3, Plenum, New York, 1976, pp. 1–28
23. D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chem. Acc.* **77** (1990) 123
24. M. Kaplun, M. Sandström, D. Boström, A. Shchukarev, P. Peresson, *Inorg. Chim. Acta* **358** (2005) 527
25. D. J. Robinson, C. H. L. Kennard, *J. Chem. Soc. A* (1970) 1008
26. X.-M. Luo, X.-H. Chen, S. Shanmuga Sundara Raj, H.-K. Fun, L.-G. Zhu, *Acta Crystallogr. C* **55** (1999) 1220
27. J. R. Wiesner, E. C. Lingafelter, *Inorg. Chem.* **5** (1966) 1770
28. A. K. Singh, J. Sooriyakumar, S. Husebye, K. W. Tornroos, *J. Organomet. Chem.* **612** (2000) 46
29. D. R. Billodeaux, F. R. Fronczek, A. Yoneda, G. R. Newkome, *Acta Crystallogr. C* **C54** (1998) 1439
30. C. S. A. Fraser, H. A. Jenkins, M. C. Jennings, R. J. Puddephatt, *Organometallics* **19** (2000) 1635
31. C. J. Adams, A. Angeloni, A. G. Orpen, T. J. Podesta, B. Shore, *Cryst. Growth Des.* **6** (2006) 411
32. M. Yamada, H. Hagiwara, H. Torigoe, N. Matsumoto, M. Kojima, F. Dahan, J.-P. Tuchagues, N. Re, S. Iijima, *Chem. Eur. J.* **12** (2006) 4536
33. J. C. Mareque Rivas, E. Salvagni, R. T. M. de Rosales, S. Parsons, *Dalton Trans.* (2003) 3339.