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

J. Serb. Chem. Soc. 74 (11) 1249–1258 (2009) UDC 546.982-386+547.171’26:542.913
JSCS–3915 *Original scientific paper*

Palladium(II) complexes with R_2edda derived ligands. Part III. Diisobutyl (*S*,*S*)-2,2’-(1,2-ethanediyldiimino)di(4-methyl-pentanoate) and its palladium(II) complex: synthesis and characterization

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(Received 3 April, revised 8 June 2009)

Abstract: A new R_2edda-type ester, diisobutyl (*S*,*S*)-2,2’-(1,2-ethane-diyldi-imino)di(4-methylpentanoate) dihydrochloride, [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2, **1**, and its palladium(II) complex, dichloro(diisobutyl (*S*,*S*)-2,2’-(1,2-ethanediyldiimino)di(4-methylpentanoate))palladium(II), [$PdCl_2${(*S*,*S*)-*i*Bu_2eddl}], **2**, were synthesized and characterized by elemental analysis, as well as IR and NMR spectroscopy. It was found that complex **2** was obtained as mixture of two diastereoisomers, observed in NMR spectra. The crystal structure of compound **1** was determined by X-ray diffraction studies and is described. The isolated crystals consisted of one dicationic species [(*S*,*S*)-H_2*i*Bu_2eddl]$^{2+}$ and two Cl^-. The crystal system was tetragonal with the space group $P4_2$. Hydrogen bonds significant for the manner of packing are N–H1N···Cl, 3.049(3) Å, 159(3)° and N–H2N···Cl, 3.100(3) Å, 164(3)°. An infinite chain was formed building a one layer structure, usual for these types of compounds. The C_2 symmetry axis of the compound passes through the C1–C1^i bond vector and lies perpendicular to the plane N_2Cl_2.

Keywords: palladium complexes; crystal structure; EDDP ligands; characterization.

INTRODUCTION

The area of present research is of consequence to studies on Pt(II/IV) and Pd(II) complexes with bis(carboxyalkylamino)ethane and -propane ligands and their derivatives. Earlier, structural and antiproliferative investigations were per-

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doi: 10.2298/JSC0911249Z

formed on complexes and esters from a family of similar compounds – H_2edda- and R_2edda-derived ligands and their transition metal complexes.[1–8]

Palladium(II) and platinum(II) have very similar chemistry and analogous coordination modes, however, palladium(II) complexes are kinetically less stable.[9,10] Therefore, palladium(II) derivatives are quite often used in attempts to discover new cytotoxic compounds and to compare and determine the influence of the central metal atoms on antiproliferative activity and structure.[11–17]

Lately, our work has been focused on complexes with branch-chained esters of a chiral acid, (*S*,*S*)-ethylenediamine-*N*,*N*'-di-2-propanoic acid hydrochloride, [(*S*,*S*)-H_3eddip]Cl (Fig. 1) and a large amount of structural information was obtained, as well as information on the antiproliferative activity of platinum(II/IV) and palladium(II) complexes.[18–20]

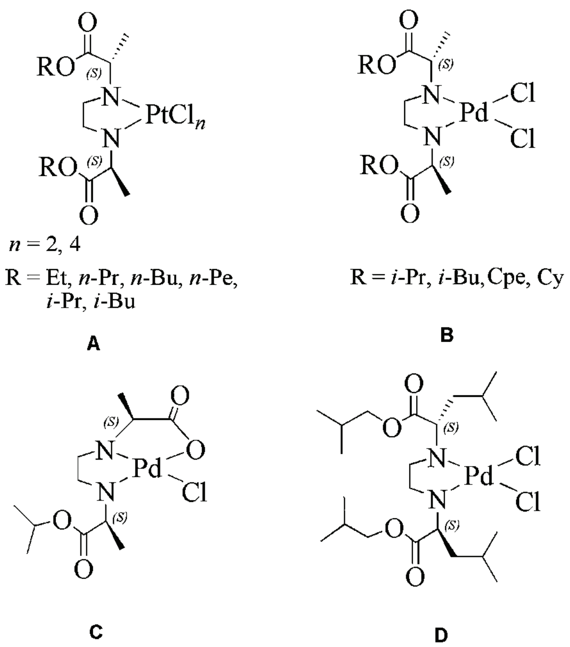
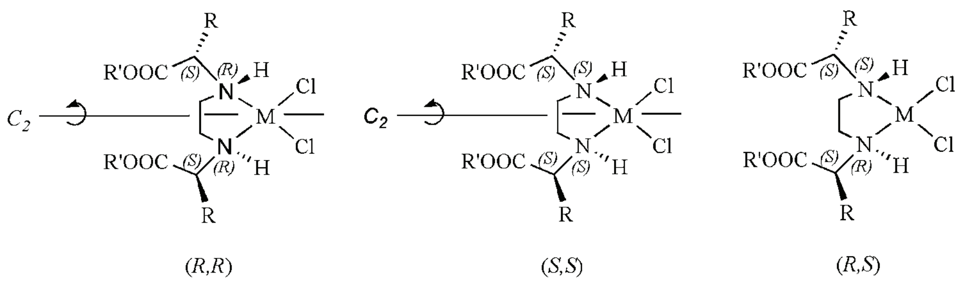


Fig. 1. Platinum and palladium complexes containing R_2edda-derived ligands.

In these complexes, three diastereoisomers could be formed (*R*,*R*), (*R*,*S* ≡ ≡ *S*,*R*) and (*S*,*S*), due to the formation of chiral centers on the coordinated nitrogen atoms (Fig. 2). Experimental data and DFT calculations showed that in the case of platinum(IV) complexes with R_2edda-type esters, a racemic mixture of (*R*,*R*) and (*S*,*S*) isomers is obtained.[1] With chiral (*S*,*S*)-R_2edda-type esters, only one diastereoisomer was isolated, the (*R*,*R*) isomer, which was determined by X-ray structure analysis[18] (Fig. 1, A). All synthesized platinum(II) and palladium(II) complexes were obtained as a mixture of two diasteroisomeric forms, *i.e.*, as (*R*,*R*) and (*R*,*S*) isomers (Fig. 1, A and B), which was verified by ^{1}H- and

^{13}C-NMR spectroscopy and supported by DFT calculations.[18–20] In a recent study, a palladium(II) complex with a partially hydrolyzed isopropyl ester of (*S*,*S*)-ethylenediamine-*N*,*N*'-di-2-propanoic acid (Fig. 1, C) was isolated and determined by X-ray structure analysis, and the (*R*,*R*)-*N*,*N*' configured isomer with the κ^2*N*,*N*',κ*O* coordination mode was found.[19] All the other complexes mentioned herein had the κ^2*N*,*N*' coordination mode of the ligand.



M = Pt(II), Pd(II); R = Me, *i*Bu; R' = *i*Pr, *i*Bu, Cpe, Cy

Fig. 2. Possible diastereoisomers of the investigated platinum(II) and palladium(II) complexes.

In this study, a new R_2edda-type ester di-isobutyl-(*S*,*S*)-2,2'-(1,2-ethane-diyldiimino)di(4-methylpentanoate) dihydrochloride, [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2, **1**, and its palladium(II) complex, diisobutyl-(*S*,*S*) 2,2'-(1,2-ethanediyldiimino)di(4-methylpentanoate))palladium(II), [$PdCl_2${(*S*,*S*)-*i*Bu_2eddl}], **2** (Fig. 1, D) were synthesized and characterized by elemental analysis, as well as IR and NMR spectroscopy. The crystal structure of **1** is also described.

EXPERIMENTAL

Materials and methods

(*S*,*S*)-2,2'-(1,2-ethanediyldiimino)di(4-methyl-pentanoic acid) dihydrochloride, [(*S*,*S*)-H_4eddl]Cl_2, was prepared using a similar method to that described in the literature.[21] $K_2[PdCl_4]$ was purchased from Merck and used without further purification. The infrared spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer using the ATR technique (4000–400 cm^{-1}). ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian "Gemini 2000" (200 MHz) spectrometer in DMSO-d_6 using tetramethylsilane as the internal standard. Elemental analyses for C, H and N were realized on a Vario EL III C, H, N, S Elemental Analyzer.

*Synthesis of [(*S*,*S*)-H_2iBu$_2$eddl]Cl_2, **1***

[(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2, **1**, was prepared using a previously described esterification reaction.[22,23]. Thionyl chloride (4.0 cm^3, 55 mmol) was introduced into a flask containing 50 ml of ice-cooled isobutanol (2-methyl-1-propanol) (anhydrous conditions) during 1 h. Subsequently, 2.0 g (5.5 mmol) of (*S*,*S*)-2,2'-(1,2-ethanediyldiimino)di(4-methyl-pentanoic acid) dihydrochloride, [(*S*,*S*)-H_4eddl]Cl_2, was added into the flask and the suspension was refluxed for 16 h. The mixture was filtered and the filtrate was stored for a few days at 4 °C. A white crystalline solid was obtained. The ester, contaminated with acid, was recrystalized from methanol. Crystals suitable for X-ray diffraction studies were obtained from the mother liquor which was stored at room temperature for several days.

*Synthesis of [PdCl$_2${(S,S)-iBu$_2$eddl}], **2***

$K_2[PdCl_4]$ (0.200 g, 0.613 mmol) was dissolved in water (20 ml) and 0.290 g (0.613 mmol) of [(*S*,*S*)-H$_2$*i*Bu$_2$eddl]Cl$_2$, **1**, was added. After 2 h of stirring, 10.2 ml of a 0.12 M solution of LiOH was added in small portions to the reaction mixture. A pale yellow precipitate was obtained, which was filtered off, dissolved in 5 ml of $CHCl_3$ and filtered. A crystalline solid of the pure complex was obtained from the mother liquor.

X-ray crystal structure determination

Data of **1** were collected with a CCD Oxford Xcalibur S (λ(Mo$_{K\alpha}$) = 0.71073 Å) using the ω and φ scans mode. Semi-empirical corrections for absorption were performed with SCALE3 ABSPACK.[24] The structure was solved by direct methods.[25] Structure refinement was realized with SHELXL-97.[26] All non-hydrogen atoms were refined anisotropically. The crystallographic details are listed in Table I. Hydrogen atoms were refined isotropically. They were placed in the calculated positions with fixed displacement parameters U_{iso}(H) = 1.2 U_{eq}(C) and U_{iso}(H) = 1.5 U_{eq}(C) (riding model), except for the hydrogen atoms attached to the nitrogen atoms which were found in the difference Fourier map and refined freely. The ORTEP-3 program was used for the presentation of the structure.[27]

The Cambridge Crystallographic Data Center, CCDC No. 723867, contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.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).

TABLE I. Crystallographic data for **1**

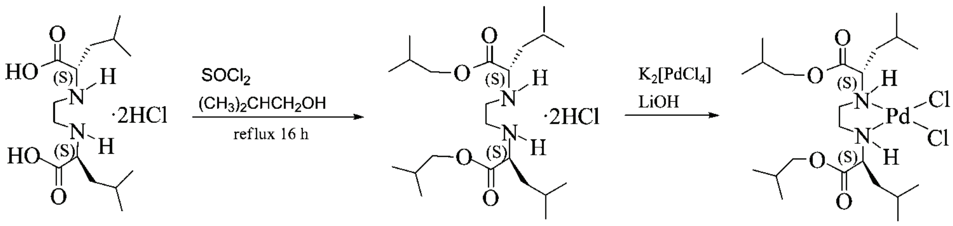
Empirical formula	$C_{22}H_{46}Cl_2N_2O_4$
M_r	473.51
Crystal system	Tetragonal
Space group	$P4_2$
a / Å	15.9708(2)
c / Å	5.2426(1)
V / Å^3	1337.21(3)
Z	2
D_{calc} / g cm^{-3}	1.176
μ(Mo-Kα) / mm^{-1}	0.27
F(000)	516
θ Range / °	2.85–25.68
Refln. collected	14178
Refln. Observed ($I > 2\sigma(I)$)	2469
Refln. independent	2002
Data/restraints/parameters	14178/3/106
Goodness-of-fit on F^2	1.349
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0588, 0.1414
$R1$, $wR2$ (all data)	0.0725, 0.1446
Flack parameter, x	–0.17(13)
Largest diff. peak and hole / e Å^{-3}	1.152/–1.018

RESULTS AND DISCUSSION

Synthesis and characterization

The ester, [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2, was synthesized using a previously described esterification reaction[17,18]. This compound is not soluble in chloroform and is poorly soluble in water. However, it is soluble in methanol and dimethyl sulfoxide.

The complex, [$PdCl_2${(*S*,*S*)-*i*Bu_2eddl}], was synthesized by combining aqueous solutions of $K_2[PdCl_4]$ and the ester. Under stirring, an aqueous solution of lithium hydroxide was added. The obtained complex is soluble in chloroform and dimethyl sulfoxide, but not soluble in water. The preparation routes of the ester and complex are shown in Scheme 1.



1 2

Scheme 1. Synthesis of the ester, **1** and the palladium complex **2**.

The analytic and spectral data for **1** and **2** are as follows (numbering as in Fig. 3):

[(S,S)-H_2iBu$_2$eddl]Cl_2 (**1**). Yield: 1.09 g (41.6 %). Anal. Calcd. for $C_{22}H_{46}Cl_2N_2O_4$: C, 55.80; H, 9.79; N, 5.92 %. Found: C, 55.84; H, 9.41; N, 5.77 %. IR (cm^{-1}): 2965, 2592, 2523, 2398, 1735, 1535, 1468, 1206, 1063, 973, 802. ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 0.90–1.00 (24H, *m*, C5H_3, C6H_3, C10H_3, C11H_3), 1.77 (6H, *m*, C3H_2, C4H), 1.94 (2H, *m*, C9H), 3.42 (4H, *m*, C1H_2), 3.98 (4H, *d*, C8H_2), 4.13 (2H, *t*, C2H), 9.90–10.40 (4H, *br*, NH_2^+). ^{13}C--NMR (50 MHz, DMSO-d_6, δ / ppm): 18.9 (C5,6), 21.4 (C10,11), 23.2 (C4), 24.5 (C9), 27.3 (C3), 41.7 (C1), 57.9 (C2), 71.8 (C8), 169.2 (C7).

[$PdCl_2${(S,S)-iBu$_2$eddl}] (**2**). Yield: 313 mg (88.4 %). Anal. Calcd. for $C_{22}H_{44}Cl_2N_2O_4Pd$: C, 45.72; H, 7.67; N, 4.85. Found: C, 45.94; H, 7.36; N, 4.97 %. IR (cm^{-1}): 3130, 2959, 2873, 1735, 1467, 1370, 1237, 1194, 1141, 976, 737. Isomer A: ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 0.90–1.10 (24H, *m*, C5H_3, 6H_3, C10H_3, C11H_3), 1.68 (6H, *m*, C3H_2, C4H), 1.90 (2H, *m*, C9H), 2.23 and 2.61 (4H, *m*, C1H_2), 3.88 (4H, *m*, C8H_2), 4.14 (2H, *m*, C2H), 6.50–6.80 (2H, *br*, NH). ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 19.0 (C5,6), 21.9 (C10,11), 23.8 (C4), 25.4 (C9), 27.3 (C3), 47.0 (C1), 58.4 (C2), 70.9 (C8), 170.1 (C7). Isomer B: ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 0.90–1.10 (24H, *m*, C5H_3, C6H_3,

C10H_3, C11H_3), 1.68 (6H, *m*, C3H_2, C4H), 1.90 (2H, *m*, C9H), 2.40 and 2.85 (4H, *m*, C1H_2), 3.88 (4H, *m*, C4H_2), 4.14 (2H, *m*, C2H), 5.85–6.25 (2H, *br*, NH). ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 19.0 (C5,6), 21.5 (C10,11), 22.9 (C4), 25.0 (C9), 27.3 (C3), 47.0 (C1), 59.1 (C2), 70.6 (C8), 171.2 (C7). Ratio of isomers A/B = 7/1.

The IR spectrum of [$PdCl_2${(*S*,*S*)-*i*Bu_2eddl}] showed specific absorption bands ν(C=O) at 1735 cm^{-1} (strong), (typical absorption for aliphatic esters), ν(C–O) at 1194 cm^{-1} (strong), ν(–CH_3, –CH_2, –CH) at 2959 and 2873 cm^{-1} (medium) (for comparison [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2: 1735, 1206, 2965 and 2871 cm^{-1}, respectively[18]). All of the mentioned bands including ν(C=O), were at similar positions to those in the spectrum of the free ligand, indicating that the oxygen atoms of the COOR moieties were not coordinated. As expected the ν(N–H) absorption bands were at 3130 cm^{-1}, (typical absorptions for secondary amino groups) and may indicate that coordination occurred *via* the nitrogen atoms.[18–20] In the ^{1}H-NMR spectrum of **2**, the broad signal of hydrogen atoms belonging to secondary amino groups appeared in the range 5.8–6.8 ppm (compared with the ammonium groups of **1**: 9.9–10.4 ppm).[18–20] The signals of the protons between the nitrogen atoms of **2** showed coordination-induced shifts in comparison with those in the spectrum of **1** and also, two signals. The situation was different in the spectrum of **1**, where only one signal was observed, which can also be confirmation of nitrogen coordination to the palladium atom. The signal for the hydrogen atom of the chiral carbon atom was observed at 4.13 ppm as a triplet for **1**, and at 4.14 ppm as a multiplet for **2**. The ^{13}C-NMR spectra of **1** and **2** exhibited signals for the carbon atom of the COO moiety at similar positions, indicating that oxygen atoms were not coordinated.[18–20] The chiral carbon atom showed a signal at 57.9 ppm for **1**, but two signals at 58.4 and 59.1 for **2**. Selected ^{1}H- and ^{13}C-NMR data of **1** and **2** are compared in Table II.

TABLE II. Selected ^{1}H- and ^{13}C-NMR data (δ / ppm, numbering as in Fig. 3 and analogous for [$PdCl_2${(*S*,*S*)-*i*Bu_2eddl}]) of [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2, **1**, and [$PdCl_2${(*S*,*S*)-*i*Bu_2eddl}], **2**

Compound		C5,6,10,11H_3	C1H_2	C2H	C10,11, C5,6	C1	C2	C7OO
1		0.90–1.00	3.42	4.13	18.9, 21.4	41.7	57.9	169.2
2	Isomer A	0.90–1.10	2.23 and 2.61	4.14	19.0, 21.9	47.0	58.4	170.1
	Isomer B	0.90–1.10	2.40 and 2.85	4.14	19.0, 21.5	47.0	59.1	171.2

*Crystal structure analysis of [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2, **1***

The compound [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2 (**1**) crystallized in the tetragonal crystal system in the chiral space group $P4_2$. The molecular structure is shown in Fig. 3. Selected bond lengths and angles are given in Table III.

The isolated crystals consisted of one dicationic species [(*S*,*S*)-H_2*i*Bu_2eddl]$^{2+}$ and two Cl^-. The most significant hydrogen bonds for the manner of packing are N–H1N···Cl, 3.049(3) Å, 159(3)° and N–H2N···Cl, 3.100(3) Å, 164(3)° and these interactions form an infinite chain (Fig. 4). The compound has a C_2 symmetry. The axis passes through the C1–C1^i bond vector and lies perpendicular to the plane N_2Cl_2.

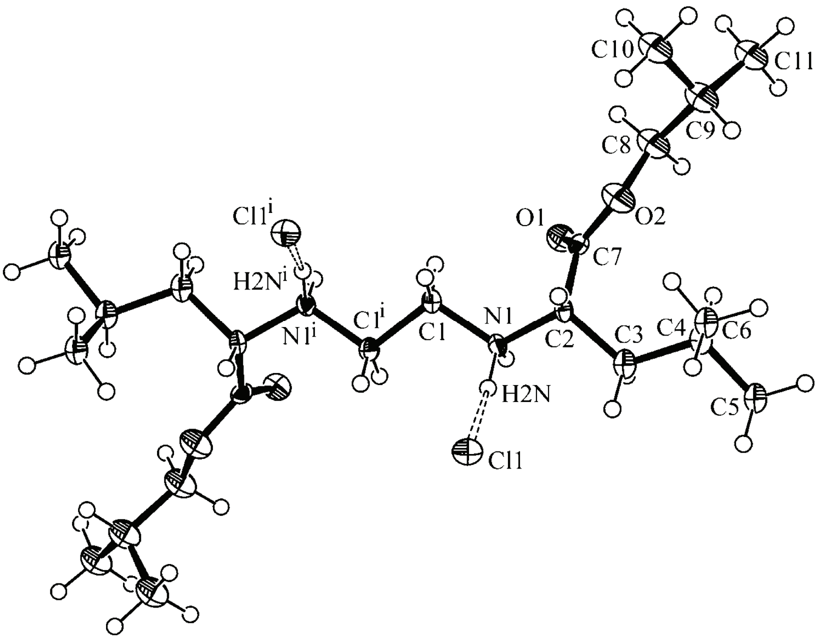


Fig. 3. ORTEP presentation of the molecular structure of **1** with the atom labeling scheme (H-bonds shown by dashed lines). The displacement ellipsoids are plotted at the 50 % probability level and the H atoms are shown as small spheres of arbitrary radii.

TABLE III. Selected bond lengths and angles for **1**

Bond	Length, Å	Bond	Angle, °
O1–C7	1.196(5)	N1–C2–C3	106.2(3)
O2–C7	1.334(5)	N1–C2–C7	110.8(3)
N1–H1N	0.99(2)	C3–C2–C7	109.9(3)
N1–H2N	0.99(2)	C7–O2–C8	115.9(4)
C3–C4	1.534(5)	C1–N1–C2	114.9(3)
C8–C9	1.507(7)	C1–N1–H1N	106(3)

Crystal structures of esters such as [(*S*,*S*)-H_2*i*Pr_2eddip]Cl_2,[18] (H_2Me_2eddp)Cl_2[28] and [(*S*,*S*)-H_2Cpe_2eddip]Cl_2[20] were previously determined. These structures are very similar to each other and to [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2 having bond lengths and angles in the same ranges, however the space groups are quite different ([(*S*,*S*)-H_2*i*Pr_2eddip]Cl_2, orthorhombic, $P22_12_1$; (H_2Me_2eddp)Cl_2, monoclinic, $P2_1/c$; [(*S*,*S*)-H_2Cpe_2eddip]Cl_2, orthorhombic, $P2_12_12$). The mentioned compounds have a C_2 symmetry axis. All of these esters form layered structures *via* hydrogen bonding similar to that shown in Fig. 4.

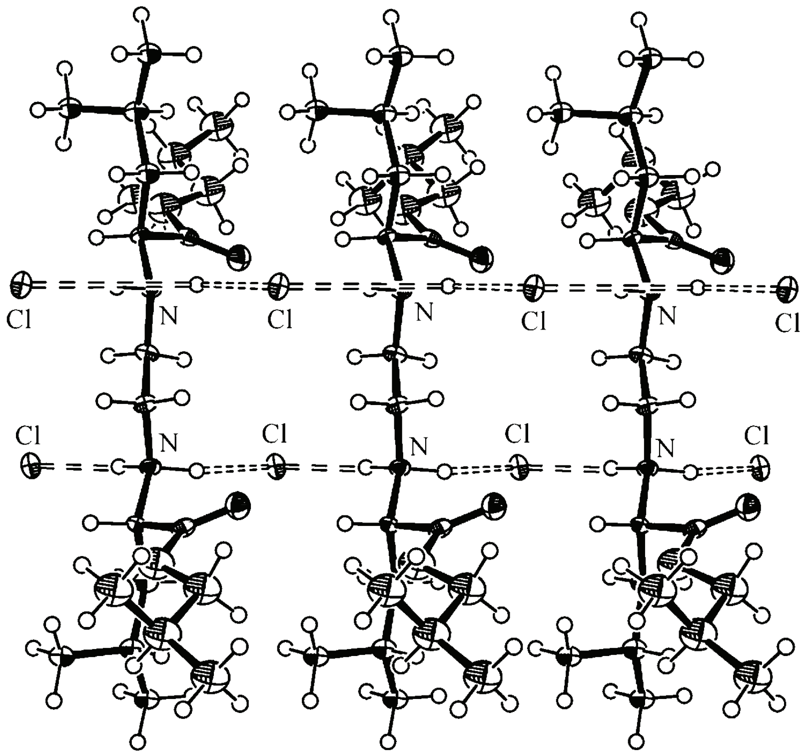


Fig. 4. ORTEP presentation of the packing *via* intermolecular hydrogen bonding of **1** viewed along the *b*-axis.

CONCLUSIONS

Two novel compounds, the R_2edda-type ester [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2, and its palladium(II) complex [$PdCl_2${(*S*,*S*)-*i*Bu_2eddl}] were synthesized and characterized by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy and elemental analysis. The crystal structure of [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2 was determined by X-ray analysis. Two diasteroisomers formed in the reaction of potassium tetrachloropalladate(II) and [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2, as was deduced from the NMR spectra.

Acknowledgements. The authors are grateful to the Ministry of Science and Technological Development of the Republic of Serbia for financial support (Grant No. 142010).

ИЗВОД

КОМПЛЕКСИ ПАЛАДИЈУМА(II) СА ЛИГАНДИМА R_2edda ТИПА. ДЕО III. ДИИЗОБУТИЛ-(*S*,*S*)-2,2'-(1,2,-ЕТАНДИИЛДИИМИНО)-ДИ(4-МЕТИЛПЕНТАНОАТ)--ДИХИДРОХЛОРИД И ЊЕГОВ КОМПЛЕКС СА ПАЛАДИЈУМОМ(II): СИНТЕЗА И КАРАКТЕРИЗАЦИЈА

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Нови естар R_2edda-типа диизобутил-(*S*,*S*)-2,2'-(1,2-етандиилдиимино)-ди(4-метилпентаноат)-дихидрохлорид [(*S*,*S*)-H_2*i*Bu_2eddl]Cl_2, **1**, и његов комплекс паладијума(II), дихлородиизобутил-(*S*,*S*)-2,2'-(1,2-етандиилдиимино)-ди(4-метилпентаноат)-паладијум(II) [PdCl_2{(*S*,*S*)-*i*Bu_2eddl}], **2**, синтетисани су и окарактерисани уз помоћ елементалне анализе, IR и NMR спектроскопије. Нађено је да је комплекс **2** добијен као смеша два дијастереоизомера, што је примећено у NMR спектрима. Кристална структура **1** је решена и описана. Изоловани кристали се састоје из једне дикатјонске врсте [(*S*,*S*)-H_2*i*Bu_2eddl]$^{2+}$ и два Cl^-. Кристални систем је тетрагоналан са просторним групом $P4_2$. Значајне водоничне везе за начин паковања су N–H1N···Cl, 3,049(3) Å, 159(3)° и N–H2N···Cl, 3,100(3) Å, 164(3)°. Тиме се формира бесконачан ланац и једнослојна структура, који су уобичајени за ове типове структура. Оса симетрије C_2 једињења пролази кроз C1–C1^i вектор везе и лежи нормално на N_2Cl_2 раван.

(Примљено 3. априла, ревидирано 8. јуна 2009)

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