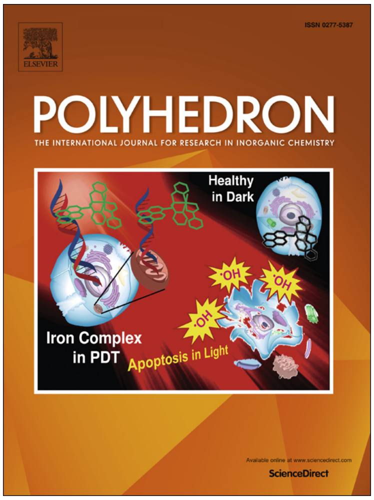

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REVISED-II

Specificity of salicylaldehyde S-alkylisothiosemicarbazones coordination in palladium(II) complexes

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Abstract

S-alkylated salicylaldehyde thiosemicarbazones (HL) form with palladium(II) the complexes **1-3** of the general formula [Pd(L)Cl], where L is monodeprotonated S-ethyl- for **1**, S-heptyl- for **2,** and S-isopropyl- for **3** derivatives of HL**.** 5-Bromosalicyladehyde S-methyl-4-phenylisothiosemicarbazone gets the complex **4 -** [Pd(L)Cl]·DMF. According to the results of X-ray investigations the **1-4** complexes reveal the square planar coordination of Pd(II). The monodeprotonated tridentate organic ligand is bound to the metal via O,N,S set of donor atoms. The fourth site is occupied by the chloride ion. This coordination mode does not allow the organic ligand to lose the second proton, keeps it as a potentially monobasic acid, does not depend on the length, topology or branching of the substituents and is a new tendency observed only for the palladium complexes.

Keywords: salicylaldehyde S-alkylisothiosemicarbazone, palladium complex, crystal structure.

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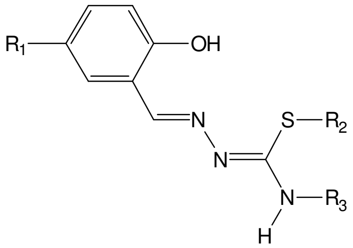
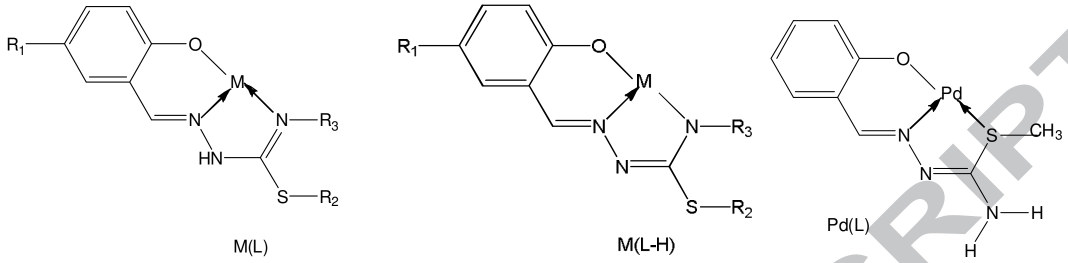
Introduction

The chemistry of the coordination compounds of thiosemicarbazones with transition metals, attracts attention due to their remarcable properties and potential applications as biologically active agents, analytical reagents, catalysts etc. [1]. As a rule, the thiosemicarbazide moiety N(1)–N(2)H–C(3)(=S)–N(4)H$_2$, in these complexes is coordinated *via* N(1),S atoms, although other binding modes have also been reported [2]. Thioalkylation of the thiosemicarbazide and its derivatives introduces a new tendency in their coordination abilities [3, 4]. The configuration of the uncoordinated salicylaldehyde S-alkylthiosemicarbazones (HL) [5] shows that HL is topologically predisposed to coordinate as an O,N,S tridentate ligand.



HL

Nevertheless, these ligands generally bind to 3d-metals *via* O,N,N donor set and behave as a monobasic acid coordinated in imino-form M(L) or as a twice deprotonated ligand in amino-form M(L-H) [6].



The survey of transition metals complexes with salicylaldehyde S-alkylthiosemicarbazones in Cambridge Structural database [7] reveals 36 complexes with O,N,N manner of coordination, and only one complex, in which this ligand is bound to the palladium(II) ion using O,N,S donor set [4] as it is shown on the scheme for Pd(L).

In order to clarify if the coordination of S-alkylthiosemicarbazones through sulphur atom is an exceptional case or it is a new trend of coordination mode of HL which occurs in palladium complexes, we have prepared and investigated the structure of four new compounds of the formulas [Pd(L)Cl] (**1**–**3**) and solvate [Pd(L)Cl]·DMF (**4**) which differ by length, topology or branching of the radicals in organic molecule. Complexes **1**–**3** differ only by R_2 in the formula HL ($R_2 = C_2H_5$ in **1**; C_7H_{15} in **2,** and *iso*-C_3H_7 in **3**), while $R_1 = R_3 = H$. The compound **4** derives from 5-bromosalicyladehyde S-methyl-4-phenylisothiosemicarbazone (R_1= Br, $R_2 = CH_3$, and $R_3 = C_6H_5$).

2. Experimental

2.1. Materials

Salicylaldehyde, 5-bromosalicylaldehyde, thiosemicarbazide, 4-phenylthiosemicarbazide, methyl iodide, ethyl iodide, iso-propyl iodide, heptyl iodide and $PdCl_2$ were purchased from Sigma-Aldrich and used as received.

2.2. Synthesis of the ligands and initial salts.

The hydroiodides of the S-alkylisothiosemicarbazides were prepared using the method reported earlier for S-methylderivative [4], refluxing 20 mmol of thiosemicarbazide and 25 mmol of the suitable alkyl iodide in 50-75 mL of dry methanol. The salicylaldehyde S-alkylisothiosemicarbazones of the general formula HL were synthesized by adding a methanol solution (40 mL) of the aldehyde (10 mmol) to the warm methanol-water (1:1) solution (100 mL) of appropriate S-alkylisothiosemicarbazides hydroiodides (10 mmol). The mixture was treated with a warm water solution (10 mL) of $NaHCO_3$ and pale yellow crystalline solids were precipitated. The resulting products were filtered, washed with methanol, diethyl ether and dried at room temperature. The purity of the products was determined by elemental C, H, and N analysis.

The salt $K_2[PdCl_4]$ was prepared according to [8].

*2.3. Synthesis of the complexes **1–4**.*

The complexes **1**–**4** were synthesized using a general method. To 10 mL of warm (65°C) water solution containing 0.326 g (1 mmol) of $K_2[PdCl_4]$, 25 mL of methanol – dimethylformamide (DMF) (1:1) solution containing 1 mmol of the respective salicylaldehyde S-alkylisothiosemicarbazones HL were added drop-wise. The mixture was maintained at this temperature during 5-7 min. Upon cooling, the obtained dark orange rhombus-shaped crystals were filtered, washed with methanol, diethyl ether, and dried in air at room temperature. The general formula of the compounds derived from salicylaldehyde S-alkylisothiosemicarbsazone is [Pd(L)Cl] (**1**–**3**). For the 5-brom derivative the formation of a solvate [Pd(L)Cl]•DMF (**4**) has been observed.

1: Orange solid, yield: 74%. *Anal.* Calc. for $C_{10}H_{12}ClN_3OPdS$: C, 32.98; H, 3.32; N, 11.54; Pd, 29.22. Found: C, 32.73; H, 3.25; N, 11.39; Pd, 29.10.

2: Orange solid, yield: 78%. *Anal.* Calc. for $C_{15}H_{22}ClN_3OPdS$: C, 41.48; H, 5.11; N, 9.67; Pd, 24.50. Found: C, 41.25; H, 5.05; N, 9.49; Pd, 24.32.

3: Orange solid, yield: 71%. *Anal.* Calc. for $C_{11}H_{14}ClN_3OPdS$: C, 34.93; H, 3.73; N, 11.11; Pd, 28.14. Found: C, 34.68; H, 3.56; N, 11.56; Pd, 28.02.

4: Orange solid, yield: 81 %. *Anal.* Calc. for $C_{18}H_{20}BrClN_4O_2PdS$: C, 37.39; H, 3.49; N, 9.69; Pd, 18.40. Found: C, 37.18; H, 3.37; N, 9.74; Pd, 18.26.

2.4. X-ray Crystallography

The X-ray intensity data for **1** and **3** were collected at a room temperature on a Xcalibur E diffractometer, and for **2** at 150K and for **4** at 100K on a Bruker-AXS SMART 1K CCD diffractometer both equipped with graphite monochromatized Mo-*K*α radiation ($\lambda = 0.71073$ Å).

The data reduction included a correction for Lorentz and polarization effects and multi-scan method of absorption correction [9a]**.** The crystal structure was solved and refined using the SHELX97 [9b] program suite. The positions of all hydrogen atoms were calculated geometrically and refined using a riding model with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C, N})$ or $1.5U_{\mathrm{eq}}(\mathrm{C(-CH_3)})$. The X-ray data and the details of the refinement of the structures are summarized in Table 1, the selected geometric parameters are given in Table 2, and hydrogen bonds geometry is given in Table 3.

Table 1
Crystal data and structure refinement parameters for compounds **1–4.**

Compound	**1**	**2**	**3**	**4**
Formula weight	364.14	434.27	378.16	578.20
Crystal system	triclinic	triclinic	triclinic	Monoclinic
Space group	$P\bar{1}$, No.2	$P\bar{1}$, No.2	$P\bar{1}$, No.2	$P2_1/c$, No.14
a (Å)	7.9960(7)	8.3345(6)	7.5233(5)	11.1525(4)
b (Å)	8.1829(4)	14.763(1)	7.7982(5)	10.8672(5)
c (Å)	11.0640(8)	15.565(1)	12.9709(9)	17.4665(5)
α (°)	99.638(5)	113.559(4)	72.564(6)	90
β (°)	90.222(6)	98.894(4)	80.118(6)	102.668(3)
γ (°)	119.126(7)	93.809(4)	66.312(6)	90
V (Å^3)	620.39(8)	1717.0(2)	663.70(8)	2065.35(13)
Z	2	4	2	4
D_{cal} (Mg/m^3)	1.949	1.680	1.892	1.859
μ (mm^{-1})	1.865	1.362	1.747	3.086
F(000)	360	880	376	1144
Crystal size (mm)	0.40x0.36x0.10	0.40x0.30x0.25	0.50x0.40x0.10	0.40x0.35x0.30
θ range for data collection (°)	2.93 – 26.50	1.46 – 25.50	2.96 – 26.50	3.28 – 25.49
Reflections collected / unique	4615 / 2560 [R(int) = 0.0294]	11135 / 6366 [R(int) = 0.0799]	4680 / 2746 [R(int) = 0.0314]	6340 / 3811 [R(int) = 0.0329]
Reflections with $I>2\sigma(I)$	2195	3818	2482	3395
Refinement method	Full-matrix least-squares on F^2			
Parameters	156	399	165	256
Completeness (%)	99.8 (θ=26.50°)	99.9 (θ=25.50°)	99.6 (θ=26.50°)	99.1 (θ=25.49°)
Goodness-of-fit on F^2	1.000	1.007	1.001	1.003
R_1, wR_2 [$I>2\sigma(I)$]	0.0344, 0.0550	0.0561, 0.1351	0.0312, 0.0703	0.0284, 0.0747
R_1, wR_2 (all data)	0.0420, 0.0602	0.1223, 0.1831	0.0359, 0.0751	0.0332, 0.0768

3. Results and discussion

The interaction of the potassium tetrachloropalladate with HL in mixed methanol-dimethylformamide solutions results in the formation of the complexes **1–4.** The ratio palladium:organic ligand in the final products is 1:1 and remains the same when the initial ratio was 1:2 or when the mixing order has been changed. Although the tridentate coordination of HL, the composition of the complexes and their square-planar structure may be anticipated, the manner of these ligands coordination to palladium ion remains unresolved, because, as we previously have shown [3, 4], the S-methyl derivative may act both as tridentate O,N,N or O,N,S ligand.

The X-ray single crystal investigation showed that crystals **1**–**4** comprise neutral [Pd(L)Cl] complexes (Fig. 1a–1d). The organic ligand in all complexes is coordinated to the palladium ion as tridentate ONS monoanion and forms with Pd(II) six-membered $PdONC_3$ and five membered PdN_2CS chelate rings. Thus, the alkylated sulfur atom is involved in coordination. It should be noted that during the formation of complexes, the ligand keeps the same configuration as in the structures of uncoordinated agent [5]. Coordination surrounding of the palladium is completed up to square-planar by the chloride anion. The distances Pd–Cl, Pd–S, Pd–N и Pd–O in **1**–**4** are in the range 2.3060(8) – 2.342(2) Å, 2.2232(4) – 2.234(3) Å, 1.969(8) – 1.979(2) Å and 2.000(9) – 2.021(6) Å, respectively, (Table 2) and close to the corresponding distances 2.311(2), 2.226(3), 1.967(7) and 1.978(6) Å in the Pd(II) complex described in [4]. The metal-ligand distances in **1**–**4** are also close to those found in the complex chloro(N-ethylsalicylidene-thisemicarbazonato)palladium(II) monohydrate [1h]. In the square planar core of all reported here complexes, the deviations of the donor atoms from their mean plane are less than 0.10 Å and Pd(II) displacement from this plane is less than 0.04 Å. The sum of bond angles at S(1) atom equals 305.1° in **1**, 302.1° in **2A**, 307.0° in **2B**, 305.9° in **3** and 308.2° in **4**. The interatomic distances in the thiosemicarbazide fragment indicate a localization of double C(8)–N(2) bond (Table 2), which is typical for the uncoordinated alkylated thiosemicarbazones molecules [5], for the coordinated twice deprotonated forms with O,N,N donor atoms [3a, 10], and tetradentate derivatives [3a, 3b, 11]. In the solvate **4** the dihedral angles between the mean planes of five-membered chelate ring and phenyl moiety attached to N(3) atom equals 8.6º. The almost coplanar mutual arrangement of these moieties is stabilized by intramolecular C(11)–H···N(2) H-bond (Table 3) [1k].

In the crystal of **1** hydrogen bonds N(3)–H···O(1) and C(4)–H···N(2) (Table 3) join complexes in the chains along [110] direction (Fig. 2a). Two metallocycles and aromatic moiety are coplanar and deviation of corresponding non-hydrogen atoms from the common plan is less then 0.04 Å. The infinite stacking interaction between this flat part of center symmetry related complexes involving aromatic moieties and both metallocycles unite chains in layers parallel to (*ab*) crystallographic plan (Fig. 2a). The interplanar separation between the plans of parallel overlapped fragments equal 3.389 and 3.399 Å. The alkyl substituents on sulphur atoms are pointed outside such layers and provide hydrophobic interactions along *c* axis.

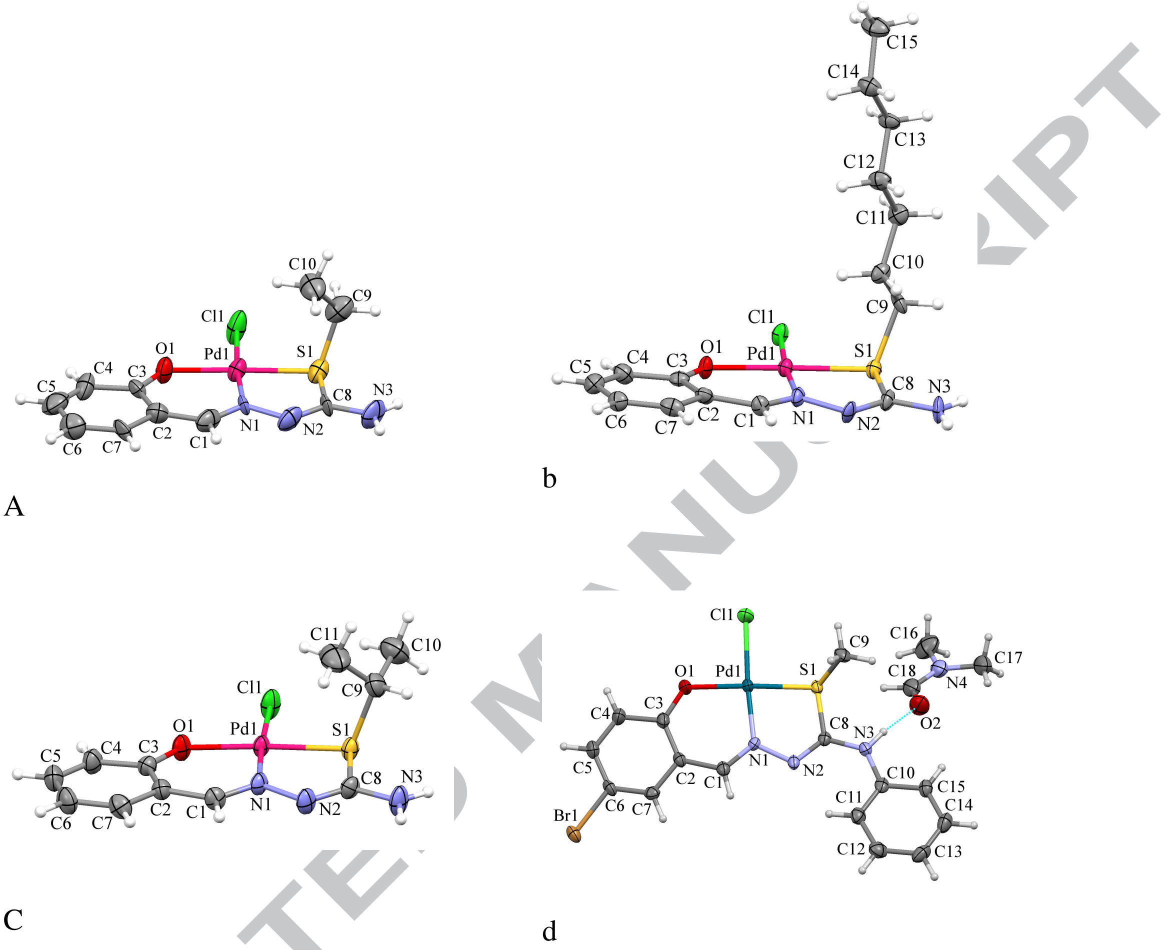


Fig. 1. ORTEP drawings for **1** (a), **2** (b), **3** (c) and **4** (d) display the formula units with atom numbering scheme. Thermal ellipsoids are shown at 50% probability level.

Table 2
Selected bond distances (Å) and angles (°) for compounds **1** – **4**

	1	**2**		**3**	**4**
		A	**B**		
Pd(1)–O(1)	2.002(2)	2.021(6)	2.013(6)	2.008(2)	2.000(2)
Pd(1)–N(1)	1.974(3)	1.969(8)	1.977(7)	1.979(2)	1.971(2)
Pd(1)–S(1)	2.2232(10)	2.234(3)	2.227(3)	2.2294(9)	2.2259(7)
Pd(1)–Cl(1)	2.3163(10)	2.342(2)	2.333(2)	2.3150(9)	2.3060(8)

	1	**2**		**3**	**4**
		A	**B**		
O(1)–Pd(1)–N(1)	93.8(1)	94.1(3)	94.0(3)	93.63(10)	94.08(9)
O(1)–Pd(1)–S(1)	178.38(7)	179.0(2)	178.9(2)	177.15(6)	174.70(6)

O(1)–Pd(1)–Cl(1)	91.40(7)	91.7(2)	91.8(2)	90.10(7)	90.04(6)
N(1)–Pd(1)–S(1)	85.24(9)	85.0(2)	85.1(2)	85.06(8)	84.94(7)
N(1)–Pd(1)–Cl(1)	174.79(9)	172.8(2)	174.1(2)	175.93(8)	173.34(7)
S(1)–Co(1)–Cl(1)	89.55(4)	89.26(9)	89.13(8)	91.14(3)	91.43(3)

	1	**2**		**3**	**4**
		A	**B**		
O(1)–C(3)	1.324(4)	1.32(1)	1.35(1)	1.317(4)	1.318(4)
N(1)–C(1)	1.297(4)	1.29(1)	1.29(1)	1.291(4)	1.303(4)
N(1)–N(2)	1.408(4)	1.383(10)	1.404(10)	1.405(3)	1.404(3)
N(2)–C(8)	1.280(4)	1.29(1)	1.30(1)	1.281(4)	1.284(4)
N(3)–C(8)	1.340(4)	1.37(1)	1.32(1)	1.336(4)	1.353(4)
N(3)–C(10)	-	-	-	-	1.409(4)
C(1)–C(2)	1.330(5)	1.42(1)	1.43(1)	1.424(5)	1.429(4)
C(2)–C(3)	1.411(5)	1.42(1)	1.43(1)	1.425(4)	1.420(4)
S(1)–C(8)	1.802(4)	1.823(10)	1.810(9)	1.806(3)	1.820(3)
S(1)–C(9)	1.814(4)	1.828(9)	1.814(10)	1.865(3)	1.813(3)

	1	**2**		**3**	**4**
		A	**B**		
C(9)–S(1)–Pd(1)	108.1(1)	107.1(3)	108.5(3)	111.0(1)	110.63(10)
C(8)–S(1)–Pd(1)	96.5(1)	96.2(3)	97.0(3)	96.3(1)	96.28(9)
C(3)–O(1)–Pd(1)	124.3(2)	124.3(6)	124.3(6)	124.7(2)	124.3(2)
C(1)–N(1)–Pd(1)	124.7(3)	123.6(7)	123.7(6)	124.6(3)	124.8(2)
N(2)–N(1)–Pd(1)	120.9(2)	121.9(6)	121.3(6)	121.0(2)	121.8(1)
C(1)–N(1)–N(2)	114.3(3)	114.4(8)	114.9(7)	114.2(3)	113.4(2)
N(1)–N(2)–C(8)	115.2(3)	115.9(8)	121.3(6)	115.2(3)	114.8(2)
N(1)–C(1)–C(2)	127.0(3)	128.6(9)	128.9(8)	127.1(3)	126.3(3)
C(1)–C(2)–C(3)	124.4(4)	124.1(9)	124.1(8)	124.8(3)	124.9(3)
O(1)–C(3)–C(2)	125.7(3)	125.2(9)	123.9(9)	124.8(3)	125.4(3)
N(2)–C(8)–N(3)	122.7(3)	122.2(9)	123.4(8)	124.0(3)	124.8(3)
N(2)–C(8)–S(1)	122.0(3)	120.9(7)	120.9(7)	122.1(2)	121.4(2)
N(3)–C(8)–S(1)	115.3(3)	116.9(8)	115.7(7)	113.9(3)	113.7(2)
C(8)–S(1)–C(9)	100.5(2)	98.8(4)	101.5(4)	98.6(2)	101.3(1)

The same hydrogen bonded chains, running along *a* axis were found in the structure of **2** for both symmetry independent complexes **A** and **B** (Table 3, Fig. 2b). Two neighboring inversion center related chains of complexes **A** are stacked in the tapes due to overlapping of parallel flat fragments each involving aromatic moiety and both metallocycles. The interplanar separation of overlapping fragments equals 3.247 Å and the non-hydrogen atoms, which constitute this fragment, deviate from the common plane within ±0.03 Å. The complex **B** does not reveal stacking interactions. The packing of tapes of complexes A and chains of complexes **B** creates the channel along *a* axis filled with cross interpenetrated bulk aryl substituents. The crystal structure of **3** is similar to **1**. The H-bounded chains run along [-110] of the unit cell (Fig. 2c, Table 3). The interplanar separation between the planes of overlapped fragments in the infinite stack equals 3.349 and 3.514 Å. In the crystal structure of **4** the molecules of DMF unite the couple of complexes in dimer *via* hydrogen bounds N(3)–H···O(2) and C(1)–H···O2 (Fig. 2d, Table 3). The crystal packing in **4** does not reveal any other specific intermolecular interactions.

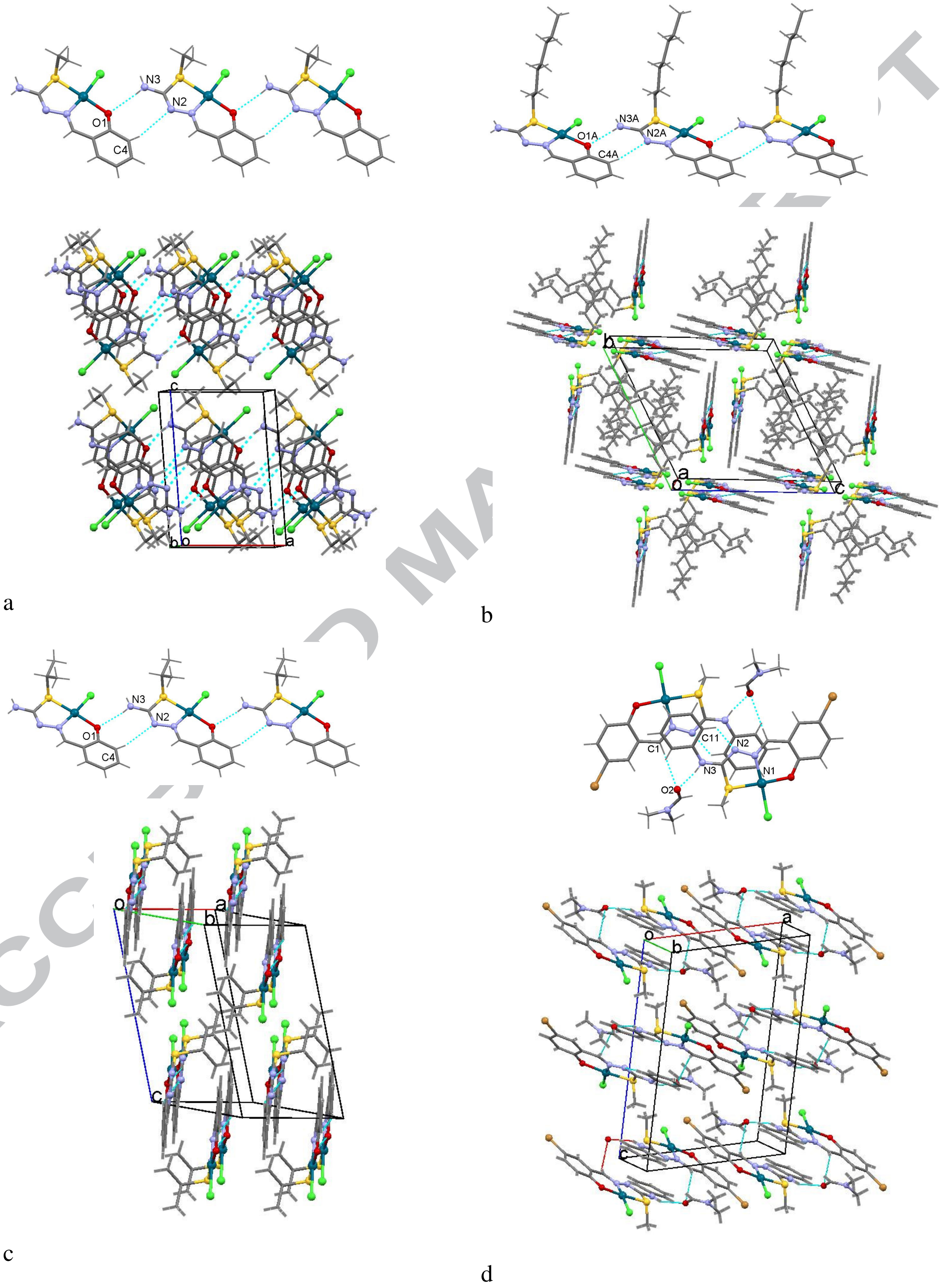


Fig. 2. Hydrogen bonded chain and packing motif in the structures **1** (a), **2** (b), **3** (c), and H-bonded dimmers and packing diagram in **4** (d).

Table 3
Selected hydrogen bond distances (Å) and angles (°) for compound **1**–**4**

D–H···A	D(H···A)	D(D···A)	∠(D–H···A)	Symmetry transformation for acceptor
		1		
N(3)–H···O(1)	2.21	2.943(4)	143	$x-1, y-1, z$
C(4)–H···N(2)	2.67	3.486	147	$x+1, y+1, z$
		2		
N(3A)–H···O(1A)	2.08	2.89(1)	157	$x+1, y, z$
C(4A)–H···N(2A)	2.61	3.527	168	$x-1, y, z$
N(3B)–H···O(1B)	2.08	2.918(10)	165	$x-1, y, z$
C(4B)–H···N(2B)	2.59	3.500	165	$x+1, y, z$
		3		
N(3)–H···O(1)	2.16	2.973(3)	152	$x+1, y-1, z$
N(3)–H···Cl(1)	2.69	3.221(3)	122	$x+1, y-1, z$
C(4)–H···N(2)	2.68	3.539	154	$x-1, y+1, z$
		4		
N(3)–H···O(2)	2.06	2.865(3)	154	x, y, z
C(1)–H···O(2)	2.70	3.440	137	$x+2, -y, -z$
C(11)–H···N(2)	2.28	2.892	123	x, y, z

4. Conclusions

Our study shows, that the treatment of the potassium tetrachloropalladate with salicylaldehyde S-alkylisothiosemicarbazones affords the square planar complexes in which monoanionic organic ligands are coordinated to Pd(II) through O,N,S donor's atom set. Regardless of the length and branching of the alkyl substituent the sulfur atom is always coordinated to Pd(II). The introduction of the substitutents in the position 5 of the salicyldehyde and 4 of thiosemicarbazide moiety influences only on the complex packing in the crystal.

Thus, we extended the knowledge about possible manner of coordination of salicylaldehyde S-alkylisothiosemicarbazones to Pd(II) from one exclusive example [4] to well defined set of complexes. Such behaviour could be treated from the positions of Pearson theory of "hard" and "soft" acids and bases [12]. Being "hard" or "intermediate" acids, the 3d-metal ions adopt the coordination of a versatile ligand as a "soft" O,N,N base, while in the case of palladium, as "soft" acid the coordination of the ligand with "hard" ONS donor is more preferable.

Acknowledgments

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Appendix A. Supplementary data

CCDC 978040 (**1**), 978041 **(2)** 978042 **(3)**, and 978039 **(4)** contain the supplementary crystallographic data for compounds **1**-**4**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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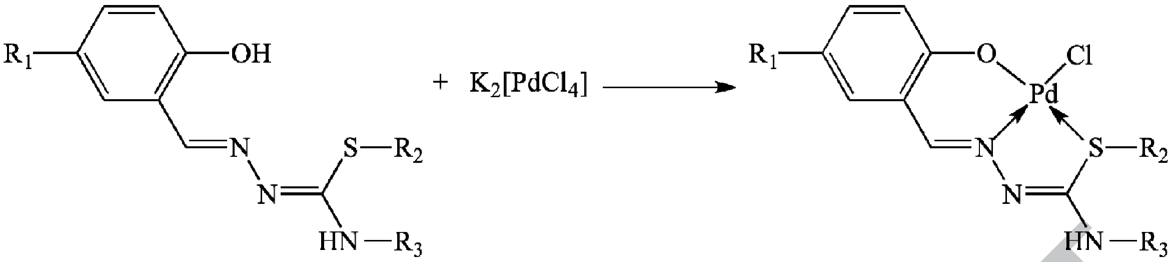
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