SYNTHESIS AND CHARACTERIZATION OF PLATINUM(IV)-COMPLEXES WITH S-ALKYL DERIVATIVES OF THIOSALICYLIC ACID AND THE CRYSTAL STRUCTURE OF THE S-BUTYL DERIVATIVE OF THIOSALICYLIC ACID

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SINTEZA I KARAKTERIZACIJA PLATINA(IV)-KOMPLEKSA SA S-ALKIL DERIVATIMA TIOSALICILNE KISELINE. KRISTALNA STRUKTURA S-BUTIL DERIVATA TIOSALICILNE KISELINE

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ABSTRACT

*New platinum(IV)-complexes with S-alkyl derivatives of thiosalicylic acid (alkyl = benzyl-(**L1**), methyl-(**L2**), ethyl-(**L3**), propyl-(**L4**), butyl-(**L5**)) have been synthesized and characterized by microanalysis, infrared spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy. The bidentate S,O ligand precursor, the S-butyl derivative of thiosalicylic acid (S-bu-thiosal), was prepared, and its crystal structure was determined. Single crystals suitable for X-ray measurements were obtained by slow crystallization from a DMSO-water system. S-bu-thiosal crystallized in a $P2_1/c$ space group of a monoclinic crystal system with a = 8.0732 (3) Å, b = 19.6769 (4) Å, c = 8.2291 (3) Å and Z = 4. S-bu-thiosal also has a coplanar geometry.*

Keywords: *S-alkyl derivative of thiosalicylic acid, platinum(IV)-complexes, IR and NMR spectroscopy, crystal structure*

SAŽETAK

*Novi platina(IV)-kompleksi sa S-alkil derivatima tiosalicilne kiseline (alkil = benzil-(**L1**), metil-(**L2**), etil-(**L3**), propil-(**L4**), butil-(**L5**)) su sintetisani i okarakterisani na osnovu rezultata mikroanalize, infracrvene i ^{1}H i ^{13}C NMR spektroskopije. Sintetisan je bidentatni S, O ligand prekursor, S-butil derivat tiosalicilne kiseline, (S-bu-thiosal), i ispitivana je njegova kristalna struktura. Kristali nagrađenog jedinjenja pogodni za rendgensku strukturnu analizu dobijeni su sporom kristalizacijom iz sistema DMSO-voda. Navedeni ligand kristališe u prostornoj grupi $P2_1/c$ monokliničkog kristalnog sistema sa dimenzijama jedinične ćelije a = 8,0732 (3) Å, b = 19,6769 (4) Å, c = 8,2291 (3) Å i Z = 4. Molekul navedenog jedinjenja poseduje koplanarnu strukturu.*

Ključne reči: *S-alkil derivati tiosalicilne kiseline, platina(IV)-kompleksi, IR i NMR spektroskopija, kristalna struktura*

ABBREVIATIONS

DNA - deoxyribonucleic acid
DMSO-d_6 - deuterated dimethyl sulfoxide
IR - infrared
K_2PtCl_6 - potassium-hexachloroplatinate(IV)
LiOH - lithium hydroxide
NMR - nuclear magnetic resonance
Pt - platinum
Ras - rat sarcoma proteins
TMS - tetramethylsilane

INTRODUCTION

Recent studies have shown important progress towards the use of transition metal complexes as drugs for the treatment of various human disorders. In the past, platinum-based drugs, mainly cisplatin and carboplatin, have dominated the treatment of various types of cancers by chemical agents because of their pharmacological properties. Relationships between structure and activity for a class of platinum coordination compounds confirmed that only those compounds having *cis* geometry block cell growth. The most active complex, cisplatin, was found to exhibit antitumor activity, while its *trans* isomer showed no such activity. Many derivatives of cisplatin also inhibit

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tumor cell growth, and these compounds have at least one N-H group that is responsible for important hydrogen-bond donor properties. However, the clinical utilization of cisplatin has often been limited by its severe side effects. Furthermore, platinum(II)-based drugs are associated with high reactivity and thus, poor biological stability (1-3).

After the discovery and use of platinum(II)-complexes, research has been directed towards complexes of platinum(IV), primarily due to the adverse effects of platinum(II)-complexes. The platinum(IV)-complexes display potential advantages due to their greater stability and bioreductive activation, thereby allowing for a greater proportion of the drug to arrive at the target intact. Currently, attention is focused on platinum(IV)-complexes with bioactive ligands because of lower toxicity, the possibility of oral administration, and the fact that they can coordinate to DNA (4). From the studies of platinum complexes in different cancer cell lines and DNA binding studies, some important structure activity rules have previously been summarized. The three important factors in designing platinum drugs appear to be chain length and flexibility, hydrogen bonding capacity, and charge of linking chain and the geometry of the chloro ligands to the linking chain (5). Two compounds of Pt(IV), iproplatin and ormaplatin, have undergone clinical trials. However, these compounds were abandoned due to severe neurotoxicity in the case of ormaplatin and the lack of superior performance in the case of iproplatin (6). Furthermore, numerous new complexes based on the platinum(IV)-ion have been synthesized, and their antitumor activities have been documented (7-9).

Thiosalicylic acid and its derivatives are used in cosmetics, for reducing hair growth, and for treatment of inflammatory, allergic and respiratory diseases. Farnesyl thiosalicylic acid, a novel Ras inhibitor, dislodges Ras proteins from the cell membrane, leading to inhibition of cell transformation and tumor growth. Ethyl mercury covalently linked to thiosalicylate, known as thimerosal, has been extensively used as a preservative in vaccines (10-13).

Our investigations presented in this paper focus on the synthesis and characterization of the corresponding Pt(IV)-complexes with S-alkyl derivatives of thiosalicylic acid. The preparation and spectral characterization of S-alkyl derivatives of thiosalicylic acid have been previously published (14,15). The structures of the isolated complexes are proposed based on elemental microanalysis, and infrared and nuclear magnetic resonance spectra. The bidentate S,O ligand precursor, S-butyl derivative of thiosalicylic acid (S-bu-thiosal), was prepared, and its crystal structure was determined and presented in this paper.

MATERIALS AND METHODS

Materials and measurements

All chemicals were obtained commercially and used without further purification. Elemental microanalyses were performed on a Vario III CHNOS Elemental Analyser, Elemental Analysensysteme GmbH. For the infrared spectra, a Perkin-Elmer Spectrum One FT-IR spectrometer was employed. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 NMR spectrometer using TMS in DMSO-d_6 as an internal reference at 22°C and with 10 mM solutions of the complexes.

Syntheses

General procedure for the synthesis of S-alkyl derivatives of thiosalicylic acid (L1)-(L5)

S-alkyl derivatives of thiosalicylic **L1**-**L5** (benzyl-(**L1**), methyl-(**L2**), ethyl-(**L3**), propyl-(**L4**), butyl-(**L5**)) were prepared (16) via alkylation of thiosalicylic acid by adding the alkyl halogenides to an alkaline water-ethanol solution. A crystal of the S-butyl derivative of thiosalicylic acid suitable for X-ray analysis was obtained after slow crystalization from a DMSO-water system.

Preparation of [$PtCl_2$(S-bz-thiosal)$_2$] (C1), a platinum(IV)-complex with the S-benzyl derivative of thiosalicylic acid

K_2PtCl_6 (0.1000 g, 0.2056 mmol) was dissolved in 10 mL of water in a steam bath, and the S-benzyl derivative of thiosalicylic acid (0.1005 g, 0.4112 mmol) was added to the solution. The resulting mixture was stirred for 2 h, and during this time, an aqueous solution LiOH (0.0099 g, 0.4112 mmol in 10 mL of water) was introduced. The complex [$PtCl_2$(S-bz-thiosal)$_2$] (C1) formed a yellow precipitate and was filtered, washed with water and air-dried, with a yield of 0.15 g (58.80%). Anal. Calc. for [$PtCl_2$(S-bz-thiosal)$_2$]=$PtC_{28}H_{22}O_4S_2Cl_2$ (Mr=752.59): C, 44.68; H, 2.95; S, 8.52. Found: C, 44.26; H, 2.88; S, 8.60. IR (KBr, cm^{-1}): 3437, 3062, 3028, 2924, 1629, 1561, 1493, 1463, 1412, 1318, 1254, 1142, 1046, 868, 799, 750, 697, 667, 652, 552. ^{1}H NMR (200 MHz, DMSO-d_6, δ ppm): 4.01 (s, 4H, CH_2), 7.23-8.24 (m, 18H, Ar и bz). ^{13}C NMR (50 MHz, DMSO-d_6,δ ppm): 17 (CH_2), 124; 125.5; 127.1; 127.4; 127.7; 133.1; 133.9; 136.2 (Ar и bz); 169.1 (COO^-).

Preparation of [$PtCl_2$(S-met-thiosal)$_2$] (C2), a platinum(IV)-complex with the S-methyl derivative of thiosalicylic acid

The complex [$PtCl_2$(S-met-thiosal)$_2$] (**C2**) was prepared as described using the S-methyl derivative of thiosalicylic acid (0.0692 g, 0.4112 mmol) instead of the S-benzyl derivative of thiosalicylic acid, with a yield of 0.12 g (56.40%). Anal. Calc. for [$PtCl_2$(S-met-thiosal)$_2$] = $PtC_{16}H_{14}O_4S_2Cl_2$ (Mr=600.40): C, 32.00; H, 2.35; S, 10.68. Found: C, 31.54; H, 2.59; S, 10.22.IR (KBr, cm^{-1}): 3436, 2923, 2794, 2439, 1634, 1581, 1552, 1469, 1423, 1361, 1290, 1274, 1149, 1116, 1056, 970, 858, 798, 754, 697, 653, 568. ^{1}H NMR (200 MHz, DMSO-d_6, δ ppm): 2.47 (s, 6H, CH_3), 7.41-8.30 (m, 8H, Ar). ^{13}C NMR (50 MHz, DMSO-d_6, δ ppm): 15.6 (CH_3), 125; 125.5; 126.4; 129.9; 134.1; 137.2 (Ar), 169.3 (COO^-).

Preparation of [$PtCl_2$(S-et-thiosal)$_2$] (C3), a platinum(IV)-complex with the S-ethyl derivative of thiosalicylic acid

The complex [$PtCl_2$(S-et-thiosal)$_2$] (**C3**) was prepared as described using the S-ethyl derivative of thiosalicylic acid (0.0749 g, 0.4112 mmol) instead of the S-benzyl derivative of thiosalicylic acid, with a yield of 0.13 g (58.10%). Anal. Calc. for [$PtCl_2$(S-et-thiosal)$_2$] = $PtC_{18}H_{18}O_4S_2Cl_2$ (Mr=828.46): C, 34.40; H, 2.89; S, 10.20. Found: C, 34.14; H, 2.71; S, 10.11. IR (KBr, cm^{-1}): 3436, 2521, 1692, 1634, 1563, 1437, 1404, 1274, 1143, 1122, 1050, 997, 872, 794, 749, 693, 643, 568. ^{1}H NMR (200 MHz, DMSO-d_6, δ ppm): 1.27 (t, 6H, CH_3), 2.81 (q, 4H, CH_2), 7.42-8.28 (m, 8H, Ar).^{13}C NMR (50 MHz, DMSO-d_6,δ ppm):12.9 (CH_3), 13.8 (CH_2), 125.1; 126.4; 126.6; 133.3; 133.8; 137.1 (Ar), 169.2 (COO^-).

Preparation of [$PtCl_2$(S-pr-thiosal)$_2$] (C4), a platinum(IV)-complex with the S-propyl derivative of thiosalicylic acid

The complex [$PtCl_2$(S-pr-thiosal)$_2$] (**C4**) was prepared as described using the S-propyl derivative of thiosalicylic acid (0.0807 g, 0.4112 mmol) instead of the S-benzyl derivative of thiosalicylic acid, with a yield of 0.13 g (56.90%). Anal. Calc. for [$PtCl_2$(S-pr-thiosal)$_2$] = $PtC_{20}H_{22}O_4S_2Cl_2$ (Mr=656.51): C, 36.59; H, 3.38; S, 9.77. Found: C, 36.17; H, 3.30; S, 9.61. IR (KBr, cm^{-1}): 3444, 3061, 2963, 2930, 2873, 2600, 1706, 1639, 1586, 1562, 1461, 1436, 1416, 1293, 1253, 1138, 1091, 1052, 863, 798, 753, 691, 652. ^{1}H NMR (200 MHz, DMSO-d_6, δ ppm): 0.90 (t, 6H, CH_3), 1.34 (m, 4H, CH_2), 2.75 (t, 4H, CH_2), 7.40-8.31 (m, 8H, Ar). ^{13}C NMR (50 MHz, DMSO-d_6, δ ppm): 13.0 (CH_3), 23,2 (CH_2), 12 (CH_2), 125.3; 126.1; 126.4; 133.2; 133.9; 136.9 (Ar), 169.1 (COO^-).

Preparation of [$PtCl_2$(S-bu-thiosal)$_2$] (C5), a platinum(IV)-complex with the S-butyl derivative of thiosalicylic acid

The complex [$PtCl_2$(S-bu-thiosal)$_2$] (**C5**) was prepared as described using the S-butyl derivative of thiosalicylic acid (0.0865 g, 0.4112 mmol) instead of the S-benzyl derivative of thiosalicylic acid, with a yield of 0.14 g (59.30%). Anal. Calc. for [$PtCl_2$(S-bu-thiosal)$_2$] = $PtC_{22}H_{26}O_4S_2Cl_2$ (Mr=684.56): C, 38.60; H, 3.83; S, 9.37. Found: C, 38.35; H, 3.71; S, 9.28. IR (KBr, cm^{-1}): 3437, 3054, 2956, 2931, 2869, 2629, 1673, 1644, 1635, 1583, 1561, 1462, 1433, 1410, 1318, 1286, 1250, 1137, 1100, 1060, 1049, 916, 863, 754, 738, 698, 652, 551. ^{1}H NMR (200 MHz, DMSO-d_6, δ ppm): 0.89 (t, 6H, CH_3), 1.43 (m, 4H, CH_2), 1.60 (m, 4H, CH_2), 2.73 (t, 4H, CH_2), 7.41-8.28 (m, 8H, Ar). ^{13}C NMR (50 MHz, DMSO-d_6, δ ppm): 13.4 (CH_3), 21.5 (CH_2), 31(CH_2), 10 (CH_2), 124.9; 125.9; 126.5; 133.1; 134.2; 136.9 (Ar), 168.9 (COO^-).

X-ray crystal structure determination

A single crystal of S-butyl thiosalicylic acid was selected and mounted on a glass fibre. Diffraction data were collected using the Oxford Diffraction Gemini S four-circle goniometer equipped with a Sapphire CCD detector. The crystal to detector distance was 45.0 mm, and graphite monochromated CuKα (λ = 1.5418 Å) radiation was used for the experiments. The data were reduced using the program CrysAlisPRO (17). A semi-empirical absorption-correction, based upon the intensities of equivalent reflections, was applied, and the data were corrected for Lorentz, polarization, and background effects (17). The structure was solved by direct methods using the Sir 97 program (18) and refined by full-matrix least-squares procedures on F^2 using SHELXL-97 programs (19) as implemented in the WinGX program suite (20). The non-H atoms were refined anisotropically. The positions of hydrogen atoms were found from the inspection of the difference Fourier maps. Crystallographic data and refinement parameters are listed in Table 1. The figures representing molecular structure were created using the ORTEP-3 (21) and PLATON (22) programs.

RESULTS AND DISCUSSION

Synthesis and chemical characterization

S-alkyl (alkyl = benzyl-(**L1**), methyl-(**L2**), ethyl-(**L3**), propyl-(**L4**), butyl-(**L5**)) derivatives of thiosalicylic acid were prepared (16) via alkylation of thiosalicylic acid by addition of the corresponding alkyl halogenides to an alkaline water-ethanol solution (Scheme 1).

Platinum(IV)-complex with S-alkyl derivatives of thiosalicylic acid, [$PtCl_2$(S-alkyl-thiosal)$_2$], were obtained via the direct reaction of K_2PtCl_6 with the S-alkyl derivatives of thiosalicylic acid (in a molar ratio of 1:2) in water (Scheme 2).

Bidentate coordination (S-O) of S-alkyl derivatives of thiosalicylic acid to the platinum(IV)-ion is expected. In the infrared spectrum of isolated ligands (15), we observed valencione asymmetric vibrations of the carboxyl groups at lower values than expected (from 1700 to 1750 cm^{-1}) (23-25), which could be explained by the presence of large R-S groups in the *ortho* position. The positions of these bands in the corresponding complexes (C1-C5) are located in the expected region (1600 to 1650 cm^{-1}), which confirms their deprotonation and coordination to the metal ion (Table 2).

The chemical shifts of hydrogen and carbon atoms of the obtained S-alkyl derivatives of thiosalicylic acid and the corresponding platinum(IV)-complexes were found to be almost the same as the expected chemical shifts. We observed only slight differences in the chemical shifts of the carbon atoms of the carboxyl group of the S-alkyl derivative of thiosalicylic acid and the corresponding platinum(IV)-complexes. These differences in the chemical shifts of the carboxyl group may be explained by the coordination of the ligands over the oxygen atom of the carboxyl group to the platinum(IV)-ion.

Based on the IR and NMR spectra of the ligands and the corresponding Pt(IV)-complexes, we concluded that the ligands are bidentately coordinated to the platinum(IV)-ion. However, based on the mentioned spectroscopic results,

Table 1. Experimental details: Crystallographic data and refinement parameters.

Crystal data	
Chemical formula	$C_{11}H_{14}O_2S$
M_r	210.28
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	8.0732 (3), 19.6769 (4), 8.2291 (3)
b (°)	119.084 (5)
V (Å^3)	1142.40 (7)
Z	4
Radiation type	Cu Ka
No. of reflections for cell measurement	4178
q range (°) for cell measurement	4.5–72.2
m (mm^{-1})	2.30
Crystal size (mm)	0.33 × 0.28 × 0.21
Data collection	
Diffractometer	Xcalibur-Gemini S diffractometer
Absorption correction	Multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.24 (release 03-12-2012 CrysAlis171 .NET) (compiled Dec 3 2012,18:21:49) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.557, 1.000
No. of measured, independent and observed [$I > 2s(I)$] reflections	6832, 2038, 1898
R_{int}	0.020
$(\sin q/l)_{max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.035, 0.100, 1.06
No. of reflections	2038
No. of parameters	183
No. of restraints	0
H-atom treatment	H atoms treated by independent refinement
ρ_{max}, ρ_{min} (e Å^{-3})	0.20, -0.16

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.24 (release 03-12-2012 CrysAlis171 .NET) (compiled Dec 3 2012,18:21:49), *SIR* 97 (Altomare *et al.* (1999) J. Appl. Cryst. 32, 115-119), *SHELXL97* (Sheldrick, 1997).

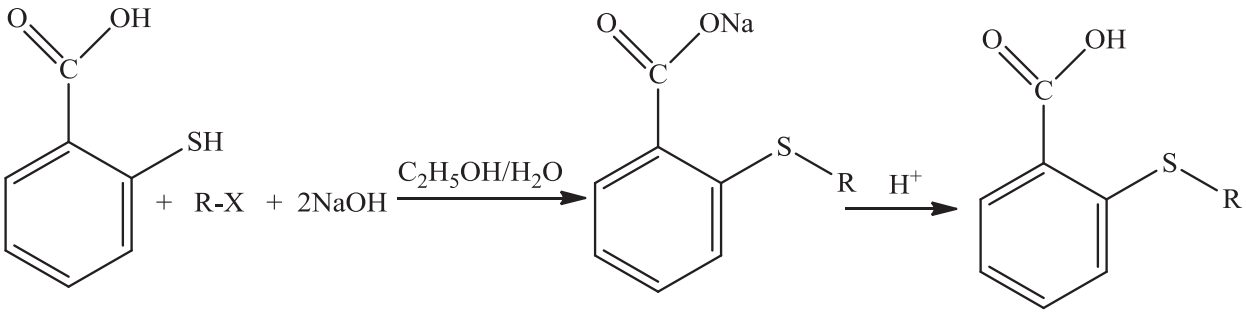
we could not conclude anything about the complex geometry.

In a previously published study of palladium(II)-complexes with S-alkyl derivatives of thiosalicylic acid (15), we have confirmed a square-planar structure with *cis*-O *cis*-S geometry of two bidentate ligands in a coordinated sphere of the metal ion. Based on these results, we can expect that octahedral platinum(IV)-complexes also contain two molecules of S-alkyl derivatives of thiosalicylic acid in the equatorial plane with *cis*-O *cis*-S geometry and two axial monodentate anionic ligands.

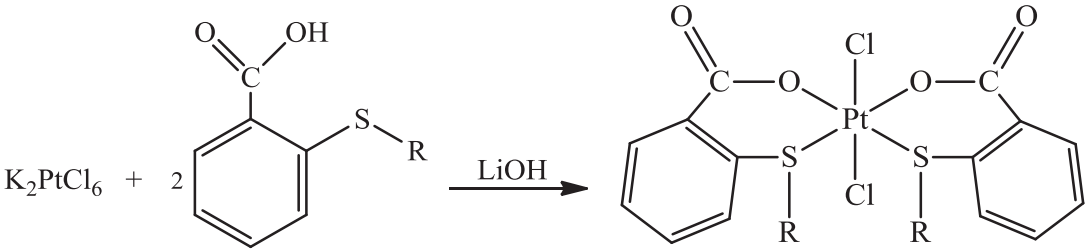
Crystal structure of the S-butyl derivative of thiosalicylic acid

S-butyl-thiosalicylic acid was prepared by the alkylation of thiosalicylic acid using the corresponding alkyl halogenide in an alkaline water-ethanol solution. The lack of S-H stretching absorption bands in the range of 2600-2550 cm^{-1} (2556 cm^{-1}) suggests the deprotonation of the S-H group in thiosalicylic acid and its alkylation with a butyl group (26). The carboxylate asymmetric stretching band from S-butyl-thiosalicylic acid (1674 cm^{-1}) is located at a lower energy range than expected (1700–1750 cm^{-1}) (26, 27). This fact could be explained by the presence of a large S-butyl group in the *ortho* position with a -COOH group. Chemical shifts arising from carbon and hydrogen atoms of this type of thioether were found at the expected positions.

The perspective view of the molecular structure of the title compound ($C_{11}H_{14}O_2S$) is shown in Figure 1. The arrangement of the molecules in the unit cell is shown in Figure 2, where broken lines represent hydrogen bonds that connect the molecules of each dimer.



Scheme 1. The preparation of the S-alkyl derivatives of thiosalicylic acid; R= benzyl-(**L1**), methyl-(**L2**), ethyl-(**L3**), propyl-(**L4**), butyl-(**L5**).



Scheme 2. The preparation of the platinum(IV)-complexes with S-alkyl derivatives of thiosalicylic acid ; R= benzyl-(**C1**), methyl-(**C2**), ethyl-(**C3**), propyl-(**C4**), butyl-(**C5**).

As expected, S-butyl thiosalicylic acid crystalizes in the same monoclinic crystal system and $P2_1/c$ space group as was found for the crystal form of benzoic acid (28). The bond lengths and angles in the title compound are within the expected ranges (Table 3). The differences between C-C bonds in the benzene ring are in the range of 0-0.035 Å, but displacement of the benzene carbon atoms is not significant, suggesting that the ring can be assumed as strictly planar. The dihedral angle between the thiosalicylic and butyl groups is -179.50(11)°, indicating a co-planar molecular geometry.

Due to the intermolecular hydrogen bonds between carboxylic groups, a dimeric form of this structure is also expected. The hydrogen bond distance of 2.634(3) in the crystal form of S-butyl thiosalicylic acid is very similar to the same distances in, for example, benzoic acid (2.64 Å)

Table 2. The most important infrared bands (cm^{-1}) of the investigated compounds.

Compound	-COO- (as)
$[PtCl_2(S\text{-bz-thiosal})_2]$ (**C1**)	1629
$[PtCl_2(S\text{-met-thiosal})_2]$ (**C2**)	1634
$[PtCl_2(S\text{-et-thiosal})_2]$ (**C3**)	1634
$[PtCl_2(S\text{-pr-thiosal})_2]$ (**C4**)	1639
$[PtCl_2(S\text{-bu-thiosal})_2]$ (**C5**)	1644,1635

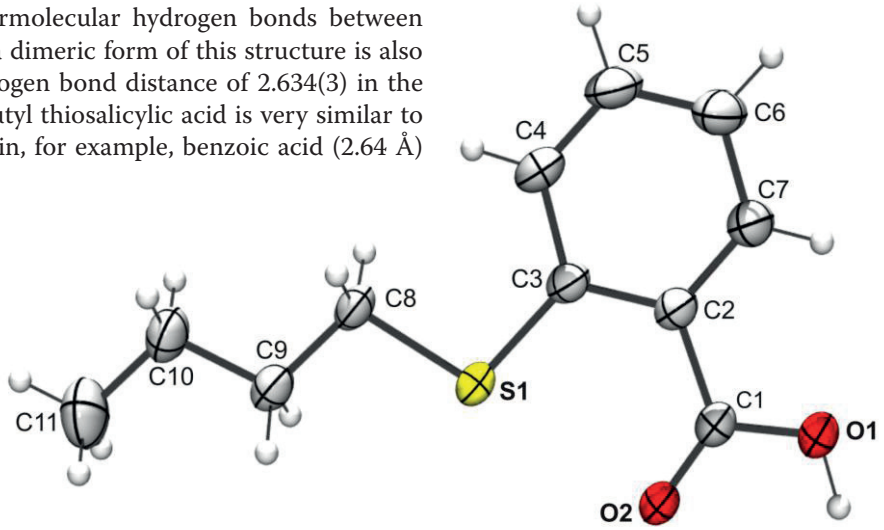


Figure 1. Molecular structure of compound $C_{11}H_{14}O_2S$ with the non-H atom numbering scheme with thermal ellipsoids at 30% probability level.

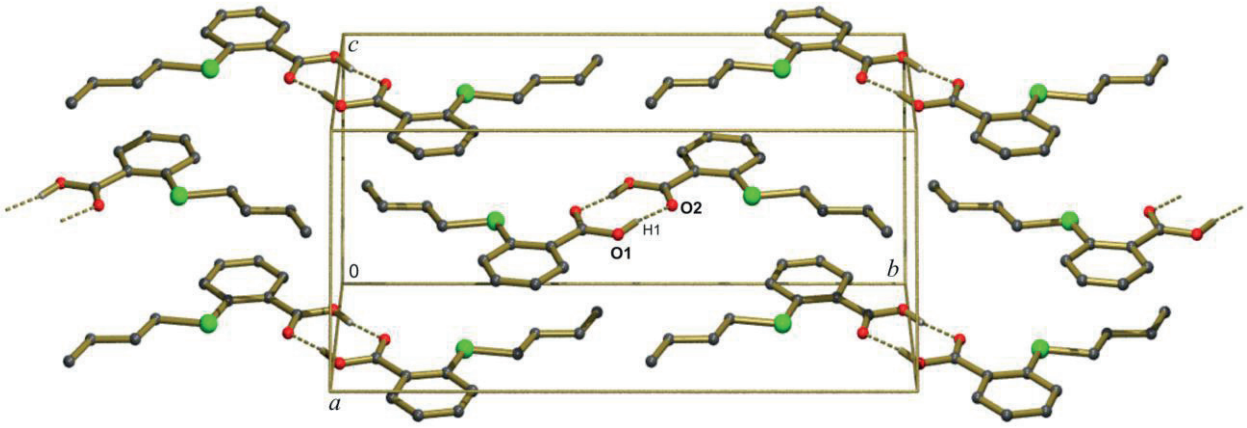


Figure 2. PLATON drawing showing crystal packing for $C_{11}H_{14}O_2S$. Intermolecular hydrogen bonds O1-H1....O2 are shown as dashed line. H atoms not involved in hydrogen bonds are not shown for clarity.

Table 3. Selected geometrical parameters for S-butyl derivative of thiosalicylic acid.

Bond lengths [Å]		Bond angles [°]	
S1—C3	1.7593 (18)	C3—S1—C8	103.82 (7)
S1—C8	1.8169 (15)	O2—C1—O1	122.10 (13)
O2—C1	1.216 (2)	O2—C1—C2	123.63 (13)
O1—C1	1.3088 (18)	O1—C1—C2	114.26 (13)
C1—C2	1.479 (2)	C7—C2—C3	120.33 (13)
C2—C7	1.399 (2)	C7—C2—C1	117.66 (14)
C2—C3	1.411 (2)	C3—C2—C1	122.01 (13)
C3—C4	1.404 (2)	C9—C8—S1	107.70 (10)
C4—C5	1.370 (3)	C6—C7—C2	121.00 (17)
C6—C5	1.364 (3)	C11—C10—C9	113.4 (2)
C8—C9	1.513 (3)	C4—C3—C2	116.58 (15)
C7—C6	1.376 (2)	C4—C3—S1	121.52 (13)
C10—C9	1.515 (2)	C2—C3—S1	121.89 (10)
C10—C11	1.507 (4)	C8—C9—C10	112.42 (14)
		C5—C6—C7	118.81 (18)
		C5—C4—C3	121.56 (17)
		C6—C5—C4	121.68 (16)

Torsion angles [°]	
O2—C1—C2—C7	-179.10 (16)
O1—C1—C2—C7	0.8 (2)
O2—C1—C2—C3	0.8 (2)
O1—C1—C2—C3	-179.33 (14)
C3—S1—C8—C9	-179.50 (11)
C3—C2—C7—C6	1.0 (3)
C1—C2—C7—C6	-179.14 (17)
C7—C2—C3—C4	-1.8 (2)
C1—C2—C3—C4	178.29 (14)
C7—C2—C3—S1	177.09 (12)
C1—C2—C3—S1	-2.8 (2)
C8—S1—C3—C4	-0.56 (15)
C8—S1—C3—C2	-179.45 (12)
S1—C8—C9—C10	176.41 (13)
C11—C10—C9—C8	-177.3 (2)
C2—C7—C6—C5	0.4 (3)
C2—C3—C4—C5	1.4 (3)
S1—C3—C4—C5	-177.57 (15)
C7—C6—C5—C4	-1.0 (3)
C3—C4—C5—C6	0.0 (3)

(28), acetic acid (2.62(2) Å) (29), nicotinic acid (2.66 Å) (30) and *o*-phtalic acid (2.67(0.05) Å) (31). The differences between the two C-O bonds are almost 0.093 Å higher than in benzoic acid (0.046 Å), but are similar to the differences in salicylic acid (0.1 Å) (32). This observation could be explained by the greater similarities of the title compound with salicylic acid than with benzoic acid.

The pair of O1—H1...O2 interactions connects inversion-related molecules into dimers (Table 4, Figure 2).

CONCLUSION

Platinum(IV)-complexes with S-alkyl derivatives of thiosalicylic acid (alkyl = benzyl-(**L1**), methyl-(**L2**), ethyl-(**L3**), propyl-(**L4**), butyl-(**L5**)) have been synthesized and characterized by microanalysis, infrared spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy. The S-butyl derivative of thiosalicylic acid was crystalized in a $P2_1/c$ space group of a monoclinic crystal system. The crystal form and crystal packing are determined by intermolecular hydrogen bonds O1-H1...O2. The S-butyl derivative of thiosalicylic acid also has a co-planar geometry.

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Table 4. Hydrogen bonding geometry for $C_{11}H_{14}O_2S$.

D-H....A	*D-H (Å)*	*H....A (Å)*	*D ....A (Å)*	*q (°)*
O1-H1....O2[a]	0.90(3)	1.75(3)	2.634(3)	172(2)

[a] 1-x,1-y,1-z

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