SYNTHESIS AND CHARACTERIZATION OF ZINC(II)-COMPLEXES WITH S-ALKYL DERIVATIVES OF THIOSALICYLIC ACID

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SINTEZA I KARAKTERIZACIJA CINK(II)-KOMPLEKSA SA NEKIM S-ALKIL DERIVATIMA TIOSALICILNE KISELINE

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ABSTRACT

*New zinc(II)-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 elemental microanalysis, IR spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy. The S-alkyl derivatives of thiosalicylic acid were prepared by alkylation of thiosalicylic acid by adding alkyl halides to an alkaline water-ethanol solution, while the corresponding zinc(II)-complexes were obtained via the direct reaction of $ZnCl_2$ with S-alkyl derivatives of thiosalicylic acid in water. Based on the microanalysis results and the IR and NMR spectra of the S-alkyl derivatives of thiosalicylic acid and the corresponding zinc(II)-complexes, we concluded that the ligands are bidentately coordinated to the zinc(II)-ion.*

Keywords: *S-alkyl derivatives of thiosalicylic acid, zinc(II)-complexes, elemental microanalysis, IR and NMR spectroscopy*

SAŽETAK

*Novi cink(II)-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 elementalne mikroanalize, IR, ^{1}H i ^{13}C NMR spektroskopije. S-alkil derivati tiosalicilne kiseline dobijeni su reakcijom alkilovanja tiosalicilne kiseline odgovarajućim alkil-halogenidima u baznom rastvoru voda-etanol dok su odgovarajući cink(II)-kompleksi dobijeni direktnom reakcijom $ZnCl_2$ i S-alkil derivata tiosalicilne kiseline u vodenom rastvoru. Na osnovu rezultata mikroanalize i infracrvenih i nuklearno-magnetno rezonancionih spektara S-alkil derivata tiosalicilne kiseline i odgovarajućih Zn(II)-kompleksa zaključili smo da su se molekuli liganada koordinovali bidentatno za cink(II)-jon.*

Ključne reči: *S-alkil derivati tiosalicilne kiseline, cink(II)-kompleksi, elementalna mikroanaliza, IR i NMR spektroskopija*

ABBREVIATIONS

CuZnSOD – copper-zinc superoxide dismutase
DNA - deoxyribonucleic acid
DMSO-d_6 - deuterated dimethyl sulfoxide
IR - infrared
LiOH - lithium hydroxide
NMR - nuclear magnetic resonance
TMS - tetramethylsilane
Zn – zinc
$ZnCl_2$ – zinc chloride

INTRODUCTION

Zinc is the most abundant trace intracellular element that plays a role in a wide range of cellular processes, including cell proliferation, reproduction, immune function, and defence against free radicals (1-4). Furthermore, the bioessential metal zinc is required for the catalytic activity of more than 300 specific enzymes and over 2000 zinc-associated transcription factors including DNA binding proteins with zinc fingers. Some well-studied zinc metalloenzymes include alcohol dehydrogenase, carbonic anhydrase, alkaline phosphatase and ribonucleic acid polymerases. Zinc also plays a structural role by stabilizing the tertiary structure of zinc metalloenzymes and other critical proteins. For example, zinc is required to stabilize the enzyme CuZnSOD (5,6).

Unlike iron and copper, zinc does not participate in redox reactions but rather functions as a Lewis acid to accept

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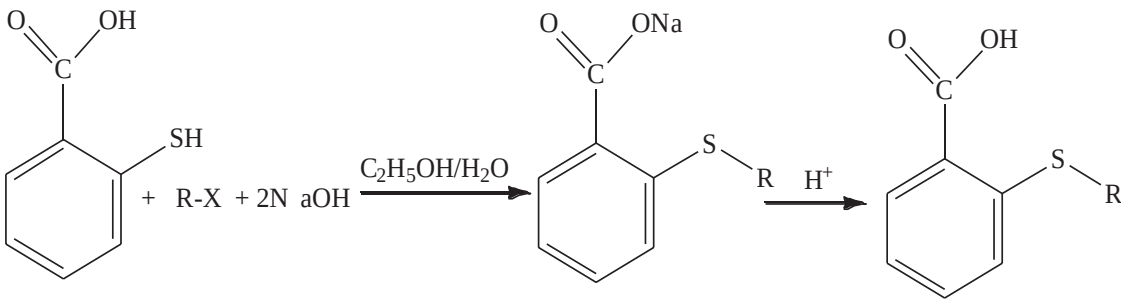

Scheme 1. The preparation of the S-alkyl derivatives of thiosalicylic acid.
R= benzyl-(**L1**), methyl-(**L2**), ethyl-(**L3**), propyl-(**L4**), butyl-(**L5**)

a pair of electrons. The coordination of zinc by four amino acid side chains to form zinc finger motifs facilitates stable protein folding to form biologically active proteins. Zinc is also known to play a direct role in the regulation of gene expression, although this role is less studied than its catalytic and structural functions (7).

Thiosalicylic acid and its derivatives are used in chemical analysis (8-11), in dermatology (12,13), and in the treatment of various diseases (14,15).

The synthesis and characterization of zinc(II)-complexes with thiosalicylic acid preceding this study focused on interactions of bioessential metals with biologically and pharmacologically active ligands. The zinc salt of thiosalicylic acid, which was isolated by the reaction of zinc chloride, thiosalicylic acid and sodium hydroxide in an alcohol-water solution, (16) has been applied to the treatment of acne and seborrheic dermatitis (17). When zinc acetate reacts with a solution of thiosalicylic acid in sodium acetate, a white precipitate of $[Zn(SC_6H_4CO_2]$ is formed, which is insoluble in all common solvents except pyridine and DMSO, in which it is more soluble, yielding the composition product $[Zn(SC_6H_4CO_2py]$ (18). Coordination chemistry of zinc with thiosalicylate and ancillary donor ligands has also been investigated (19). In more recent work, dimeric Zn(II)-complexes with 1,10-phenanthroline was structurally characterized and found to contain carboxylate bridges (20).

The aim of our present study was to synthesize and characterize five new zinc(II)-complexes with S-alkyl derivatives of thiosalicylic acid (alkyl = benzyl-(**L1**), methyl-(**L2**), ethyl-(**L3**), propyl-(**L4**), butyl-(**L5**)). The chemical characterization of S-alkyl derivatives of thiosalicylic acid has been previously published (21,22). The composition and structure of synthesized complexes was predicted based on elemental microanalysis and infrared and nuclear magnetic resonance spectra.

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 Analyzer, Elemental Analysensysteme GmbH. For the infrared spectra, a Perkin-Elmer Spectrum One FT-IR spectrometer was employed. ^1H 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)

The S-alkyl derivatives of thiosalicylic acid ligands (alkyl = benzyl-(**L1**), methyl-(**L2**), ethyl-(**L3**), propyl-(**L4**), butyl-(**L5**)) were prepared (22) by alkylation of thiosalicylic acid via addition of the corresponding alkyl halide in an alkaline water-ethanol solution (Scheme 1).

Preparation of $[Zn(S\text{-}bz\text{-}thiosal)_2]$ (C1), a zinc(II)-complex with the S-benzyl derivative of thiosalicylic acid

$ZnCl_2$ (0.1000 g, 0.7337 mmol) was dissolved in 10 cm^3 of water in a steam bath, and the S-benzyl derivative of thiosalicylic acid (0.3585 g, 1.4674 mmol) was added to the solution. The resulting mixture was stirred for 2 h, and during this time, an aqueous solution of LiOH (0.0352 g, 1.4674 mmol in 10 cm^3 of water) was introduced. The complex $[Zn(S\text{-}bz\text{-}thiosal)_2]$ (C1) as a white precipitate was filtered, washed with water and air-dried, with a yield of 0.25 g (61.22%). *Anal.* Calc. for $[Zn(S\text{-}bz\text{-}thiosal)_2]$ = $ZnC_{28}H_{22}O_4S_2$ (Mr = 551.978): C, 60.92; H, 4.02; S, 11.62. Found: C, 60.53; H, 3.94; S, 11.71. IR (KBr, cm^{-1}): 3428, 3059, 2922, 1598, 1580, 1437, 1403, 1282, 1259, 1063, 1044, 846, 744, 697. ^1H NMR (200 MHz, DMSO-d_6, δ ppm): 4.03 (s, 4H, CH_2), 7.26-8.25 (m, 18H, Ar и bz). ^{13}C NMR (50 MHz, DMSO-d_6, δ ppm): 26 (CH_2), 125; 126.4; 126.8, 127.2; 127.3; 128.9; 133.5; 134.3; 137.7, 138.6 (Ar и bz); 169.2 (COO^-).

Preparation of $[Zn(S\text{-}met\text{-}thiosal)_2]$ (C2), a zinc(II)-complex with the S-methyl derivative of thiosalicylic acid

The complex $[Zn(S\text{-}met\text{-}thiosal)_2]$ (**C2**) was prepared as described above using the S-methyl derivative of thiosalicylic acid (0.2467 g, 1.4674 mmol) instead of the

S-benzyl derivative of thiosalicylic acid, with a yield of 0.19 g (64.29%). *Anal.* Calc. for [Zn(S-met-thiosal)$_2$] = $ZnC_{16}H_{14}O_4S_2$ (Mr = 399.794): C, 48.06; H, 3.53; S, 16.04. Found: C, 47.69; H, 3.78; S, 15.71. IR (KBr, cm^{-1}): 3436, 2917, 2859, 1593, 1576, 1435, 1399, 1280, 1256, 1156, 1065, 953, 847, 744, 654. ^{1}H NMR (200 MHz, DMSO-d_6, δ ppm): 2.47 (s, 6H, CH_3), 7.42-8.30 (m, 8H, Ar). ^{13}C NMR (50 MHz, DMSO-d_6, δ ppm): 15.6 (CH_3), 126; 126.3; 126.8; 133.4; 134.3; 137.2 (Ar), 169.4 (COO^-).

Preparation of [Zn(S-et-thiosal)$_2$] (C3), a zinc(II)-complex with the S-ethyl derivative of thiosalicylic acid

The complex [Zn(S-et-thiosal)$_2$] (**C3**) was prepared as described above using the S-ethyl derivative of thiosalicylic acid (0.2673 g, 1.4674 mmol) instead of the S-benzyl derivative of thiosalicylic acid, with a yield of 0.18 g (58.47%). *Anal.* Calc. for [Zn(S-et-thiosal)$_2$] = $ZnC_{18}H_{18}O_4S_2$ (Mr = 427.846): C, 50.53; H, 4.24; S, 14.99. Found: C, 50.17; H, 4.07; S, 14.88. IR (KBr, cm^{-1}): 3432, 2954, 2765, 1595, 1563, 1436, 1404, 1273, 1149, 1122, 1054, 995, 871, 784, 739, 693, 655. ^{1}H NMR (200 MHz, DMSO-d_6, δ ppm): 1.27 (t, 6H, CH_3), 2.81 (q, 4H, CH_2), 7.43–8.27 (m, 8H, Ar). ^{13}C NMR (50 MHz, DMSO-d_6, δ ppm): 13.9 (CH_3), 13 (CH_2), 125.1; 126.6; 126.5; 133.3; 134.2; 137.1 (Ar), 169.3 (COO^-).

Preparation of [Zn(S-pr-thiosal)$_2$] (C4), a zinc(II)-complex with the S-propyl derivative of thiosalicylic acid

The complex [Zn(S-pr-thiosal)$_2$] (**C4**) was prepared as described above using the S-propyl derivative of thiosalicylic acid (0.2879 g, 1.4674 mmol) instead of the S-benzyl derivative of thiosalicylic acid, with a yield of 0.20 g (62.19%). *Anal.* Calc. for [Zn(S-pr-thiosal)$_2$] = $ZnC_{20}H_{22}O_4S_2$ (Mr = 455.898): C, 52.69; H, 4.86; S, 14.07. Found: C, 52.27; H, 4.78; S, 13.91. IR (KBr, cm^{-1}): 3443, 3061, 2965, 2931, 2863, 2559, 1591, 1562, 1462, 1435, 1312, 1294, 1252, 1137, 1092, 1055, 867, 794, 755, 692, 652. ^{1}H NMR (200 MHz, DMSO-d_6, δ ppm): 0.90 (t, 6H, CH_3), 1.35 (m, 4H, CH_2), 2.77 (t, 4H, CH_2), 7.41–8.32 (m, 8H, Ar). ^{13}C NMR (50 MHz, DMSO-d_6, δ ppm): 13.0 (CH_3), 24.2 (CH_2), 22 (CH_2), 125.3; 126.6; 126.5; 133.4; 134.2; 138.7 (Ar), 169.1 (COO^-).

Preparation of [Zn(S-bu-thiosal)$_2$] (C5), a zinc(II)-complex with the S-butyl derivative of thiosalicylic acid

The complex [Zn(S-bu-thiosal)$_2$] (**C5**) was prepared as described above using the S-butyl derivative of thiosalicylic acid (0.3085 g, 1.4674 mmol) instead of the S-benzyl derivative of thiosalicylic acid, with a yield of 0.21 g (60.12%). *Anal.* Calc. for [Zn(S-bu-thiosal)$_2$] = $ZnC_{22}H_{26}O_4S_2$ (Mr = 483.950): C, 54.60; H, 5.42; S, 13.25. Found: C, 54.33; H, 5.19; S, 13.17. IR (KBr, cm^{-1}): 3436, 3053, 2952, 2934, 2867, 2529, 1614, 1594, 1582, 1565, 1467, 1430, 1408, 1312, 1291, 1252, 1139, 1098, 1063, 1051, 918, 853, 754, 733, 697, 652, 551. ^{1}H NMR (200 MHz, DMSO-d_6, δ ppm): 0.88 (t, 6H, CH_3), 1.44 (m, 4H, CH_2), 1.60 (m, 4H, CH_2), 2.77 (t, 4H, CH_2), 7.42-8.28 (m, 8H, Ar). ^{13}C NMR (50 MHz, DMSO-d_6, δ ppm): 13.4 (CH_3), 21.6 (CH_2), 32 (CH_2), 20 (CH_2), 124.9; 126.6; 126.8; 133.3; 134.2; 138.5 (Ar), 168.8 (COO^-).

RESULTS AND DISCUSSION

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

The corresponding zinc(II)-complexes were obtained via the direct reaction of $ZnCl_2$ with the appropriate S-alkyl derivative of thiosalicylic acid (in a molar ratio 1:2) in water.

Infrared spectra of the obtained complexes were analyzed to determine the coordination mode of the ligands to the zinc (II) ion. Based on previous results (18-20), we expected a bidentate coordination of S-alkyl derivatives of thiosalicylic acid through S and O donor atoms. Asymmetric stretching frequencies of the carboxyl groups in the infrared spectrum of isolated ligands (22) are observed 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 frequencies in the infrared spectrum of the corresponding zinc(II)-complexes (C1-C5) are located in the expected region (1580 to 1620 cm^{-1}), which confirms their coordination to the zinc(II)-ion (Table 1).

Hydrogen and carbon chemical shifts of the S-alkyl derivatives of thiosalicylic acid and the corresponding zinc(II)-complexes were found at almost the same positions. Only minor differences in the chemical shifts of the carbon atoms from the carboxyl group of the S-alkyl derivative of thiosalicylic acid and the corresponding zinc(II)-complexes were observed. These differences in the chemical shifts of the carboxyl group may be explained by ligand coordination through the oxygen atom of the carboxyl group to the zinc (II) ion (Table 2).

Based on the microanalysis results and the IR and NMR spectra of the ligands and the corresponding Zn(II)-complexes, we concluded that the ligands are bidentately coordinated to the zinc(II)-ion through S and O donor atoms. However, based on these results, we could not conclude anything about the complex geometry. The precise molecular structure of the obtained zinc(II)-complexes can only be determined using X-ray analysis.

CONCLUSION

Zinc(II)-complexes with S-alkyl derivative of thiosalicylic acid (R = 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

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

Compound	-COO- (as)
[Zn(S-bz-thiosal)$_2$] (C1)	1598, 1580
[Zn(S-met-thiosal)$_2$] (C2)	1593
[Zn(S-et-thiosal)$_2$] (C3)	1595
[Zn(S-pr-thiosal)$_2$] (C4)	1591
[Zn(S-bu-thiosal)$_2$] (C5)	1614,1594

Table 2. ^{1}H and ^{13}C NMR spectra of the ligands (22) and corresponding Zn(II)-complexes

Ligands		^{1}H	^{13}C	Zn(II)-complexes		^{1}H	^{13}C
(L1)	CH_2-bz Ar and bz COOH	4.17 7.21-8.14 -	35.9 124.1-141.3 167.5	(C1)	CH_2-bz Ar и bz COOH	4.03 7.26-8.25 -	26.0 125.0-138.6 169.2
(L2)	CH_3- Ar COOH	2.48 7.16-8.18 -	15.6 123.5-144.4 171.6	(C2)	CH_3- Ar COOH	2.47 7.42-8.30 -	15.6 126.0-137.2 169.4
(L3)	CH_3- CH_2- Ar COOH	1.42 2.97 7.16-8.17 -	13.1 26.2 124.0-142.6 171.4	(C3)	CH_3- CH_2- Ar COOH	1.27 2.81 7.43-8.27 -	13.9 13.0 125.1-137.1 169.3
(L4)	CH_3- CH_2- CH_2- Ar COOH	1.1 1.74 2.92 7.15-8.15 -	13.8 21.6 34.1 123.8-143.1 171.6	(C4)	CH_3- CH_2- CH_2- Ar COOH	0.90 1.35 2.77 7.41-8.32 -	13.0 24.2 22.0 125.3-138.7 169.1
(L5)	CH_3- CH_2- CH_2- CH_2- Ar COOH	0.96 1.46 1.78 2.94 7.15-8.16 -	13.7 22.3 30.2 31.9 123.8-143.1 171.4	(C5)	CH_3- CH_2- CH_2- CH_2- Ar COOH	0.88 1.44 1.60 2.77 7.42-8.28 -	13.4 21.6 32.0 20.0 124.9-138.5 168.8

spectroscopy. Based on the microanalysis and spectroscopic results of the obtained compounds, we concluded that the ligands are bidentately coordinated to the zinc(II)-ion, but we could not yet conclude anything about the complex geometry.

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