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COORDINATION COMPOUNDS OF 3d-METALS 5-SULFOSALICYLATES

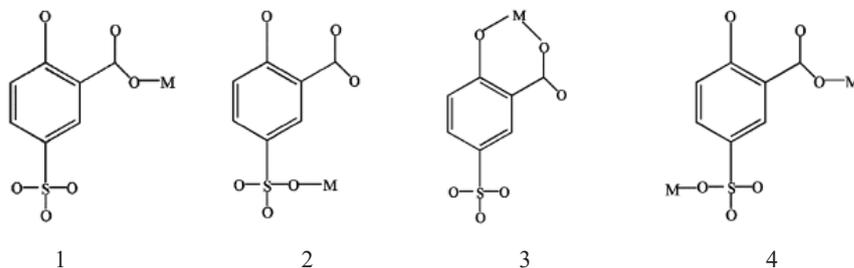
The review is devoted to the characteristic of 3d-metal coordination compounds with 5-sulfosalicylate anions and their mixed-ligand complexes. Their preparation, structure, properties and applications are considered.

Keywords: coordination compound, complex, 3d-metal, 5-sulfosalicylate

1. GENERAL CHARACTERISTICS OF 5-SULFOSALICYLIC ACID AND 5-SULFOSALICYLATES

5-Sulfosalicylic acid shows biological activities such as antiulcer, antifungal, anti-inflammatory, antitumor and antimicrobial [1]. Furthermore, its metal complexes with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and VO(II) exhibit antimicrobial activity stronger than that of the free ligand [2–4].

5-Sulfosalicylic acid molecule H_3SSal has three functional groups, SO_3H , $COOH$, and OH . 6 forms of 5-sulfosalicylic acid may exist: (1) neutral, (2) singly deprotonated at the sulfo group $-SO_3H$, (3) singly deprotonated at the carboxy group $-CO_2H$, (4) doubly deprotonated at the sulfo $-SO_3H$ and carboxy $-CO_2H$ groups, (5) rarely doubly deprotonated at the $-SO_3H$ and the $-OH$ groups, and (6) triply (completely) deprotonated [5]. Thence it possesses versatile coordination modes (fig. 1). Simultaneously it can participate in additional bonding interactions (hydrogen bonding or other molecular contacts) at peripheral sites. It has the ability to construct a novel metal-organic supramolecular network through specific and directional hydrogen bonds as well as π - π stacking due to the presence of aryl rings (fig. 1) [4]. It can form coordination polymers with diverse architectures, such as linear or zigzag chains, ladders, helices, honeycombs, square grids, brick walls, and interwoven diamondoids leading to different functional properties [6].



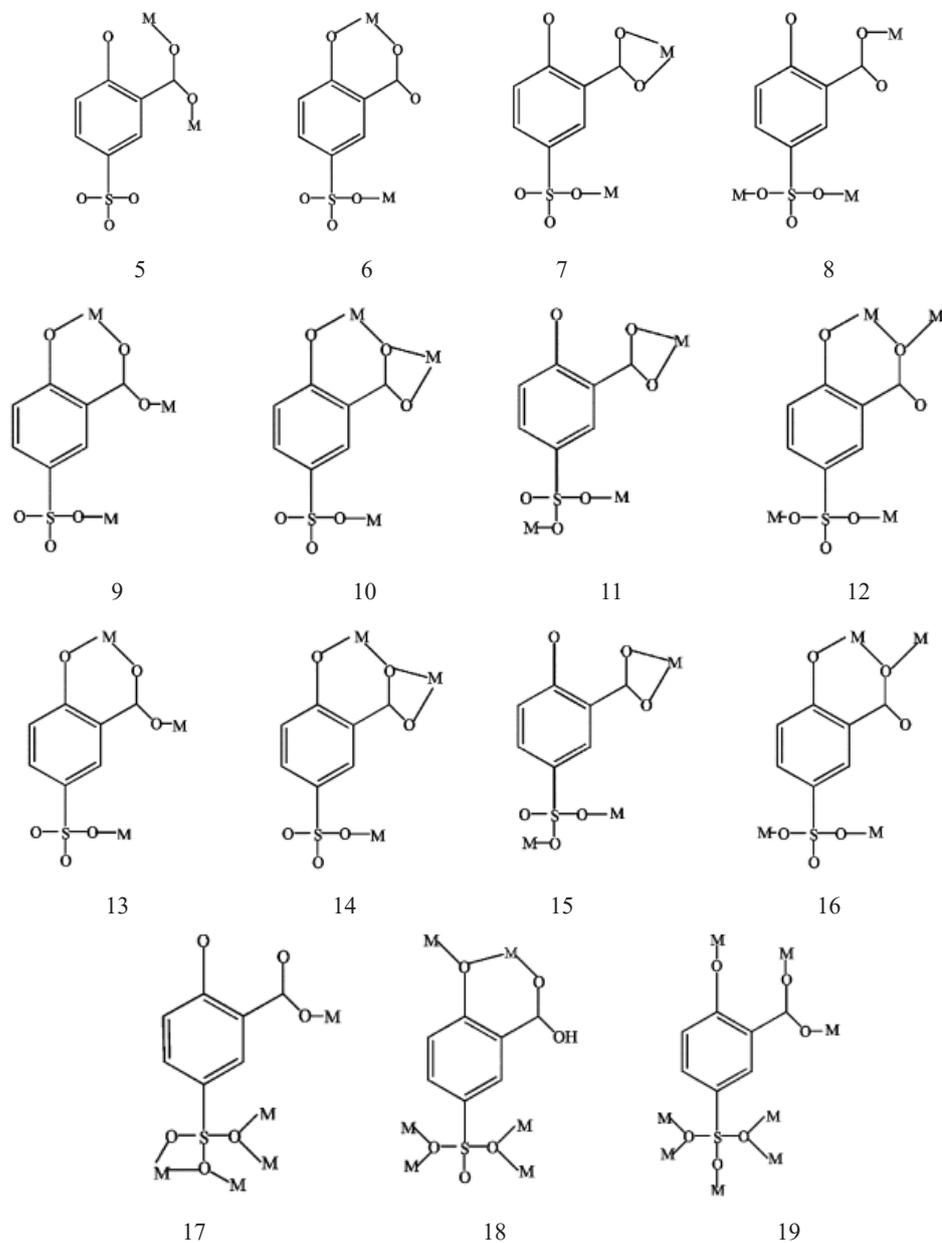


Fig. 1. Coordination modes of 5-sulfosalicylates.

The 5-sulfosalicylate can provide different superexchange pathways transmitting magnetic interactions between paramagnetic metal centers owing to the diversity of their bonding modes [7].

2. PREPARATION OF 5-SULFOSALICYLATE SALTS AND COMPLEXES

Simple metal 5-sulfosalicylate salts can be prepared by the action of 5-sulfosalicylic acid on metal oxides [8, 9], hydroxides [10] or carbonates [11–13] in water.

Hydrated Fe(III)(Ssal) was synthesized by adding of Na_2HSsal to $\text{Fe}(\text{NO}_3)_3$ with subsequent action of NaOH and isopropanol [10].

The most often studied ligands in complexes with 5-sulfosalicylates were nitrogen-containing molecules, primarily bipyridines.

The reaction of copper diacetate, sulfosalicylic acid and 2,2'-bipyridine in methanol yields a trinuclear complex, $[\text{Cu}_3(\text{SSal})_2(\text{Bipy})_2(\text{H}_2\text{O})_4]4\text{H}_2\text{O}$, which incorporates the sulfosalicylate entity as a completely deprotonated trianionic group. Two of the three Cu atoms are chelated by the heterocyclic ligand [14]. However, a similar synthesis carried out with the sodium salt of the acid instead of the acid itself and copper nitrate in water yields the mononuclear salt-like compound $[\text{Cu}(\text{H}_2\text{Ssal})(\text{Bipy})](\text{H}_2\text{Ssal})$, containing two mono-deprotonated sulfosalicylate groups. One of them is covalently bonded to the bis-chelated Cu atom, whereas the other exists in the outer coordination sphere [15].

The reaction of zinc diacetate and sulfosalicylic acid in water and 2,2'-bipyridine in methanol yields the polymeric compound $[\text{Zn}(\text{HSsal})(\text{Bipy})(\text{H}_2\text{O})_2]$ [16].

The combination of synthesis strategies, solvents, reaction temperature, starting materials, and molar ratios can largely influence the formation of final products and enables to obtain complexes with various topologies. It is not possible to synthesize 2,2'-bipyridine copper-5-sulfosalicylate complexes using copper(II) chloride or copper(II) sulfate as a reactant. The starting material used in the syntheses can be copper acetate or copper nitrate. The higher the pH of the solution is, the easier the deprotonation of the ligand H_3Ssal is [6].

The supramolecular 4,4'-bipyridine and 4,4'-dipyridyl-N, N'-dioxide Mn complexes with 5-sulfosalicylate dianion have been synthesized by adding to an aqueous solution of Na_2HSsal and Mn chloride a methanolic solution of ligand [17].

The 5-sulfosalicylate three functional groups provide a huge potential ability for in situ ligand synthesis. Except the sulfosalicylate of partly or fully deprotonated, the 5-sulfosalicylate can be decarboxylated. Decarboxylation is any chemical reaction in which a carboxyl group is split off from a compound as carbon dioxide. In generally, chemical decarboxylation reactions often require hydrothermal synthetic method, extensive heating in high boiling solvents or presence of a catalyst. From the decarboxylation of 5-sulfosalicylic acid under the hydrothermal conditions 4-hydroxybenzenesulfonate arises and its Mn and Co complexes with 4,4'-bipyridine have been synthesized [18].

The hydrothermal procedure for the synthesis of 5-sulfosalicylate Cu and Cr complexes with 2,2'-bipyridine and 1,10-phenanthroline was carried out in water [4].

The reaction of cobalt nitrate and 5-sulfosalicylic acid mixture in water and 1,10-phenanthroline in water – methanol mixture yields the cobalt(II) complex $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2](\text{HSsal})\cdot 4\text{H}_2\text{O}$. Its reaction with copper acetate led to a novel complex $[\text{Co}(\text{phen})(\text{H}_2\text{O})_4][\text{Cu}_2(\text{Ssal})_2(\text{phen})_2]\cdot 5\text{H}_2\text{O}$ [19].

The pH value of the solutions containing titanium tetrachloride, 5-sulfosalicylic acid and 1,10-phenanthroline have important effect on the formation of titanium coordination

complexes. Moreover, solvent has played an important role in synthesis design for the formation of high quality crystals [20].

$[\text{Cu}_4(\text{L})_2(\text{HL})_2(\text{H}_2\text{O})_2](\text{HSSal})$ (H_2L = Schiff base ligand 2-ethoxy-6-[(1-hydroxy-methyl-propylimino)-methyl]-phenol) has been obtained by adding to a methanolic solution of Et_3N and H_2L methanolic solution of copper perchlorate and then a mixture of methanol–water solution of disodium sulfosalicylate [21].

A mixed-valence complex with di-2-pyridylamine (dpa) $[\text{Cu}^{\text{II}}(\text{Ssal})_2(\text{dpa})_2] \cdot [\text{Cu}^{\text{I}}(\text{dpa})_2] \cdot 2\text{H}_2\text{O}$ has been obtained under hydrothermal conditions from copper acetate, 5-sulfosalicylic acid, di-2-pyridylamine and NaOH in water [22]. Hydrothermal reactions of mixed ligands 5-sulfosalicylic acid and macrocyclic oxamide complex (CuL , H_2L = 2,3-dioxo-5,6,14,15-dibenzo-1,4,8,12-tetraazacyclopentadeca-7,13-diene) with $\text{Mn}(\text{ClO}_4)_2$ afford complexes, including Mn^{II} and Mn^{III} [7].

Metal-organic framework (MOF) has been synthesized under hydrothermal conditions from zinc acetate, 5-sulfosalicylic acid and 1,10-(1,4-butanediyl)bis(imidazole) [23].

By adding of benzohydrazide to metal 5-sulfosalicylate salts in water Cu, Ni, Co, Zn benzohydrazide – 5-sulfosalicylate complexes have been synthesized. After dissolving under boiling in water/ethanol (1:1) mixture Ni complex added ethanol molecules, and Co complex contained water [5, 24]. Co, Ni and Zn complexes with phenylacetylhydrazide were prepared similarly; this ligand was dissolved in methanol [25].

By reaction of thiosemicarbazide with an aqueous solution of preliminarily prepared 3d-metal 5-sulfosalicylates were synthesized Cu, Ni and Co thiosemicarbazide – 5-sulfosalicylates complexes [26, 27]. We obtained two isomeric Ni(II) complexes. Prolonged reaction of nickel(II) 5-sulfosalicylate with an equimolar amount of thiosemicarbazide afforded green complex, whereas pink complex was rapidly formed in the reaction of nickel(II) 5-sulfosalicylate with 2 equiv of thiosemicarbazide [27].

3. STRUCTURES OF 5-SULFOSALICYLATES COMPOUNDS

Complexes structure determinations reveal 5-sulfosalicylates can form structurally diverse complexes with different coordination polyhedrons.

In simple metal 5-sulfosalicylate salts $[\text{M}(\text{H}_2\text{O})_6](\text{H}_2\text{Ssal})_2 \cdot n\text{H}_2\text{O}$ anions do not coordinate to metals, but act as counter-anions. The crystal structure is composed of alternating layers of $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ cations and H_2Ssal^- anions. The $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ cations, water molecules and H_2Ssal^- anions are connected through a complex pattern of H-bonding interactions [8, 9, 11–13].

In $\text{Na}[(\text{H}_2\text{O})_3(\text{Ssal})\text{Cu}(\text{II})] \cdot 2 \times 0.5\text{H}_2\text{O}$ the 5-sulfosalicylate anion, (Ssal^{3-}), coordinates rather unusually in the syn–syn coordination mode since it binds bidentately the Cu(II) ion through the carboxylic and the phenolic oxygens [3].

A mixed-valence $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ anion-cation complex bis[1-5-sulfosalicylato(3-)]bis[(di-2-pyridylamine)-copper(II)] bis[bis(di-2-pyridylamine)copper(I)] dihydrat $[\text{Cu}^{\text{II}}_2(\text{Ssal})_2(\text{C}_{10}\text{H}_9\text{N}_3)_2][\text{Cu}^{\text{I}}(\text{C}_{10}\text{H}_9\text{N}_3)_2] \cdot 2\text{H}_2\text{O}$ consists of anionic Cu^{II} moieties, cationic Cu^{I} species and uncoordinated water molecules. The anionic dimeric unit consists of one fully deprotonated 5-sulfosalicylate anion, a di-2-pyridylamine group and a Cu^{II} atom. Each Cu^{II} atom is 5-coordinate within a square-pyramidal geometry. The basal plane of the square-pyramidal geometry of the Cu^{II} center is occupied by two N atoms of a dpa

ligand and two O atoms of the fully deprotonated Ssal^{3-} ligand, while the apical position is taken by the phenoxo O atom of a second Ssal^{3-} ligand. Only one carboxylate O atom from the Ssal^{3-} ligand is directly bonded to the Cu^{II} atom, and the coordination mode of the carboxylate moiety is obviously anti monodentate. In the cationic monomer, the Cu^{I} atom adopts tetrahedral geometry. The cations and anions are connected by $\text{O-H}\cdots\text{O}$ and $\text{N-H}\cdots\text{O}$ hydrogen bonds [22].

Two 5-sulfosalicylic acid and 1,10-phenanthroline substituted titanium-oxo-clusters, $[\text{Ti}_6\text{O}_8(\text{Hssal})_2(\text{Phen})_6(\text{H}_2\text{O})_4]\cdot 4\text{OH}\cdot 21\text{H}_2\text{O}$ (TOC-1) and $[\text{Ti}_4\text{O}_4(\text{Hssal})_4(\text{Phen})_4]\cdot 18\text{H}_2\text{O}\cdot 4\text{NH}_3$ (TOC-2) have been synthesized [20]. The structure of TOC-1 is a hexanuclear cluster containing a $\{\text{Ti}_6(\mu_2\text{-O})_8\}$ core, where all titanium ions can be described in a distorted octahedral geometry with both 1,10-phenanthroline and 5-sulfosalicylate serving as chelating ligands, while TOC-2 consists of a tetranuclear $\{\text{Ti}_4(\mu_2\text{-O})_4\}$ skeletons forming an approximate plane quadrilateral where both 5-sulfosalicylate and 1,10-phenanthroline ligands chelate to the titanium atom and oxygen atom bridges two titanium atoms [20].

The Cu atom in the compound $[\text{Cu}(\text{H}_2\text{Ssal})(\text{Bipy})](\text{H}_2\text{Ssal})$ [15] is chelated by the two N-heterocycles and is covalently bonded to the sulfonate O atom of the sulfosalicylate ion in a trigonal-bipyramidal geometry. The uncoordinated sulfosalicylate anion interacts with adjacent anions, forming a linear hydrogen-bonded chain; the mononuclear cations are appended to the chain by hydrogen bonds. The uncoordinated anion uses its carboxylic acid H atom to form a hydrogen bond to the sulfonate O atom of another uncoordinated anion, resulting in a relatively strong hydrogen-bonded chain. The mononuclear cations are appended to the chain, also through a carboxylic acid/sulfonate hydrogen bond that is marginally weaker.

Two structurally diverse complexes, $[\text{Cu}_4(\text{CH}_3\text{COO})_2(\text{Ssal})_2(2,2'\text{-bipy})_4(\text{H}_2\text{O})_2]6\text{H}_2\text{O}$ (1) and $\{[\text{Cu}(\text{Ssal})(2,2'\text{-bipy})][\text{Cu}_2(\text{Ssal})(2,2'\text{-bipy})_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})\}_n$ (2) have been characterized by single crystal X-ray analyses. The structure of complex 1 is a tetranuclear species where both the carboxyl and phenoxo chelate to the copper atom and the carboxyl also bridges two copper atoms, while complex 2 features a charge transfer species with two cationic and anionic chains, in which both the carboxyl and sulfonyl are coordinated to copper atoms. In (1) the geometry of the Cu1 atom is completed by two nitrogen donors from one 2,2'-bipy, one carboxyl oxygen atom, and two phenoxo oxygen atoms from two Ssal^{3-} ligands. The coordination environment of the Cu2 atom consists of two nitrogen atoms of one 2,2'-bipy, one carboxylate oxygen atom of one Ssal^{3-} ligand, one oxygen atom from one water molecule, and one oxygen atom from the acetate ligand. The Ssal^{3-} ligand is fully deprotonated and uses the carboxyl and phenoxo groups to coordinate three metal atoms while the sulfonyl group is noncoordinating. The carboxylate of Ssal^{3-} acts as a bridging linker with anti-screw mode. The phenoxo oxygen atom bridges two copper atoms. The tetramers are stacked by face-to-face π - π interactions between 2,2'-bipyridine ligands and between 2,2'-bipyridine and 5-sulfosalicylate.

In the complex 2 cation, the coordination geometry around Cu1 is completed by two nitrogen atoms from one 2,2'-bipy and three oxygen atoms from one carboxyl, one phenoxo, and one sulfonyl of two Ssal^{3-} ligands. The carboxylate of the Ssal^{3-} in the cation bridges Cu1 and Cu2. The Ssal^{3-} ligand links three copper atoms and extends the

cation into one-dimensional chain. In the anionic unit of complex 2, the square pyramidal geometry for Cu3 is similar to the environment of Cu1, but the Ssal³⁻ coordination mode is different from that of the cation. The Ssal³⁻ ligand only links two copper atoms and extends the anion into a one-dimensional chain [6].

The structure of metal-organic framework (MOF) [Zn(HSsal)(biim-4)]₃·0.5H₂O (biim-4 = 1,10-(1,4-butanediyl)bis(imidazole)) contains one Zn(II) atom, one HSsal²⁻ anion, one biim-4 ligand, and half a lattice water molecule. The Zn1 atom is four-coordinated by two oxygen atoms from one carboxylate group and one sulfonate group and two nitrogen atoms from one biim-4 ligand in a distorted tetrahedral geometry. The carboxylate group and sulfonate group of HSsal²⁻ anions are deprotonated. The Zn(II) atoms are bridged by HSsal²⁻ anions to form an infinite 1D chain. The chains are further connected by biim-4 ligands in zigzag conformations to yield a 3D framework [23].

In [Mn^{II}₂Mn^{III}(Ssal)₂(CuL)₂(OH)(H₂O)₃]_n (H₂L = 2,3-dioxo-5,6,14,15-dibenzo-1,4,8,12-tetraazacyclo-pentadeca-7,13-dien, CuL is macrocyclic oxamide complex) the Mn1 has a distorted octahedral geometry with two oxygen atoms from one oxamido ligand, one oxygen atom from a water molecule, one carboxylate oxygen atom, one phenolato oxygen atom and one sulfonate oxygen atom from three different Ssal³⁻ anions. The central three manganese ions are bridged by carboxylate group and hydroxyl oxygen atoms, which form [Mn₃O₄] clusters. The [Mn₃(Ssal)₂(CuL)₂(OH)(H₂O)₃] units are bridged by Ssal³⁻ creating a 1D ladderlike chain of clusters. In the 1D ladderlike structure, the Ssal³⁻ act as a tridentate connector to bridge the manganese(II) atoms.

Complex [Cu₂(HSsal)₂(CuL)₄]_n·2H₂O is a metallamacrocycle assembled by a pair of bridging ligands oxamide and HSsal²⁻. These ligands successfully link two trinuclear copper motifs by bridging copper atoms in adjacent trinuclear units [7].

In the compound [Zn(HSsal)(Bipy)(H₂O)₂]_n, the Zn atom adopts an octahedral geometry defined by two N-atom donors from one 2,2'-bipyridine ligand, two O atoms from one sulfonyl and one carboxyl group of two HSsal²⁻ ligands and two O atoms from two water molecules that are cis to each other. The 5-sulfonatosalicylate dianion uses the carboxyl and the sulfonyl groups to bridge two Zn atoms, producing a chain structure. Moreover, the water molecules and uncoordinated carboxyl O atoms are engaged in hydrogen bonding only within each chain, while water molecules and sulfonyl O atoms form hydrogen bonds between chains, generating a two-dimensional hydrogen-bonding network [16].

In Cu₄(OH)₂(Ssal)₂(phen)₄·7H₂O Cu1 is located in a plane consisting of two nitrogen atoms from a chelating phen molecule and two hydroxides, and the axial position is occupied by the phenolato oxygen atom. For Cu2, the plane is composed of two nitrogen atoms from the phen molecule, one carboxylate oxygen and one phenolato oxygen atom, and the corresponding axial position is taken by one hydroxide ion. Each Cu₄(OH)₂(Ssal)₂(phen)₄ molecule is linked to four neighboring tetrameric units to form a 2D supramolecular layer of rhombic windows through hydrogen bonding between μ₃-hydroxo groups and the uncoordinated sulfonate oxygen atoms. Interestingly, the water heptamers and sulfonate anions are interconnected into a 2D supramolecular layer with very large rhombic windows through hydrogen bonding [4].

In Cr(Ssal)(bipy)(H₂O)₂·2H₂O the Cr(III) center exhibits a distorted octahedral surrounding, in which the basal plane is formed by two nitrogen atoms from a

chelating 2,2'-bipy ligand and one carboxylate oxygen and one phenolic oxygen from a Ssal³⁻ ligand. The most remarkable feature of this 2D layer is that there exist a supramolecular ring consisting of four coordinated water molecules, six lattice water molecules, three Ssal³⁻ anions and three Cr³⁺ ions, formed through covalent bonds and hydrogen bonds [4].

In Cr(Ssal)(phen)₂ the Cr(III) center exhibits a distorted octahedral surrounding, in which the basal plane is formed by two nitrogen atoms from two different phen ligands and two bidentate chelating coordination oxygen atoms from one carboxylate oxygen and one phenolic oxygen. π - π -interactions between the aromatic rings of different ligands stabilize the 2D puckered supramolecular layer [4].

Complex $\{[\text{Mn}(\text{HCOO})(\text{H}_2\text{O})_2(4,4'\text{-bipy})]_2[\text{Mn}(4,4'\text{-bipy})(\text{Hssal})_2(\text{H}_2\text{O})_2]\}_n$ consists of a cation and an anion where both the Mn(II) atoms adopt an octahedral geometry. In the anion, the coordination geometry around Mn ion is completed by two N atoms from two 4,4'-bipy ligands in the apical positions, and four O atoms from two Hssal²⁻ ligands and two water molecules, respectively, occupying the basal plane. The Hssal²⁻ is doubly deprotonated and monodentate to Mn(II) atom by carboxyl group. In the anionic motif $[\text{Mn}(4,4'\text{-bipy})(\text{Hssal})_2(\text{H}_2\text{O})_2]^{2-}$, hydrogen bonding O-H \cdots O interactions among Hssal²⁻ and coordinated water molecules lead to a two-dimensional anionic network. Moreover, the anions and cations form hydrogen bonds among carboxylate group, sulfonate group and coordinated water molecules, and these hydrogen bonds create a three-dimensional architecture [18].

Complex $\{[\text{Mn}_2(\text{HSsal})_2(\text{dpyo})_3(\text{H}_2\text{O})_6]\cdot 2(\text{H}_2\text{O})\}$ is a rare Mn dinuclear species realized with bridging dpyo [dpyo = 4,4'-dipyridyl N,N'-dioxide] and coordinated HSsal²⁻ ligands to form a 3D architecture through H-bonding and π - π interactions.

In complex $\{[\text{Mn}(4,4'\text{-bipy})(\text{H}_2\text{O})_4]\cdot(\text{HSsal})\cdot(\text{H}_2\text{O})\}_n$, Mn(H₂O)₄ fragments are bridged by 4,4'-bipy, giving rise to a 1D chain. Its crystallographic independent unit comprises the metal unit Mn(4,4'-bipy)(H₂O)₄, in addition to the 5-sulfosalicylate dianion and a lattice water molecule. The manganese(II) ion presents a slightly distorted octahedral geometry with a O6 chromophore comprising three aqua ligands, two oxygen donors from different dpyo ligands (one mono-coordinated, the other bridging) and a carboxylic oxygen of the 5-sulfosalicylate ligand. The 5-sulfonatosalicylate dianions are encapsulated among the polymeric chains between the py planes to give rise to a 3D structure through an ordered H-bonded with the sulfonate oxygen and lattice water molecule atoms and π - π interactions. [17].

In $[\text{Cu}_3(\text{Ssal})_2(2,2'\text{-bipy})_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$ the three copper atoms are joined together by two carboxylate group from 5-sulfosalicylate anions in bidentate syn-anti fashion to form an almost perfect basal plane with terminal 2,2'-bipyridine ligands. The four short bonds are to oxygens of two water molecules and two carboxylate oxygens from different 5-sulfosalicylate anions, which form an approximate square plane that is perpendicular to the basal plane of the trinuclear copper. The another carboxylate oxygen atom of each 5-sulfosalicylate anion is bonded to the axial coordination sites at slightly long distance, being in agreement with the expected distance of weakly bonded oxygen. The apical positions are occupied by one water molecule and oxygen atom from sulfonic group at a weak coordination length. In the trinuclear entity, the three copper ions are arranged in a strict linear fashion. In the complex the 5-sulfosalicylate

acid has now lost all its three protons, behaves as a bridging ligand between each of two trimer units coordinating to one trimer through the carboxylate and the phenolato oxygen and to other trimer through the sulfonic oxygen. Consequently, copper trimer units are connected together through this weak coordination of sulfonic oxygens to external Cu(II) ions to give an infinite chain along a-axis. The oxygen atoms of the carboxylates and the sulfonic groups further form hydrogen bond with lattice water molecules in the structure, to give a three-dimensional network structure [14].

In $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2](\text{HSsal}) \cdot 4\text{H}_2\text{O}$ cationic motif $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ forms hydrogen bonds with carboxylate group, sulfonate group, and lattice water molecules through coordinated water molecules. The strong stacking interactions can be observed among 1,10-phenanthroline and Hssal^{2-} ligands.

Complex $\{[\text{Co}(\text{phen})(\text{H}_2\text{O})_4][\text{Cu}_2(\text{phen})_2(\text{Ssal})_2] \cdot 5\text{H}_2\text{O}$ consists of $[\text{Cu}_2(\text{phen})_2(\text{Ssal})_2]^{2-}$, $[\text{Co}(\text{phen})(\text{H}_2\text{O})_4]^{2+}$ and water molecules. The Ssal^{3-} ligand is fully deprotonated in which the carboxyl group adopts monodentate mode and the phenolate oxygen donor adopts bridging mode, while the sulfonate group does not coordinate metal atom. The cationic motif of $[\text{Co}(\text{phen})(\text{H}_2\text{O})_4]^{2+}$ forms hydrogen bonds with anionic motif $[\text{Cu}_2(\text{phen})_2(\text{Ssal})_2]^{2-}$ through coordinated water molecules, carboxyl groups, and sulfonate groups, therefore cationic and anionic motifs create a 2-D network. Then the lattice water molecules hold 2-D sheets into 3-D hydrogen-bonding architecture [19].

$[\text{Cu}_4(\text{L})_2(\text{HL})_2(\text{H}_2\text{O})_2](\text{Ssal})$ [$\text{H}_2\text{L} = 2\text{-ethoxy-6-}[(1\text{-hydroxymethyl-propylimino)-methyl] \text{-phenol}$] is tetranuclear with double open cubane core framework, and C-H \cdots π interactions results the formation of 1D supramolecular structure [21].

Crystals of thiosemicarbazide complex $[\text{Cu}(\text{TSC})_2(\text{H}_2\text{SSal})_2]$ are composed of doubly charged $[\text{Cu}(\text{TSC})_2]^{2+}$ cations and $(\text{H}_2\text{SSal})^-$ anions monodeprotonated at the sulfate moiety of 5-sulfosalicylic acid. The coordination polyhedron of the Cu atom is completed to a prolate tetragonal bipyramid (4 + 2) by Cu–O bonds of the sulfate moieties of both anions, which form together with hydrogen bonds the $[\text{Cu}(\text{TSC})_2(\text{H}_2\text{SSal})_2]$ supermolecule.

The anion $\text{H}_2\text{SSal}^{2-}$ favors the formation of numerous hydrogen bonds, which can be combined in cyclic fragments capable of strengthening of the structure due to π - π stacking interaction.

The H_2SSal^- anion in $[\text{Cu}(\text{TSC})_2(\text{H}_2\text{SSal})_2]$ contains the sulfate and salicylate moieties bonded through the carbon atom. Hydrogen bond closes a six-membered ring so that the salicylate moiety transforms into two fused rings. Both rings are involved in formation of π - π stacking ensembles. In addition, H_2SSal^- anions are combined by a centrosymmetric pair of hydrogen bonds into planar dimers, which, like bricks, form wallslayers running through the entire crystal.

Parallel to the anionic layers in complex structure, there are layers of cationic cores of supermolecules linked with each other also through hydrogen bonds, involving the N atoms of the thiosemicarbazide ligand and the O in the sulfate moieties of neighboring supermolecules [26].

The nature of the metal is the deciding factor in the formation of coordination compounds. So, benzohydrazide – 5-sulfosalicylate compounds have compositions

$[M^{II}(\text{Bhz})_2(\text{H}_2\text{SSal})_2]$ for Cu and Zn whereas $[M^{II}(\text{Bhz})_3](\text{HSSal})_3$ correspond to Ni and Co [5, 24].

IR spectroscopy data can be useful to determine the nature of binding of 5-sulfosalicylate anions. The IR spectrum of free 5-sulfosalicylic acid contains the following absorption bands (cm^{-1}): $\nu(\text{C}=\text{O})$ 1678; $\nu(\text{C}=\text{C}_{\text{arom}})$ 1477, 1439; $\nu_{\text{as}}(\text{SO}_2)$ 1234, 1203, 1165, 1134; $\nu_{\text{s}}(\text{SO}_2)$ 1084, 1065, 1026; $\nu(\text{S}-\text{O})$ 663. If the $\nu(\text{C}=\text{O})$ band remains almost unaltered this is evidence of a free carboxylic acid group. Proton abstraction from the carboxy group should lead to disappearance of carbonyl absorption band and appearance of two new bands at considerably lower frequencies due to antisymmetric and symmetric vibrations of carboxylate group (COO^-) where two oxygen atoms are equivalent. The values of $\Delta\nu(\text{COO}^-) = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$ equal to 130–160 cm^{-1} indicate that the carboxylate group remains free (outer sphere) in the coordination compound [5, 24–27]. $\Delta\nu$ 230–260 cm^{-1} indicates that the carboxylate groups in complexes are coordinated to metal ions in a monodentate mode, 160–190 cm^{-1} shows chelating-bridging coordination mode [18].

The peaks about 3500–3600 cm^{-1} may be attributed to the stretching vibrations of O-H (H_2SSal^-) of a free carboxylic acid group, and if they are absent, this indicates that both protons are deprotonated. In all cases, insignificant variations in the absorption pattern of aromatic C=C bonds are detected.

The decrease in the number of absorption bands can arise from symmetric vibrations of the sulfo group most likely due to the fact that it becomes more symmetric, which is caused by deprotonation of the SO_3H group [5, 24–27].

4. PROPERTIES AND APPLICATIONS OF 5-SULFOSALICYLATES COMPOUNDS

A large number of 5-sulfosalicylate compounds are *luminescent* [5, 6, 17, 18, 21, 23, 25, 28–30].

An intense fluorescent emission of copper(II) complexes with 5-sulfosalicylate and 2,2'-bipyridine about 470 nm was observed in the solid state at room temperature, which is red-shifted about 20 nm compared to that of H_3Ssal ligand (450 nm). Peaks in complexes $\{[\text{Cu}_3(\text{Ssal})_2(2,2'\text{-bipy})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}\}_n$ and $[\text{Cu}(\text{HSSal})(2,2'\text{-bipy})(\text{H}_2\text{O})_2]_n$ are stronger than those in complexes $[\text{Cu}_4(\text{CH}_3\text{COO})_2(\text{Ssal})_2(2,2'\text{-bipy})_4(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ and $\{[\text{Cu}(\text{Ssal})(2,2'\text{-bipy})][\text{Cu}_2(\text{Ssal})(2,2'\text{-bipy})_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})\}_n$. Such fluorescent feature is assigned to the ligand-to-metal charge transfer with some σ -donations from the cooperation of 2,2'-bipyridine and 5-sulfosalicylate ligands. Moreover, the emissions in complexes are stronger than that of free ligand, which is probably caused by the enhancement of the conformational rigidity of coordinated ligands and reduces the irradiative decay of the intra-ligand excited states. Therefore, this study suggests that these complexes might be excellent candidates for potentially photoactive materials [6].

$[\text{Zn}(\text{HSSal})(\text{biim-4})_3] \cdot 0.5\text{H}_2\text{O}$ [$\text{biim} = 1,10\text{-}(1,4\text{-butanediy})\text{bis}(\text{imidazole})$] shows blue shift relative to the free organic acid. This may be attributed to the coordination effects of the salicylate ligands to metal atoms, which increases the ligand conformational rigidity and reduces the nonradiative decay of the intraligand [23].

The excitation spectra of 5-sulfosalicylate – benzohydrazide complexes $[\text{Zn}(\text{Bhz})_2(\text{H}_2\text{SSal})_2]$ and $[\text{Ni}(\text{Bhz})_3](\text{HSSal})_3 \cdot 7.5\text{H}_2\text{O} \cdot 0.5(\text{C}_2\text{H}_5\text{OH})$ contain broad

bands in the UV region with maxima at 220–330 nm, which correspond to $n-\pi^*$ and $\pi-\pi^*$ transitions of organic ligands. The excitation maxima (290, 335 nm) and the shape of the excitation spectrum of $[\text{Zn}(\text{Bhz})_2(\text{H}_2\text{SSal})_2]$ correspond to those for crystalline sodium sulfosalicylate. This means that the organic counterion in the inner coordination sphere of the coordination compound is responsible for the emission of this compound. This is also confirmed by the fact that coordination compounds in which there are no aromatic anions are characterized by much lower emission intensity. The most intense luminescence is revealed for the Zn(II) compound, because this ion has a filled 3d-sublevel and has no allowed d-d transitions capable of absorbing the energy of excited state. Ni(II) compound is significantly inferior in emission intensity to Zn(II) compound, which is explained by the quenching of inter-ligand charge transfer due to energy transfer to excited levels of the central atom. Thus, the $[\text{Zn}(\text{Bhz})_2(\text{H}_2\text{SSal})_2]$ and $[\text{Ni}(\text{Bhz})_3]_3(\text{HSSal})_3 \cdot 7.5\text{H}_2\text{O} \cdot 0.5(\text{C}_2\text{H}_5\text{OH})$ can be potential luminescent materials [5].

3d-metal 5-sulfosalicylates complexes with phenylacetylhydrazide (L) $[\text{Co}(\text{L})_3]\text{HSSal} \cdot 3\text{H}_2\text{O}$, $[\text{Ni}(\text{L})_3]\text{HSSal} \cdot 3\text{H}_2\text{O}$, and $[\text{Zn}(\text{L})_3]\text{HSSal} \cdot 6\text{H}_2\text{O}$ are luminescent. $[\text{Zn}(\text{L})_3]\text{HSSal} \cdot 6\text{H}_2\text{O}$ has the brightest luminescence with a maximum at 416 nm, which results in the blue color of the radiation. In complexes $[\text{Co}(\text{L})_3]\text{HSSal} \cdot 3\text{H}_2\text{O}$ and $[\text{Ni}(\text{L})_3]\text{HSSal} \cdot 3\text{H}_2\text{O}$, the radiation is considerably quenched, which is related to the energy transfer from the sulfosalicylate ion to the central metal ions [25].

Many soluble complexes with sulfosalicylates are used in *quantitative analysis*.

Sulfosalicylic acid forms colored compounds with iron(III) ions, which are very stable chelate complexes. Therefore, it is used as an indicator in the complexometric titration of iron(III) [31]. It has been known as a reagent for the colorimetric determination of iron(III) [32]. Its ability of forming complexes with the metallic elements (Cu, Ni, Co, U) can be used to mask these elements in solution [33]. An investigation on the separation of the lanthanides from each other and from other trivalent metals by ion-exchange displacement methods applied to their sulfosalicylate complexes has been carried [10]. Fe(III)-sulfosalicylate (FeSSA) could be used as an efficient colorimetric chemosensor to detect oxalic acid [34].

A sulfosalicylate copper–nickel electrolyte can be used for *obtaining nanostructures* comprising alternate magnetic and nonmagnetic layers by a single-bath method. A variation of compositions allows to obtain, in one solution, multilayered structures that comprise alternating magnetic and nonmagnetic layers with a substantially different content of the nonmagnetic component in the magnetic layer and to effect on, for example, magnetotransport properties of such structures [35].

Fine-grained copper *deposits with high adhesion to the surface* can be obtained from sulfosalicylate (pH 6.6) solution in which the electrodeposition proceeds at high polarization due to low discharge rate constants of the anionic copper complexes [36].

Titanium-oxo-clusters [20] exhibit excellent *catalytic performance* in the oxidation of sulfides to sulfoxides with H_2O_2 as oxidant. In particular, TOC-1 is an efficient homogeneous catalyst and very interestingly it can be recovered by filtration upon cooling and then reused at least fourth times without losing activity, which is very rare in the oxygenation of organic sulfide.

Some sulfosalicylate complexes exhibit *anticancer activity*. Several researchers suggested that Cu(II)–salicylate complexes are able, like SOD, to disproportionate the

superoxide anion O_2^- into O_2 and H_2O_2 , reducing in this manner the concentration of superoxide anion that is responsible for the metabolic activation of some carcinogens and is a necessary component in tumor promotion. Moreover, the quick reaction of complex $Na[(H_2O)_3(SSal)Cu(II)] \cdot 2 \times 0.5H_2O$ with adenine suggests that a possible mechanism of action of the Cu(II)–salicylato complexes resides on their capability to react with the active site of SOD re-establishing the normal copper level in SOD and thus the normal SOD levels in neoplastic cells. Alternatively, a second hypothesis may be advanced: since adeninato ligand is able to substitute easily the 5-sulfosalicylate anion producing the stable Cu(II)–adeninato complex $[Cu_2(Ade)_4(H_2O)_2] \cdot 2H_2O$ (Ade⁻ = adeninato monoanion), authors of [3] suggest that a possible mechanism of the cytotoxic and anti-tumor action of Cu(II)–salicylato complexes should be based on their ability to form a strong Cu(II)–nitrogen bond with DNA nucleobases.

Various sulfosalicylic acid proton transfer salts and their novel proton transfer Cu(II) complexes were prepared from 5-sulfosalicylic acid and 2-aminopyridine derivatives and the inhibitory effects of these compounds on hydratases hCA I, hCA II, carbonic anhydrases CA IX (a hypoxia-inducible protein) and CA XII (another carbonic anhydrase isoenzyme which shows an increase in tumor cells) were examined in vitro. Starting compounds, simple salts and proton transfer salts have no inhibition effects on the hydratase activities of the isoenzymes. The novel compounds have remarkable inhibition effects on CA XII isoenzyme. Such compounds may, therefore, be considered as a new class of compounds for the development of isoform-selective inhibitors. With more detailed structure–activity studies, more effective compounds can be developed and these might be of potential use as drug ingredients [37].

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КООРДИНАЦІЙНІ СПОЛУКИ 5-СУЛЬФОСАЛІЦИЛАТІВ 3d-МЕТАЛІВ

Огляд присвячений методам добування, будові, властивостям та застосуванню координаційних сполук 5-сульфосаліцилатів 3d-металів та змішанолігандних комплексів на їх основі.

5-Сульфосаліцилова кислота виявляє різні види біологічної активності: противіразкову, протигрибкову, протизапальну, протипухлинну та протимікробну. Її металокомплекси з Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) та VO(II) виявляють сильнішу антимікробну активність, ніж вільний ліганд.

Молекула 5-сульфосаліцилової кислоти H₃SSal має три функціональні групи: SO₃H, COOH та OH. Можуть існувати 6 форм 5-сульфосаліцилової кислоти: (1) нейтральна, (2) одноразово депротонувана по сульфогрупі -SO₃H; (3) одноразово депротонувана по карбоксильній групі -CO₂H, (4) двічі депротонувана по сульфо- SO₃H і карбокси -CO₂H групах, (5) рідко двічі депротонувана по -SO₃H та -OH групах і (6) тричі (повністю) депротонувана. Отже, вона здатна до різних способів координації.

Прості солі 5-сульфосаліцилатів металів можна добути дією 5-сульфосаліцилової кислоти на оксиди, гідроксиди або карбонати металів у воді.

Найчастіше досліджуваними лігандами у комплексах з 5-сульфосаліцилатами були азотовмісні молекули, насамперед біпіридин. Добуто також змішанолігандні комплекси з фенантроліном, шиффовими основами, ди-2-піридиламіном, похідними імідазолу, бензгідразидом, фенілацетгідразидом, тіосемікарбазидом.

5-сульфосалицилати можуть утворювати структурно різноманітні комплекси з різними координаційними поліедрями. У простих 5-сульфосалицилатах металів аніони не координуються з металами, а діють як протіаніони. 5-сульфосалицилат-аніон здатний бути анти-монодентатним, бидентатно-хелатним, містковим. Можливе утворення 1D, 2D, 3D структур, що включають ланцюги та у ряді випадків кільцеві структури. Велику роль у цьому відіграють водневі зв'язки за участю аніонів, ко-лігандів та зв'язаної води. Можливий прояв стекінгової взаємодії.

Описано поведінку смуг поглинання в інфрачервоних спектрах при різних способах зв'язування 5-сульфосалицилат-аніону. Багато комплексів 5-сульфосалицилатів є люмінесцентними.

5-Сульфосалицилова кислота та її металеві похідні застосовуються в кількісному аналізі як індикатори, в колориметрії, для маскування та розділення йонів металів.

5-Сульфосалицилати можуть застосовуватися в процесах електроосадження, каталітичних процесах.

Деякі солі і комплекси сульфосалицилової кислоти мають протиракову активність.

Ключові слова: координаційна сполука, комплекс, 3d-метал, 5-сульфосалицилат

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