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COMPLEXES OF METALS WITH DIHYDRAZONES OF SUCCINIC ACID DIHYDRAZIDE

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Abstract: *Bis-(3,5-di-tert-butyl-salicylidene) dihydrazone of succinic acid dihydrazide was synthesized and its analogue-reduced azomethine bond. The complexes of Mn (II) and Fe (II) with these ligands were obtained. Based on the data of IR-, electron spectroscopy and elemental analysis, of the obtained complexes is assumed the binuclear structure. The possibility of catalytic reduction of the azomethine bond with $NaBH_4$ to the corresponding succinic acid bis-(2-hydroxybenzyl) succinic dihydrazide was shown. It was found that all obtained compounds have high bactericidal and fungicidal activities.*

Keywords: *hydrazides, succinic acid hydrazones, Mn(II), Fe(II) complexes.*
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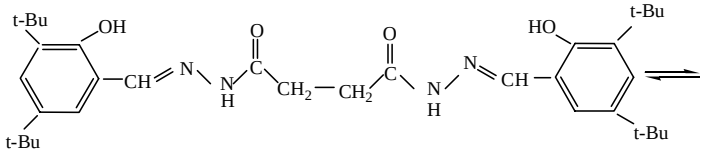
Introduction

Complexes of metals with salicylidene dihydrazones succin acid dihydrazide exhibit catalytic activity in the oxidation reaction of alkenes [1], are able to bind to DNA [2], and possess antimicrobial activity [3]. Salicyliden dihydrazone dihydrazide succinic acid, like dihydrazone derivatives of other dibasic acids, is potentially hexadentate and 4 anionic, due to deprotonation of two phenolic hydroxyls and two enolic groups, as in structure E.



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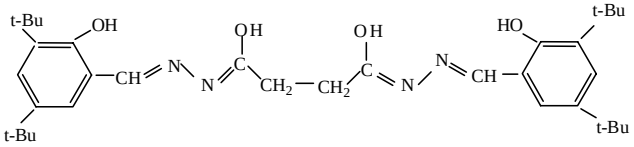


E

Therefore, this ligand is capable to form complexes of various compositions and structures. To date, binuclear copper (II) complexes [4], binuclear Fe(III) complexes [2], heterobinuclear complexes Zn(II), Cu(II), and Ni(II), [5,7] and binuclear complexes Mo(IV) [8] are known. Bi- and tetra-nuclear helicate compounds Eu (III) [9], helicate clusters of lanthanides and the influence of anions on their configuration [10] and dimeric and polymer complexes of Sn [11] were also obtained.

Obtaining new complexes of dihydrazones of this series is of interest from the point of view of search of compounds with biological activity, in particular, antimicrobial and fungicidal. In this case, metal complexes with hydrazones reduced on the azomethine group can be of considerable interest.

Earlier, we studied complexes with schiff bases hydrogenated at the azomethine group obtained from salicylic acid hydrazide and 3,5-ditretbutyl salicylic aldehyde [12].In this work, we synthesized and studied complexes of manganese and iron with dihydrazone derivatives of succinic acid dihydrazide and sterically hindered salicyl aldehyde-3,5-ditret-butyl salicylic and its reduced analog.

Experimental part

Obtaining bis(salicylidene) dihydrazone succinic acid dihydrazide(L^1).

Succinic acid dihydrazide was prepared by boiling succinic acid diethyl ether and a 60% aqueous solution of hydrazine for 5 hours. Mp = 180^0C. The Schiff base, bis(3,5-di-tretbuthyl-salicyliden)dihydrazone succinic acid L^1, was obtained by condensation of 1 mole of succinic acid dihydrazide and 2 moles of 3,5-ditretbuthyl salicylic aldehyde in alcohol solution at the boil for 1 hour. After recrystallization from ethanol Mp> 250^0 C.

For $C_{34}H_{88}N_4O_4$

Calculated,%: C 66.23; H 14.29; N 9.09; O 10.39.

Found,%: C 66.20; H14.25; N, 9.12; O 10.37.

Obtaining a complex of Mn(II) with the ligand L^1.

10^{-3}mol (0.616 g) of the ligand dissolved in 30 ml of ethanol was mixed with a methanol solution of 10^{-3}mol (0.245 g) of Mn $(CH_3COO)_2 \cdot 4H_2O$. The solution turned brown. It was heated to a boil and allowed to crystallize. After 15 minutes, small brown crystals precipitated, which were separated and washed with ethanol. After drying in vacuum Mp> 250^0C.

For $C_{68}H_{172}O_8N_8Mn_2$

Calculated:C 61.00; H 12.86; O 9.57; N, 8.37; Mn 8.21.

Found: C 60.99; H 12.85; O 9.58; N, 8.36; Mn 8.20.

Obtaining of Fe(II) complex with ligand L^1.

10^{-3}mol (0.616 g) of the ligand dissolved in 40 ml of ethanol was mixed with a methanol solution of 10^{-3}mol (0.392 g) of Mohr's salt in 5 ml of water. Through for half an hour, the solution was filtered off and after prolonged standing dark gray crystals gradually precipitated. Mp> 250^0C.For $C_{68}H_{172}N_8O_8Fe_2$

Calculated: C 60.90; H 12.84; N, 8.36; O 9.55; Fe 8.36.

Found: C 60.92; H 12.81; N, 8.34; O 9.56; Fe 8.37.

Reduction of bis(3,5-di-tretbuthyl-salicyliden)dihydrazone succinic acid (L^2).

6.16 g (10^{-2}mol) of Schiff's base and 0.2 g of $PdCl_2$ were suspended in 40 ml of methanol, and $NaBH_4$ (1 g) was added in small portions (until bleaching) with vigorous stirring. After adding the entire amount of borohydride, stirring was continued for another 0.5 hours.

The solution was filtered, diluted with three times the amount of water and acidified with a 10% aqueous HCl solution to pH ~ 7. The precipitated substance was separated on a porous filter, washed with water, recrystallized from ethanol-water (1: 1), and dried in air. Mp> 250^0C.

For $C_{34}H_{92}N_4O_4$

Calculated: C 65.81; H 14.84; N, 9.03; O 10.32.

Found: C 66.09; H 14.52; N, 9.10; O 10.32.

The $Mn_2(L^2)_2$ and $Fe_2(L^2)_2$ complexes were obtained by a similar procedure for $Mn_2(L^1)_2$ and $Fe_2(L^1)_2$, by the interaction of the L^2 ligand with the $Mn(CH_3COO)_2 \cdot 4H_2O$ salts and the Mohr salt.

For $C_{68}H_{180}N_8O_8Mn_2$

Calculated: C 60.63; H 13.37; N, 8.32; O 9.51; Mn 8.16.

Found: C 60.64; H 13.38; N, 8.31;O 9.50; Mn 8.17.

For $C_{68}H_{180}N_8O_8Fe_2$

Calculated: C 60.53; H 13.35; N, 8.31; O 9.50; Fe 8.31.

Found: C 60.52; H 13.37; N, 8.29; O 9.48; Fe 8.32.

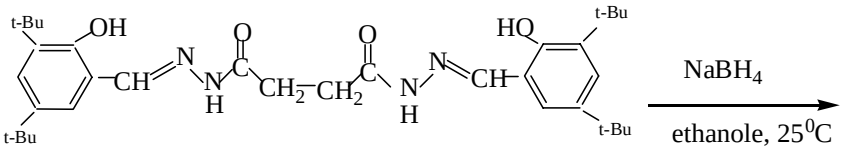
The antimicrobial activity of the investigated compounds was studied by the zonal diffusion method according to GOST 9.085-78. Mixtures of pure bacteria and fungi were taken for research.

Bacteria: - Mycobacteriumlacticolium–VKMB - 365, Pseudomonas aeruginosa

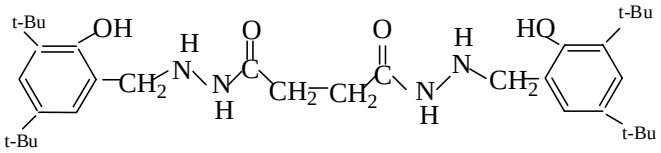
VKMV - 588 and Staphylococcus aureus. The following fungal cultures were used to test fungal activity: Aspergillusniger VKM-1119, Penicillium Cyclone - VKM-109; Cladosporium - Geosmin - VKM - 1701.

The discussion of the results

(3,5-ditretbutyl salicyliden) dihydrazone of succinic acid dihydrazide L1, unlike other derivatives of salicylic aldehyde dihydrazones, is readily soluble in various organic solvents, including lowpolar ones. An attempt to directly hydrogenate the double azomethine bond in dihydrazone L_1 with sodium borohydride is unsuccessfully and insignificant amounts of the reduced ligand are observed in the reaction products, despite the fact that Schiff bases of various amines and aldehydes are usually easily converted to secondary amines by the action of $NaBH_4$ in alcohol and other solutions. Therefore, we carried out catalytic reduction using palladium chloride as a catalyst.



L^1



L^2

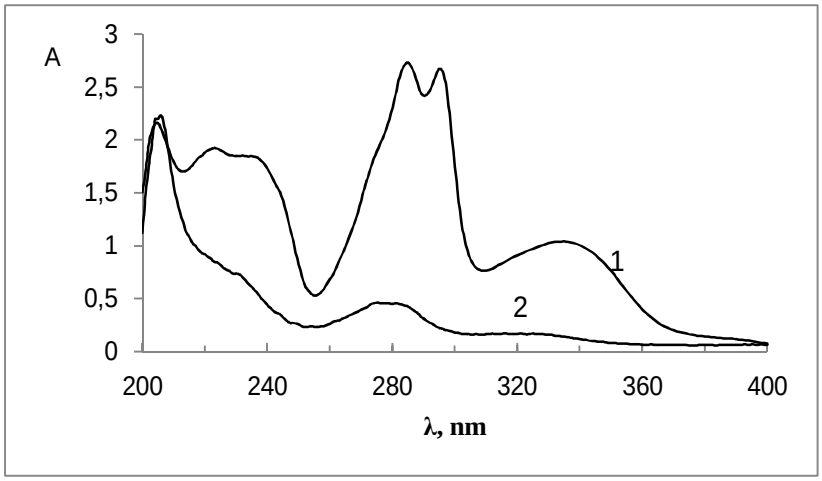


Fig.1. Electronic absorption spectra in solutions of ethyl alcohol: 1-dihydrazone succinic acid with 3,5-ditretbutyl salicylic aldehyde L^1, 2-reduced dihydrazone L^2.

Figure 1 shows electronic absorption spectra. The electronic spectrum L^1 in the ultraviolet region contains π-π * absorption band at 285 nm due to the aromatic ring and n-π * in the azomethine group C = N at 330 nm. In the reduced dihydrazone L^2 the band at 330nm disappears due to the reduction of the double bond C = N andπ - π *band of the aromatic ring is observed at 275 nm (Fig. 1).

The electronic spectrum of the absorption complex in the visible region contains absorption bands at 430 nm and 560 nm.

When dihydrazone L^1 is complexed with Mn(II), the band of the amide carbonyl group observed at 1640–1660 cm^{-1} (in the starting ligand) disappears and the band of the azomethine group is shifted from 1620 cm^{-1} to 1605 cm^{-1}.

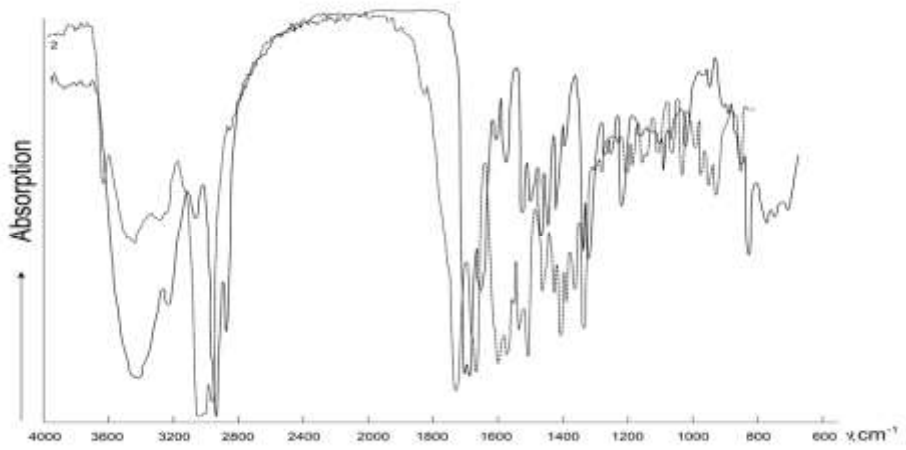
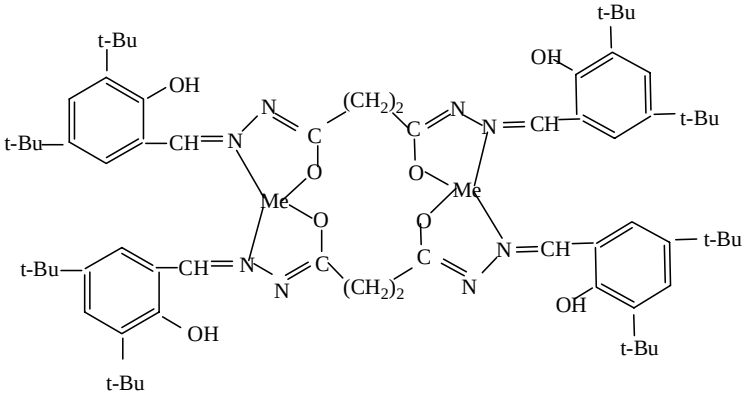


Fig.2. IR absorption spectra: 1-dihydrazone succinic acid L^1, 2- IR spectrum of the complex with $Mn_2(L^1)_2$.

There received data point to participation in the coordination of both of these groups, and the amide group coordinates the metal ion in enol form. The phenolic band OH, located in the initial ligand at 3440 cm^{-1}, strongly decreases in intensity (≈ 2 times) upon complexation. Thus, the Mn(II) ion is coordinated with the ligand through the oxygen atom of the amide group in the enol form and the nitrogen atom of the azomethine group.

Elemental analysis indicates a metal ligand ratio of 1:1.



The Fe(II) complex with this ligand has the similar structure, the electronic and IR spectra of which coincide with the manganese complex.

We have studied the bactericidal and fungicidal properties of the synthesized compounds. As you know, lubricating oils during storage in conditions (elevated temperatures and humidity) are exposed to microorganisms action, that alter the composition of the oils, increasing their acidity, and accordingly, corrosion ability.

To suppress the possibility of bacterial growth, additives in the form of pure chemical compounds or mixtures that have bactericidal properties are introduced into lubricating oils.

Currently, a large number of chemical compounds of various classes with bactericidal properties are known. However, metal complexes with reduced ligands have not yet

been studied as antimicrobial and fungicidal preparations. This section presents the test results of Schiff and reduced Schiff bases, their complexes with metals.

As can be seen from the table, all tested compounds have antimicrobial and antifungal activity. Among the tested compounds. Among the compound, the Fe(II) complex with reduced succinic acid dihydrazone was most active.

It should be noted that high activity remains with decrease in the concentration of the substance (see table).

Table. Antimicrobial properties of dihydrazone succinic acid L^1, reduced dihydrazone L^2 and their complexes.

№	Conc. %	Chemical formula	Zone diameter, sm	Inhibition
			Bacterium in MPA (meat peptide agar)	Fungi in CA medium (wort agar)
1	1 0.5 0.25	L^1	2.0-2.2 1.6-1.8 1.4-1.4	1.0-1.2 0.8-1.0 + +
2	1.0 0.5 0.25	$Mn_2(L^1)_2$	2.2.-2.4 1.8-2.0 1.4-1.6	1.2-1.4 1.0-0.9 0.9-1.0
3	1.0 0.5 0.25	L^2	2.3-2.5 1.9-2.0 1.6-1.8	2.0-2.4 1.4-1.6 1.0-1.4
4	1.0 0.5 0.25	$Fe_2(L^2)_2$	2.7-2.8 2.0-2.6 1.8-1.9	2.2-2.6 1.6-1.8 1.4-1.5

+ - lack of activity

Thus, in this work, it was shown that bis (3,5-ditretbutylsalicylidene) dihydrazone of succinic acid dihydrazide (L^1), its reduced analog (L^2) forms binuclear complexes of the composition $M^2(L^{1,2})_2$ with ions Mn(II) and Fe(II)), in which the coordination of the ligand with the metal ion occurs through the oxygen of the carbonyl group, which is in enol form and the nitrogen atom of the azomethine group. It was found that all obtained compounds have high bactericidal and fungicidal activities.

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KƏHRƏBA TURŞUSUNUN DİHİDRAZİDİNİN DİHİDRAZONLARI İLƏ METAL KOMPLEKSLƏRİ

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Kəhrəba turşusunun dihidrazidi ilə bis-(3,5-ditretbutilsalisiliden) dihidrazonu və onun azometin rabitəsi üzrə reduksiya olunmuş analoqu alınmış, onların Mn(II) və Fe(II) kompleksləri sintez olunmuşdur. İQ-spektroskopiya, elektron spektroskopiya, element analizi nəticələrinə əsasən alınmış komplekslərin ikinüvəli olduğu müəyyən olunmuşdur. Göstərilmişdir ki, azometin rabitəsinin $NaBH_4$-lə katalitik reduksiyası yolu ilə kəhrəba turşusunun bis-(2-hidroksibenzil)dihidrazonunun alınması mümkündür. Müəyyən olunmuşdur ki, alınmış birləşmələr antimikrob və funqisid aktivliyə malikdirlər.
Açar sözlər: *hidrazidlər, kəhrəba turşusunun hidrazonları, Mn(II), Fe(II) kompleksləri.*

КОМПЛЕКСЫ МЕТАЛЛОВ С ДИГИДРАЗОНАМИ ДИГИДРАЗИДА ЯНТАРНОЙ КИСЛОТЫ

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Синтезирован бис-(3,5-ди-третбутил-салицилиден)дигидразон и его аналог, восстановленный по азометиновой связи. Были получены комплексы Mn(II) и Fe(II) с этими лигандами. На основе данных ИК, электронной спектроскопии и элементного анализа предложено биядерное строение полученных комплексов. Показана возможность каталитического восстановления азометиновой связи с помощью $NaBH_4$ в соответствующий бис-(2-гидроксибензил) дигидразид янтарной кислоты. Было обнаружено, что все полученные соединения обладают высокой бактерицидной и фунгицидной активностью.
Ключевые слова: *гидразиды, гидразоны янтарной кислоты, комплексы Mn(II), Fe(II*