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SYNTHESIS, STRUCTURE AND PROPERTIES OF COMPLEXES Cu(II) Co (II), Ni(II), VO(II) WITH (3,5-DITRETBUTYL-2-HYDROXYBENZYL)-2-HYDROXYBENZOYL-HYDRAZIDE

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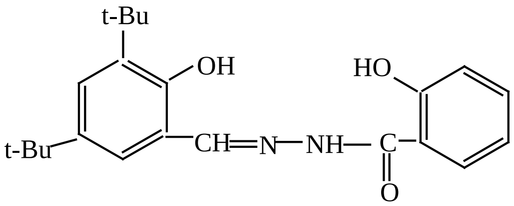
New Cu(II), Co(II), Ni(II) and VO(II) complexes with reduced Schiff bases were obtained from salicylic acid hydrazide and 3,5-di-tert-butyl salicylic aldehyde. The structure of these complexes was studied by means of IR- ,UV VIS spectrometry, thermosgravimetry and elemental analysis. It was found, that the coordination of the metal ions is due to oxygen of the amide group in the enol form, the nitrogen atom of the hydrazine group and oxygen atom of the salicylaldiminate fragment and the complexes have compositions with metal: ligand ratio is 1: 1.

Keywords: *hydrazides, hydrazones, Cu(II), Co(II), Ni(II) and VO(II) complexes, magnetic susceptibility, thermal analysis.*

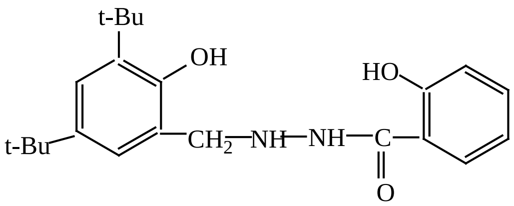
INTRODUCTION

There is a critical need for the development of new and inexpensive drugs for the treatment of many diseases. In the last two decades, profound interest has been shown in the synthesis of compounds, containing hydrazide and hydrazone groups and their complexes with transition metal ions . This interest is caused by their possible use in medicine (for the treatment of tuberculosis), in biological systems and analytical chemistry [1-4]. Acylhydrazones and their complexes with metal ions have pronounced biological and pharmaceutical effect as antitumor [5-7], antimicrobial [8], antitubercular [9] and antimalarial [10] agents.

We have obtained new Cu(II), Co(II), Ni(II), and VO(II) complexes with reduced Schiff base derived from salicylic acid hydrazide and 3,5-di-tert-butyl salicylic aldehyde. It should be noted, that there are no data on such compounds in the literature.



L^1H_4



L^2H_4

EXPERIMENTAL PART

IR spectra were recorded on a Nicolet IS10 spectrophotometer, electronic absorption spectra on a UV-VIS Evolution 60S spectrophotometer, and thermogravimetric

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analysis was performed using the NETZSCH STA 449F3 derivatograph.

Preparation of salicylic acid hydrazide

Salicylic acid hydrazide was prepared according to the procedure [11].

The preparation of Schiff base from salicylic acid hydrazide and 3,5-di-tert-butyl salicylaldehyde (L^1H_4)

To solution of 1.52 g (0.01 mol) salicylic acid hydrazide in 20 ml of ethyl alcohol 2.34 g (0.01 mol) of 3,5-di-tert-alicylic aldehyde in 25 ml of ethanol was added. The reaction mixture was refluxed during 10 min and allowed to crystallize. Yellow crystals dropped out which were separated and dried. $T_m = 235^0$C.

For $C_{22}H_{28}N_2O_3$

Calculated: C 71.74; H 7.61; N 7.61; O 13.04

Found: C 71.60; H 7.48; N 7.54; O 13.12

Hydrogenation of the Schiff base, prepared from salicylic acid hydrazide and 3,5-di-tert-butyl salicylaldehyde (L^2H_4)

3.69 (0.01 mol) Schiff base ***L1H4*** was dissolved in 30 ml of ethyl alcohol, and sodium borohydride was added portion wise with vigorous stirring until the yellow color disappeared completely (~ 0.015 mol $NaBH_4$). The reaction solution was diluted with 100 ml of water and acidified with 1N HCl solution of HCl to pH = 7. White crystals precipitated off which were separated, dried and recrystallized from ethanol $T_m = 162^0$C.

For $C_{22}H_{30}N_2O_3$

Calculated: C 71.35; H 8.11; N 7.57; O 12.97.

Found: C 71.20; H 8.00; N 7.44; O 12.82.

Preparation of the Cu complex with ligand L^2H_4

The solution of 10^{-3} mole (0.199 g) of $Cu(CH_3COO)_2 \cdot H_2O$ in 10 ml of methanol was added to solution of 10^{-3} moles (0.371 g.) reduced Schiff base L^2H_4 in 30 ml ethanol with stirring and heating at 50^0C. The resulting solution was filtered and allowed to crystallize. When cooled, dark green crystals $T_m > 250^0$C dropped out of it.

For $C_{22}H_{28}N_2O_3Cu$

Calculated: C 61.11; H 6.48; N 6.48; O 11.11; Cu 14.81.

Found: C 61.20; H 6.38; N 6.24; O 11.00; Cu 14.70.

Preparation of the Ni complex with ligand L^2H_4

A mixture of 10^{-3} mole (0.371 g) of L^2H_4 in 20 ml of ethanol and 10^{-3} moles of nickel acetate ($Ni(CH_3COO)_2$ $4H_2O$) in 10 ml of methanol was stirred with a magnetic stirrer at temperature of 40-50^0 C during 15-20 minutes. After cooling the reaction mixture to room temperature, a shallow-crystalline powder of a dark brown color precipitated with $T_m = 240^0$C.

For $C_{22}H_{28}N_2O_3Ni$

Calculated: C 61.87; H 6.56; N 6.56; O 11.25; Ni 13.76.

Found: C 61.70; H 6.28; N 6.42; O 11.05; Ni 14.70.

Similarly, the Co (II) complex was obtained. Complex has light brown color with $T_m > 250^0$C.

For $C_{22}H_{28}N_2O_3Co$

Calculated: C 61.84; H 6.56; N 6.56; O 11.25; Co 13.80.

Found: C 61.70; H 6.33; N 6.42; O 11.15; Co 14.85.

Preparation of VO^{+2} complex with ligand L^2H_4

The vanadyl complex synthesis was carried out by the interaction of L^2H_4 with $VOSO_4$ in a methanol solution and a molar ratio of 1: 1. The dark brown complex with $T_m > 250^0$C was obtained.

For $C_{22}H_{28}N_2O_4V$

Calculated: C 60.70; H 6.44; N 6.44; O 14.71; V 11.71.

Found: C 60.65; H 6.32; N 6.40; O 14.55; V 11.80.

The resulting complexes dissolve in methanol, ethanol, chloroform and benzene.

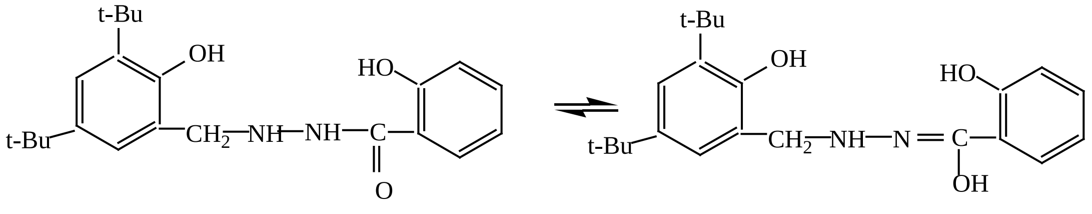
RESULTS AND DISCUSSION

The reduced Schiff base N-(3,5-di-tert-butyl-2-hydroxybenzylidene) salicyloylhydrazone L^2H_4 was obtained under mild conditions (in methanol solution at room temperature by sodium borohydride reducing. In the electronic absorption spectra of the Schiff base, the absorption bands at 210, 225 (bend), 265, 310, and 350 nm are observed which can be attributed to π-π * transitions in the salicylic hydrazone fragment (bands at 205 and 265 nm) and π-π * transitions in the di-tert-butyl-2-hydroxybenzylidene fragment (bands at 225 and 265 nm) The band at 350 nm refers to the n-π * transition in the C=N conjugated with the benzene ring.

In the reduced Schiff base L^2H_4, the band at 260 nm disappears and a broad peak with maximum absorption at 295 nm with bends at 285 and 320 nm is observed.

The IR spectrum of the Schiff base L^1H_4 contains the vibration bands of the C= N and C=O groups at 1612 cm^{-1} and 1634 cm^{-1}, respectively. The absorption bands at 3072 and 3196 cm^{-1} can be attributed to the vibrations of N-H and HO-C=N groups. In the reduced L^2H_4, the vibrational band at 1612 cm^{-1} which belongs to the azomethine group disappeared, while the carbonyl group CO band is observed at 1639 cm^{-1}. The vibrational band of the NH group in this ligand is at 3285 cm^{-1}, and the band at 3079 cm^{-1} has a very low intensity. The origin of the last band is attributed to the enolization of the carbonyl group (see below).

As noted above, this band is also observed in the Schiff base L^1H_4, but its intensity is much higher. This may indicate a higher degree of enolization in the Schiff base compared to its hydrogenated analogue L^2H_4.



L^2H_4-ketone form

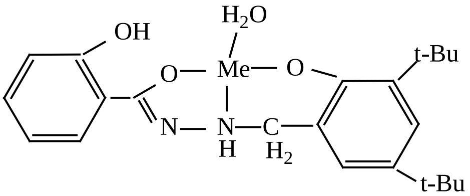
L^2H_4-enol form

In the Co(II), Ni(II), VO(II), and Cu(II) complexes with the L^2H_4 ligand, an additional band appears in the electronic absorption spectra in the region of 400 nm which depends on the nature of metal ion. This absorption band can be attributed to the ligand-metal charge transfer band. In the Cu(II) complex, it is at 410 nm, in the Ni(II) complex at 423 nm and in the Co(II) complex at 435 nm. Along with this band, d-d transitions are observed in the visible region which has wide low-intensity absorption bands for the Cu(II) complex at 620 nm, for Co(II) at 560 nm and Ni(II) at 530 nm.

IR spectra indicate, that the coordination of the ligand with the metal ion is performed with the oxygen atom of the carbonyl group in the enol state. Indeed, the absorption band of the amide group at 1639 cm^{-1} disappears when complexing. At the same time, at 3488 cm^{-1}, an absorption band of the hydroxyl group of the salicylhydrazide fragment is observed to indicate that this group does not participate in the coordination.

Derivatographic analysis confirms the elemental analysis data. From him follows also, that the metal: ligand ratio in the complexes is 1: 1. In addition, according to thermogravimetric data, the molecules of the Ni (II), Cu (II) complexes contain one water molecule, that lose in the temperature ranges between 120-250^{0}C. Further, several stages of weight loss of 300-420^{0}C (37-58%), 420-500^{0}C (4.5-22%) are observed.

Taking into account the data of elemental analysis, IR, electronic spectroscopy, as well as derivatography, the following structures can be attributed to the obtained complex:



According to the above structure, the coordination sphere of the metal ion is formed from oxygen atom of the amide group in the enol form, the nitrogen atom of the hydrazine group and the oxygen atom of the salicylaldiminate fragment.

Thus, the reduced Schiff base, the derivative of 3,5-di-tert-butyl phenol and salicylic aldehyde form stable complexes with Co(II), Ni(II), VO(II) and Cu(II) ions, soluble in polar and nonpolar organic solvents. The complexes obtained have compositions in which the metal: ligand ratio is 1: 1.

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СИНТЕЗ, СТРОЕНИЕ И СВОЙСТВА КОМПЛЕКСОВ Cu(II,) Co(II), Ni(II), VO(II) С (3,5-ДИТРЕТБУТИЛ-2-ГИДРОКСИБЕНЗИЛ)-2-ГИДРОКСИБЕНЗОИЛ-ГИДРАЗИДОМ

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Получены новые комплексы Cu(II), Co(II), Ni(II) и VO(II) с гидрированными по азометиновой группе шиффовыми основаниями, полученными из гидразида салициловой кислоты и 3,5-дитретбутил салицилового альдегида. Методами ИК-электронной спектрометрии, термогравиметрии и элементного анализа изучено строение этих комплексов. Показано, что координация иона металла осуществляется за счет кислорода амидной группы в енольной форме, атома азота гидразиновой группы и атома кислорода салицилальдиминатного фрагмента, и коммплексы имеют составы, в которых отношение металл:лиганд равно 1:1.

Ключевые слова: *гидразиды, гидразоны, комплексы Cu(II), Co(II), Ni(II) и VO(II), магнитная восприимчивость, термический анализ.*

Co(II), Ni(II),VO(II), Cu(II) METALLARININ (3,5-DİTRETBUTİL-2-HİDROKSİBENZİL)-2-HİDROKSİBENZOİL-HİDRAZİDLƏ KOMPLEKSLƏRİNİN SİNTEZİ, QURULUS VƏ XASSƏLƏRİ

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Salisil turşusunun hidrazidi və 3,5-ditretbutil salisil aldehidi əsasında yeni liqand alınmışdır. Bu liqandla Cu(II), Co(II), Ni(II) и VO(II) kompleksləri sintez olunmuşdur. İQ-, electron spektroskopiyası, termoqravimetriya və element analizi üsulları ilə bu komplekslərin quruluşu öyrənilmişdir. Göstərilmişdir ki, metal ionunun koordinasiyası enol formasında olan amid qrupunun oksigeni, hidrazin qrupunun azotu, salisilaldiminat fraqmentinin oksigeni hesabına formalaşır. Komplekslərin tərkibində metal:liqand nisbəti 1:1-dir.

Açar sözlər: *hidrazidlər, hidrazonlar, Cu(II), Co(II), Ni(II) и VO(II) kompleksləri, maqnit nüfuzlugu, termiki analiz.*