

Tetiana Panchenko, Maria Evseeva and Anatoliy Ranskiy

COPPER(II) AND NICKEL(II) WITH *N,N'*-BIS(SALICYLIDENE)THIOSEMICARBAZIDE HETEROMETAL COMPLEX COMPOUNDS

Vinnitsia National Technical University

Khmelnytske Ave., 21021 Vinnitsia, Ukraine; tpanchenko88@gmail.com

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Abstract. New heterometal coordination compounds of copper(II), nickel(II), and alkaline-earth metals with *N,N'*-bis(salicylidene)thiosemicarbazide have been synthesized. Using elemental analysis, IR-spectroscopy, molecular conductivity, magneto-chemical, and thermogravimetric investigations the composition and structure of the complexes of the general formula $E[ML']_2 \cdot xH_2O$ ($M^{2+} = Cu, Ni$; $E^{2+} = Ca, Sr, Ba$; $x = 1-4$; $H_3L' = N,N'$ -bis(salicylidene)thiosemicarbazide) have been examined. It has been shown that the synthesized compounds have semi-conducting properties.

Keywords: heterometal complex compounds, copper(II), nickel(II), salicylic anhydride thiosemicarbazone, semiconductor.

1. Introduction

The Schiff's bases as the organic ligands occupy the leading place of the modern coordination chemistry. The reason is that they contain a series of nucleophilic centers and functional groups in their structure, which coordinate with metal cation first of all and form new mono-, bi-, or polynucleolus complexes with various properties. Such compounds are widely used in nanotechnologies while forming different molecular devices, as well as in biochemistry, medicine, and microelectronics [1-4].

Thiosemicarbazones of aromatic and heterocyclic aldehydes, which form different complexes with 3d-metal ions, are of special interest among Schiff's bases [5-9]. In the mentioned compounds the initial thiosemicarbazones are one- or dibasic acids with tridentate coordination [10-15]. Moreover, it is shown in [16] that in alkali medium thiocarbazonates and their derivatives are capable of template synthesis over Cu(II), Ni(II), and VO(IV) matrices followed by the formation of tetradentate organic

ligand, the direct synthesis of which is impossible under other conditions. Earlier [17] we synthesized a series of heterometal complex compounds of Cu(II), Ni(II), Co(II), and alkaline-earth elements with *N,N'*-bis(salicylidene)semicarbazide *via* template synthesis and investigated their structure, composition, and properties. The purpose of this work is study of the complex formation of copper(II), nickel(II), and alkaline-earth elements with *N,N'*-bis(salicylidene)thiosemicarbazide and determination of composition and structure of resulted coordinated compounds.

2. Experimental

Salicylic aldehyde thiosemicarbazone was obtained *via* interaction between water-ethanol (1:1) mixture of thiosemicarbazide with salicylic aldehyde with the ratio 1:1 by the procedure described in [18]. $MCl_2 \cdot nH_2O$ ($M^{2+} = Cu, Ni$; $n = 2, 6$) and $E(OH)_2$ ($E^{2+} = Ca, Sr, Ba$) of P.A. purity were used to synthesize the compounds I-VI.

The content of metals in the resulted products was determined after the complex previous thermal decomposition: copper – by iodometric method [19]; nickel, barium, and strontium – by gravimetric method [19, 20]; calcium – by complexometric titration [21] and nitrogen – by Dumas method [22].

FT-IR analysis was performed using Nicolet iS10 spectrometer within the range of 4000–375 cm^{-1} . The samples were examined as received, without pretreatment. Derivatographic analysis was carried out using Paulic-Paulic-Erdey MOM OD-102 derivatograph in the atmosphere of air. The rate of temperature change was 2.5°/min within 293–773 K and 5°/min – within 293–1273 K. Molar electric conductivity of $1 \cdot 10^{-3}$ M solution in DMFA was determined using P-38 slidewire

bridge at 293 K. Magnetic susceptibility of the compounds was determined by Gui method at room temperature. $\text{Co}[\text{Hg}(\text{CNS})_4]$ was used as the calibration standard. Diamagnetic corrections were calculated in accordance with [23]. The effective magnetic (dipole) moments were calculated according to the formula $m_{ef} = (8c_m T)^{1/2}$. The electric properties of the investigated compounds were studied for pressed samples using E6-13A teraohmmeter (measurement range is $10\text{--}10^{14} \Omega$). The temperature was controlled using copper-constantan thermocouple and PP-63 potentiometer. The characteristics of semi-conductive materials were calculated in accordance with the formulas given in [24].

Calcium di[N,N'-bis(salicylidene)thiosemicarbazide] dihydrate(II) (I). The sample of salicylic aldehyde thiosemicarbazone (1.95 g; 10 mmol) is dissolved in 20 ml of water-ethanol mixture (1:1) in water bath at ≈ 343 K. The $\text{Ca}(\text{OH})_2$ aqueous solution is added by portions till pH = 8 and then 1.22 g (10 mmol) of salicylic aldehyde is added. The mixture is heated to 343 K and 1.71 g (10 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in 20 ml of ethanol is introduced. After the transparent solution is formed the aqueous solution of calcium hydroxide is continued to be added under constant stirring and heating (333–343 K) till pH = 9–10. The fine-crystalline sediment of green and then brown color is formed. The reaction mixture is kept in water bath for 1 h and then cooled. The sediment is kept under mother liquor for 12 h and then filtered using Schott's filter. The formed sediment of brown color is washed by cold ethanol and ether and dried in desiccator with CaCl_2 till the mass becomes constant. The yield is 2.35 g (59 %).

The other heterometal compounds II–VI are synthesized in the same manner. The results of elemental analysis and physico-chemical properties of the compounds I–VI are given in Table 1.

3. Results and Discussion

It was shown earlier that salicylic aldehyde thiosemicarbazone (H_2L) forms strong chelate complexes with Co(III) [12], Cr(III), and Fe(III) [25], as well as with Cu(II) and Ni(II) [26]. In these compounds H_2L is a tridentate ligand that joins the metal central atom *via* oxygen of phenoxyl radical, nitrogen of hydrazine residual, and sulfur of thicarbonyl group and forms stable five- and six-membered cycles. At the same time it was assumed that in the alkali medium H_2L enters into additional condensation with salicylic aldehyde over copper(II), nickel(II), and oxovanadium(IV) matrices by nitrogen of amide group [16, 27, 28]. As a result of such

unusual condensation a new organic molecule H_3L is formed. It is a tetradentate ligand which forms strong chelate compounds with the metal central atom. The resulted complexes have plane structure where sulfur atom is chemically bounded not with the central atom of 3d-element but with metal cation of external sphere. It should be noted that the synthesis of new ligand H_3L occurs only in the alkali medium and over matrices Cu(II), Ni(II), and VO(IV). To continue these investigations of new heterometal coordination compounds of Cu(II), Ni(II), and alkali-earth elements with *N,N'*-bis(salicylidene)thiosemicarbazide were synthesized. Physico-chemical properties and results of elemental analysis of the synthesized compounds of the general formula $\text{E}[\text{ML}']_2 \cdot x\text{H}_2\text{O}$ ($\text{M}^{2+} = \text{Cu}, \text{Ni}$; $\text{E}^{2+} = \text{Ca}, \text{Sr}, \text{Ba}$; $x = 1\text{--}4$; $\text{H}_3\text{L}' = \text{N,N}'\text{-bis(salicylidene)thiosemicarbazide}$) are given in Table 1. Depending on the nature of 3d-element the complexes have different colors: I–III – brown-colored and IV–VI – cherry-colored. On the basis of elemental analysis we observe the ratio $\text{M}:\text{E}:\text{L}' = 2:1:2$ ($\text{M}^{2+} = \text{Cu}, \text{Ni}$; $\text{E}^{2+} = \text{Ca}, \text{Sr}, \text{Ba}$; $\text{H}_3\text{L}' = \text{N,N}'\text{-bis(salicylidene)thiosemicarbazide}$) irrespective of the ion nature of 3d-metal.

The compounds I–VI have good solubility in DMFA and DMSO, worse solubility in ethanol and acetone, and are practically not dissolved in water, chloroform, acetonitrile, and tetrachlormetan.

For the compounds I–VI dissolved in DMFA we determined the molar electric conductivity (Table 1). They are found to be three-ion electrolytes.

On the basis of magneto-chemical investigations of nickel-containing compounds IV–VI we determined their diamagnetic nature. While measuring molar magnetic susceptibility of the compounds I–III (Table 1) we observe that their m_{ef} values are similar to spin value ($m_{ef} = 1.73$ B.M.) of one unpaired electron. It indicates the absence of exchange between Cu^{2+} ions in the synthesized complexes.

The thermal stability of the obtained compounds I–VI was investigated using thermogravimetric analysis. Within the range of 343–373 K we observe an endothermal effect which corresponds to the detachment of water crystallization molecules by the value of mass loss on TG curve (Table 2). The compounds I–VI are stable to the temperatures of 583–633 K. The further heating leads to the oxidative destruction of the complexes accompanied by a series of strong exothermal effects on DTA curve. The process is finished at 723–773 K by complete combustion of organic residues. The analysis of derivatograms for the compounds I–VI testifies to their complete destruction within 683–713 K regardless of 3d- and s-elements nature.

Table 1

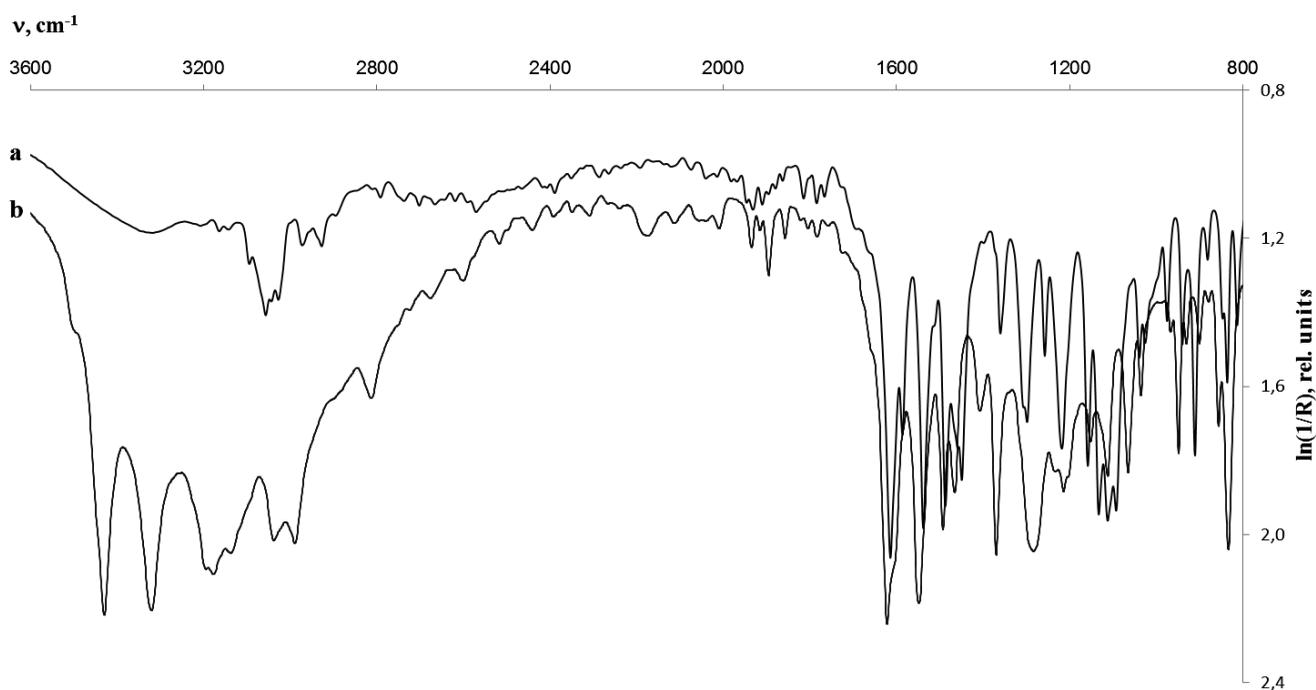
Elemental analysis and physico-chemical properties of the compounds I–VI

Compound	Name	Yield, %	Founded, % Calculated			Gross-formula	μ_{ef} , B. M. (293 K)	Molar electric conductivity, $\text{Ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
			N	M ²⁺ (Cu, Ni)	E ²⁺ (Ca, Sr, Ba)			
I	Calcium di[<i>N,N'</i> -bis(salicylidene)thiosemicarbazidatocuprate(II)] dihydride	59	$\frac{10.68}{10.57}$	$\frac{15.79}{15.97}$	$\frac{5.27}{5.03}$	$\text{C}_{30}\text{H}_{24}\text{N}_6\text{O}_6\text{S}_2\text{Cu}_2\text{Ca}$	1.73	252
II	Strontium di[<i>N,N'</i> -bis(salicylidene)thiosemicarbazidatocuprate(II)] tetrahydride	57	$\frac{9.62}{9.56}$	$\frac{14.37}{14.45}$	$\frac{9.96}{10.01}$	$\text{C}_{30}\text{H}_{28}\text{N}_6\text{O}_8\text{S}_2\text{Cu}_2\text{Sr}$	1.71	245
III	Barium di[<i>N,N'</i> -bis(salicylidene)thiosemicarbazidatocuprate(II)] monohydride	61	$\frac{9.70}{9.61}$	$\frac{14.59}{14.53}$	$\frac{15.73}{15.67}$	$\text{C}_{30}\text{H}_{22}\text{N}_6\text{O}_5\text{S}_2\text{Cu}_2\text{Ba}$	1.77	242
IV	Calcium di[<i>N,N'</i> -bis(salicylidene)thiosemicarbazidatonickolate(II)] trihydride	60	$\frac{10.38}{10.46}$	$\frac{14.57}{14.62}$	$\frac{5.04}{4.98}$	$\text{C}_{30}\text{H}_{26}\text{N}_6\text{O}_7\text{S}_2\text{Ni}_2\text{Ca}$	diamagn.	250
V	Strontium di[<i>N,N'</i> -bis(salicylidene)thiosemicarbazidatonickolate(II)] trihydride	59	$\frac{9.73}{9.87}$	$\frac{13.72}{13.80}$	$\frac{10.34}{10.29}$	$\text{C}_{30}\text{H}_{26}\text{N}_6\text{O}_7\text{S}_2\text{Ni}_2\text{Sr}$	diamagn.	261
VI	Barium di[<i>N,N'</i> -bis(salicylidene)thiosemicarbazidatonickolate(II)] monohydride	63	$\frac{9.68}{9.72}$	$\frac{13.55}{13.59}$	$\frac{15.24}{15.36}$	$\text{C}_{30}\text{H}_{22}\text{N}_6\text{O}_5\text{S}_2\text{Ni}_2\text{Ba}$	diamagn.	244

Table 2

Thermogravimetric investigations of the compounds I–VI

Compound	Peak on the DTA curve	Peak characteristics on DTA curve	ΔT , K	Δm , %		T_{dec} , K
				Founded/calculated, %	Corresponds to H ₂ O detachment	
I	1	endo	358–368	5.01/4.53	2 H ₂ O	693
	2	exo	583–753			
II	1	endo	353–368	7.74/8.19	4 H ₂ O	713
	2	exo	613–773			
III	1	endo	358–363	2.31/2.06	1 H ₂ O	703
	2	exo	613–743			
IV	1	endo	343–353	6.41/6.72	3 H ₂ O	683
	2	exo	593–723			
V	1	endo	353–363	6.72/6.35	3 H ₂ O	703
	2	exo	623–753			
VI	1	endo	363–373	1.96/2.08	1 H ₂ O	713
	2	exo	633–763			

Fig. 1. IR-spectra of complex VI (a) and salicylic aldehyde thiosemicarbazone (H₂L) (b)

It should be noted that heterometal *N,N'*-bis(salicylidene)thiosemicarbazidates of Cu(II) and Ni(II) are more thermostable by 333–353 K than those compounds based on semicarbazides [17].

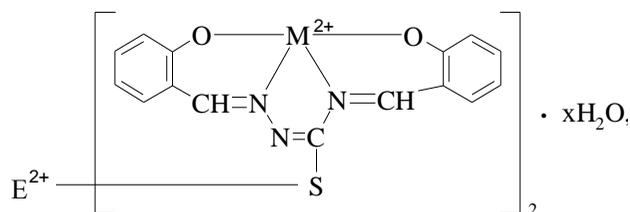
To determine the method of ligand coordination we compared the IR-spectra of salicylic aldehyde thiosemicarbazone (H₂L) and synthesized complexes I–VI (Fig. 1). To exclude the overlapping of the compounds I–VI stretching vibrations typical of H₂O molecules with

some absorption bands of the ligand in the area of $\nu(\text{H-O-H})$ 3550–3200 cm⁻¹ and $\delta(\text{H-O-H})$ 1630–1600 cm⁻¹ the synthesized complexes were previously kept in the desiccator at 378 K till the mass became constant. In the IR-spectra of the compounds I–VI the band of deformation vibrations of aromatic cycle OH-group is absent in the range of 1270–1215 cm⁻¹ (Fig. 1). The reason is OH-group deprotonation and formation of covalent bond with the metal atom [30].

Moreover, the disappearance of $\delta(\text{NH}_2)$ at 1610 cm^{-1} and $\nu_{\text{as}}(\text{NH}_2)$ at 3410 cm^{-1} in the bands of I–VI complexes compared with those of H_2L indicates the participation of amide group nitrogen in the reaction of H_2L condensation with salicylic aldehyde over M^{2+} matrix ($\text{M}^{2+} = \text{Cu}, \text{Ni}$) and formation of new tetradentate ligand similar to that described in [31]. The presence of absorption bands in the range of $1620\text{--}1400\text{ cm}^{-1}$ for the synthesized complexes

confirms the above-mentioned facts. According to [32, 33] they are related to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{N})$. In comparison with IR-spectra of H_2L they are shifted to the low field by $40\text{--}30$ and $50\text{--}40\text{ cm}^{-1}$, respectively. The reduction of $\nu(\text{C}-\text{S})$ frequencies by 30 cm^{-1} compared with IR-spectrum of H_2L ($830\text{--}820\text{ cm}^{-1}$) [34] also confirms the formation of *N,N'*-bis(salicylidene)thiosemicarbazide in the complexes I–VI.

The obtained physico-chemical data allow to propose the following coordination of metal cations in the compounds I–VI:



where **I:** $\text{M}^{2+} = \text{Cu}; \text{E}^{2+} = \text{Ca}; x = 2;$ **II:** $\text{M}^{2+} = \text{Cu}; \text{E}^{2+} = \text{Sr}; x = 4;$ **III:** $\text{M}^{2+} = \text{Cu}; \text{E}^{2+} = \text{Ba}; x = 1;$
IV: $\text{M}^{2+} = \text{Ni}; \text{E}^{2+} = \text{Ca}; x = 3;$ **V:** $\text{M}^{2+} = \text{Ni}; \text{E}^{2+} = \text{Sr}; x = 3;$ **VI:** $\text{M}^{2+} = \text{Ni}; \text{E}^{2+} = \text{Ba}; x = 1.$

Table 3

Characteristics of semi-conducting properties for the compounds I–VI

Compound	Operational temperature, K	Change of the specific resistance within the range of operational temperatures, $\text{Ohm}\cdot\text{cm}$	$-\text{TCR}$ at 333 K, %/K	B , K
I	313–403	$3\cdot 10^{14} - 4.4\cdot 10^8$	16.97	18823
II	323–413	$1.2\cdot 10^{12} - 3.6\cdot 10^7$	13.91	15430
III	313–413	$6\cdot 10^{12} - 3.4\cdot 10^8$	11.39	12630
IV	313–403	$2.4\cdot 10^{14} - 2.7\cdot 10^8$	17.32	19201
V	323–413	$0.8\cdot 10^{12} - 1.7\cdot 10^7$	14.38	15947
VI	313–413	$2.5\cdot 10^{12} - 3.2\cdot 10^8$	10.45	11587

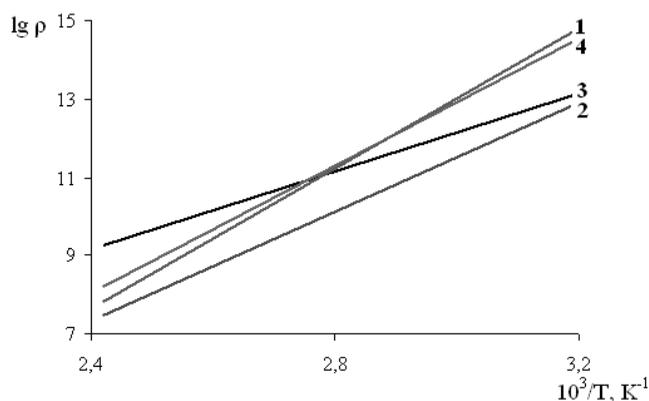


Fig. 2. The dependence of specific resistance on temperature for the compounds I (1), II (2), III (3) and IV (4)

It is known from the literature [35] that heterometal complexes are of semi-conducting type. Therefore we

investigated the electric properties of the synthesized compounds in the pressed form. For this purpose the compounds I–VI were kept in the desiccator at 378 K till the mass became constant. The study of temperature (T) effect on specific resistance (r) of the compounds I–VI within the temperature range of 313–413 K shows the linear dependence between r and T typical of semi-conducting materials. The dependence of specific resistance on temperature for the compounds I – III and IV is shown in Fig. 2.

The experimental data are given in Table 3. One can see that the parameters of semi-conducting material (TCR – temperature coefficient of resistance and B – sensitivity) are affected by only the nature of s -element. Compound IV is most sensitive to the temperature change. Moreover, depending on the nature of s -element the semi-conducting characteristics decrease in the row: $\text{Ca} > \text{Sr} > \text{Ba}$ (Table 3).

4. Conclusions

The new heterometal complexes of copper(II), nickel(II), and alkali-earth elements with *N,N'*-bis(salicylidene)thiosemicarbazide were synthesized. Using elemental analysis, IR-spectroscopy, molecular conductivity, magneto-chemical, and thermogravimetric investigations the composition and structure of the synthesized compounds were established. The dependence of specific resistance on the temperature of the synthesized compounds was investigated and it was found that they have the properties of semi-conducting materials, whose parameters are affected only by the nature of s-element.

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ГЕТЕРОМЕТАЛЕВІ КОМПЛЕКСНІ СПОЛУКИ КУПРУМУ(II) ТА НІКОЛУ(II) З *N,N'*-БІС(САЛІЦИЛІДЕН) ТІОСЕМІКАРБАЗИДОМ

Анотація. Синтезовано нові гетерометалеві координаційні сполуки купруму(II), ніколу(II) і лужно-земельних елементів з *N,N'*-біс(саліциліден)тіосемікарбазидом. На основі даних елементного аналізу, ІЧ-спектроскопічного, магнетохімічного, термогравіметричного досліджень і даних молярної електропровідності встановлено склад та будову комплексів загальної формули $E[ML]_2 \cdot xH_2O$ ($M^{2+} = Cu, Ni$; $E^{2+} = Ca, Sr, Ba$; $x = 1 - 4$; $H_3L' = N,N'$ -біс(саліциліден)тіосемікарбазид). Показано, що синтезовані сполуки володіють напівпровідниковими властивостями.

Ключові слова: гетерометалеві комплексні сполуки, купрум(II), нікол(II), тіосемікарбазон саліцилового альдегіду, напівпровідники.