

## SYNTHESIS AND SPECTROSCOPIC STUDY OF SOME COORDINATIVE COMPOUNDS OF Co(III), Ni(II) AND Cu(II) WITH DIANILINE- AND DISULFANILAMIDEGLYOXIME

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**Abstract:** Directed synthesis of dianiline- (DAnH<sub>2</sub>) and disulfanilamidglyoximes (DSamH<sub>2</sub>) has been accomplished by condensation of dichloroglyoxime with aniline or sulfanilamide in 1:2 molar ratio, as well as their corresponding Co(III), Ni(II) and Cu(II) coordinative compounds. Composition, structure and some properties of dioximes and complexes have been established by using elemental analysis, UV-Vis, IR and NMR- spectroscopies. Dioxime coordination at the central atom and structure of complexes depends on pH of reaction medium: at pH=5-6 - *bis*-dioximates, whilst at pH=2 - *tris*-dioximines are obtained. In the case of the corresponding *tris*-dioximines increment of the functional groups number in dioxime fragments, which can form intermolecular hydrogen bonds, leads to the augment of the stability of complexes.

Keywords:  $\alpha$ -dioximes, coordinative compounds, 3d metals, spectroscopy.

### Introduction

Actually *vic*-dioximates are appreciated as coordinative compounds possessing a broad spectrum of applications in branches as: analytical, biological, medicinal and pigment's chemistries. *vic*-Dioximes and the important role of their complexes, especially with 1,2-dioxime, have been widely investigated, while the substitution of some fragments of dioxime can significantly influence the structure and stability of complexes [1-4].

On interaction of amines or thiols with dichloroglyoxime or cyanogen-di-N-oxide different symmetrically substituted derivatives of diamine- or dithioglyoxime have been obtained. New optically active *vic*-dioximes have been described and the syntheses of mono- and dinuclear complexes on their basis have been performed [5, 6].

Cobaloximes containing *bis*-(thiophenyl)glyoxime in equatorial plane have been studied [7]. It has been noted that the orientation of thiophenyl groups with respect to the dioximine plane varies depending on the size of axial ligand and influences the values of chemical shifts in NMR-spectra. The *cis*-position of thiodioxime from the equatorial plane reflects upon Co-C bond reactivity in these complexes. A study with the use of cyclic voltametry has demonstrated that reduction Co(III)/Co(II) and Co(II)/Co(I) occurs easier in ClCo(dSPhgH)<sub>2</sub>Py (dSPhgH - dithiophenylglyoxime) in comparison with other chlorocobaloximes (gH - glyoxime, dmgH -dimethylglyoxime, dpgh - diphenylglyoxime). Thus, the general investigations in this field clearly suggest that many of the axial ligand's chemical properties: spectroscopic, geometry, kinetics significantly depend on the changes in equatorial ligand.

Gumus *et. al.* [8] have shown that inclusion of hexilamine radical in dioxime fragment permits to obtain Ni(II) and Pd(II) dioximates and in their crystalline structure tubular channels with diameter ~16 Å were found.

Recent investigations have demonstrated the biostimulator activity of Co(III) dioximates upon fungi [9,10]. Supplementation the nutritive medium of these microorganisms with the mentioned compounds causes an enhancement of the outcome of enzyme production and in some cases the technological cycle of cultivation the producer has been diminished [11].

On the basis of biostimulator effects in enzymogenesis processes of Co(III) complexes containing aniline or sulfanylamine on axial coordinate, their inclusion in dioximine moiety has been considered, aimed at obtaining the new dioximates of transition metals, which will accentuate these properties, as expected. Furthermore, the mobility of the „wings” of these dioximes can open interesting structural opportunities for obtaining the supramolecular systems. Preparation of dioximates with bulky ligands could make possible the formation of gaps in the crystalline structure [8], which is favourable for the intake of small molecules.

### Materials and methods

Composition, structure and properties of oximes and complexes have been established on the basis of elemental analysis, as well as IR, UV-Vis and NMR spectroscopies data. IR-spectra of compounds were recorded at FT-IR Perkin Elmer *Spectrometer 100* in vaseline oil at 4000–400 cm<sup>-1</sup> and ATR at 4000–650 cm<sup>-1</sup>. UV-Vis spectra were recorded at Perkin Elmer *Lambda 25* spectrophotometer in water solutions of compounds of 0.5·10<sup>-4</sup> mol/L. NMR-spectra were recorded on a Bruker spectrometer at 400.13 MHz for <sup>1</sup>H and 100.61 MHz for <sup>13</sup>C in DMSO-d<sub>6</sub> using TMS as an internal reference. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and are referenced to the residual non-deuterated solvent peak (2.49 for <sup>1</sup>H and 39.70 for <sup>13</sup>C).

**Experimental part****Synthesis of coordinative reagents**

**Glyoxime** has been synthesized according to the literature procedure [12] in 67% yield.

**Dichloroglyoxime** has been prepared as reported by Dutta *et al.* [7] in ~35% overall yield. Compound is soluble in alcohols, DMF, DMSO.

**Disulfanilamideglyoxime (DSamH<sub>2</sub>)**. The solution of 3.14 g (0.02 mol) dichloroglyoxime in 15 ml ethanol was added to a solution of 6.89 g (0.04 mol) sulfanilamide in 40 ml ethanol at room temperature (rt) under continuous stirring. The reaction mixture was cooled in ice bath for 10 min, and then 3.20 g (0.03 mol) sodium carbonate was added. The mixture was stirred for 6 hr, then diluted with 20 ml water and left in refrigerator for the next day. The obtained precipitate was filtered off, washed with cold water and dried in air. Yield: 63%. Found, %: C 39.14; H 3.58; N 19.54. Calculated for C<sub>14</sub>H<sub>16</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub>, %: C 39.25; H 3.76; N 19.62.

**Dianilineglyoxime (DAnH<sub>2</sub>)** was prepared, in 93% yield, according to the procedure as described for preparation of disulfanilamideglyoxime. Found, %: C 62.15; H 5.09; N 20.66. Calculated for C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>, %: C 62.21; H 5.22; N 20.73.

**Synthesis of coordinative compounds.**

**[Ni(DAnH<sub>2</sub>)<sub>3</sub>]Cl<sub>2</sub>·6CH<sub>3</sub>OH (1)**. To the warm solution of 0.27 g (1.0 mmol) DAnH<sub>2</sub> in 30 ml methanol the solution of 0.12 g (0.5 mmol) NiCl<sub>2</sub>·6H<sub>2</sub>O in 20 ml methanol was added. The obtained mixture was stirred for 5-10 min, then filtered and left at rt. After 2-3 days the crystals have appeared in solution of emerald color. The crystals are soluble in diethyl ether, alcohols, DMSO and DMF. The reaction yield constituted 46 %. Found, %: C 50.78; H 5.81; N 14.76. Calculated for C<sub>48</sub>H<sub>66</sub>Cl<sub>2</sub>N<sub>12</sub>NiO<sub>12</sub>, %: C 50.90; H 5.87; N 14.84.

**[Ni(DAnH<sub>2</sub>)<sub>2</sub>]·H<sub>2</sub>O (2)**. A solution of 0.27 g (1.0 mmol) DAnH<sub>2</sub> in 30 ml methanol was added to a solution of 0.12 g (0.5 mmol) NiCl<sub>2</sub>·6H<sub>2</sub>O in 20 ml methanol and the mixture was stirred for 10 min at 40-50°C. Ammonia (1-2 drops, 25%) was added while stirring. The color of solution changed from green to brown and a precipitate of the same color has been formed. The precipitate was filtered off, washed with cold methanol, ether and dried at rt. The reaction yield constituted 56%. The complex is soluble in DMF and weakly soluble in methanol and DMSO. Found, %: C 54.59; H 4.45; N 18.09. Calculated for C<sub>28</sub>H<sub>28</sub>N<sub>8</sub>NiO<sub>5</sub>, %: C 54.66; H 4.59; N 18.21.

**[Cu(DAnH<sub>2</sub>)<sub>3</sub>]SO<sub>4</sub>·3H<sub>2</sub>O (3)**. For the synthesis of this complex similar conditions as for compound (1) were applied, but the solubilisation of Cu(II) salt in a minimal amount of water has preceded the addition of methanol. The reaction yield constituted 42%. Compound is soluble in DMSO, DMF and alcohols. Found, %: C 49.16; H 4.67; N 16.32. Calculated for C<sub>42</sub>H<sub>48</sub>CuN<sub>12</sub>O<sub>13</sub>S, %: C 49.24; H 4.72; N 16.41.

**[Co(DAnH<sub>2</sub>)<sub>2</sub>(Thio)<sub>2</sub>][TiF<sub>6</sub>]·2DMF·H<sub>2</sub>O (4)**. Dianilineglyoxime, 0.27g (1.0 mmol) and thiocarbamide, 0.08 g (1.0 mmol) were dissolved in a mixture of 10 ml DMF and 40 ml methanol. The mixture was refluxed at ~60°C, under stirring. Chrystalhydrate CoTiF<sub>6</sub>·6H<sub>2</sub>O, 0.17 g (0.5 mmol) was dissolved in 10 ml water and added by dropping funnel (~ 1 drop in 4-5 sec.) to the initial solution and stirring was continued for 3 hr. Ammonia solution (1:4) was dropped into reaction to adjust its pH to ~5 and this value was maintained till the end of reaction. The stirring was stopped and the reaction medium was left for slow evaporation. Dark brown monocrystals were obtained that were unstable at air. Reaction yield constituted 19%. Compound is soluble in DMF, DMSO and less soluble in alcohols. Found, %: C 43.31; H 4.52; N 19.81. Calculated for C<sub>66</sub>H<sub>84</sub>Co<sub>2</sub>F<sub>6</sub>N<sub>26</sub>O<sub>11</sub>S<sub>4</sub>Ti, %: C 43.42; H 4.64; N 19.95.

**[Co(DAnH<sub>2</sub>)<sub>3</sub>][TiF<sub>6</sub>]·1.5DMF (5)**. This compound has been synthesized as afore-described for (4), without the addition of ammonia solution. The results of investigations have shown that thiocarbamide moiety does not enter the complex and three molecules of non-deprotonated dioxime are bound to the central atom. Reaction yield constituted 32%. Product is soluble in alcohols, DMF and DMSO. Found, %: C 45.38; H 3.96; N 15.11. Calculated for C<sub>88.5</sub>H<sub>94.5</sub>Co<sub>2</sub>F<sub>18</sub>N<sub>25.5</sub>O<sub>13.5</sub>Ti<sub>3</sub>, %: C 45.53; H 4.08; N 15.30.

**[Ni(DSamH<sub>2</sub>)<sub>2</sub>]·2H<sub>2</sub>O (6)**. To the warm solution of 0.21 g (0.50 mmol) disulfanilamideglyoxime in 30 ml methanol 0.06 g (0.25 mmol) NiCl<sub>2</sub>·6H<sub>2</sub>O in 15 ml methanol were added and the mixture was stirred for 15 min at 60°C. While stirring few drops of ammonia was added and a brown precipitate appeared that was separated, washed with cold methanol then diethyl ether and dried at air. Reaction yield constituted 43%. Complex is soluble in DMF and DMSO and weakly soluble in methanol. Found, %: C 35.41; H 3.54; N 17.62. Calculated for C<sub>28</sub>H<sub>34</sub>N<sub>12</sub>NiO<sub>14</sub>S<sub>4</sub>, %: C 35.41; H 3.61; N 17.70.

**[Cu(DSamH<sub>2</sub>)<sub>3</sub>]SO<sub>4</sub>·5H<sub>2</sub>O (7)**. Disulfanilamideglyoxime, 0.21 g (0.50 mmol) was dissolved in 40 ml methanol and heated in water bath at 60°C. Crystalhydrate CuSO<sub>4</sub>·5H<sub>2</sub>O, 0.06 g (0.25 mmol) dissolved in a minimum amount of water and 20 ml methanol was added dropwise to the solution of ligand, then heating was removed and the solution was left at rt. The slow evaporation gave dark-brown crystals. Reaction yield constituted 52%. Compound is soluble in DMF and DMSO. Found, %: C 32.72; H 3.71; N 16.34. Calculated for C<sub>42</sub>H<sub>58</sub>CuN<sub>18</sub>O<sub>27</sub>S<sub>7</sub>, %: C 32.86; H 3.81; N 16.42.

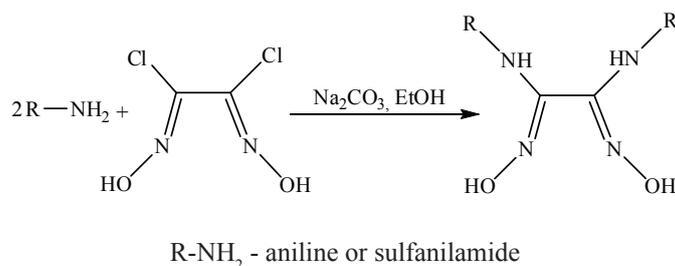
**[Co(DSamH<sub>2</sub>)<sub>2</sub>(Thio)<sub>2</sub>][ZrF<sub>6</sub>]·DMF·H<sub>2</sub>O (8)**. A mixture of 0.21 g (0.5 mmol) disulfanilamideglyoxime in 30 ml methanol and 0.04 g (0.5 mmol) thiocarbamide in 10 ml methanol was refluxed at 60°C with stirring. To this mixture a solution of 0.1 g (0.25 mmol) CoZrF<sub>6</sub>·6H<sub>2</sub>O in 20 ml of water/methanol (1:1) was added. The reaction mixture was stirred for 3 hrs, while maintaining the pH of solution at 4.5-5.5 value by dropping ammonia solution (1:3). A

dark brown precipitate was formed that was filtered off, washed with cold methanol and diethyl ether. Reaction yield constituted 36%. Compound is soluble in methanol, DMF and DMSO. Found, %: C 31.02; H 3.46; N 18.91. Calculated for  $C_{63}H_{85}Co_2F_6N_{33}O_{26}S_{12}ZrS$ , %: C 31.16; H 3.53; N 19.03.

**[Co(DSamH)<sub>2</sub>(Thio)<sub>2</sub>][TiF<sub>6</sub>]<sub>2</sub>·1.5DMF·2H<sub>2</sub>O (9).** This compound was prepared according to the procedure as described for preparation of compound 8, by using CoTiF<sub>6</sub>·6H<sub>2</sub>O instead of Zr crystalhydrate. Found, %: C 31.64; H 3.61; N 19.08. Calculated for  $C_{64.5}H_{90.5}Co_2F_6N_{33.5}O_{27.5}S_{12}Ti$ , %: C 31.75; H 3.74; N 19.23.

## Results and discussion

As a result of the condensation between dichloroglyoxime and various organic amines, a series of  $\alpha$ -aminodioximes can be obtained, according to the following scheme:

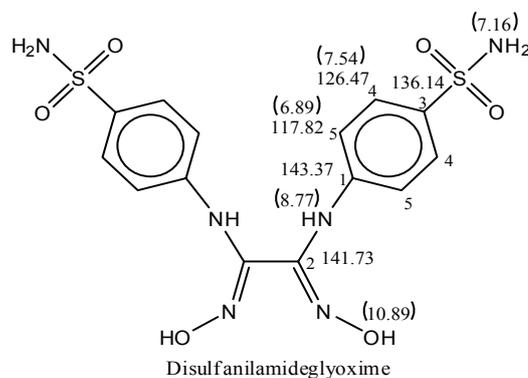


This approach served as basic for the obtaining of DANH<sub>2</sub> and DSamH<sub>2</sub>, the latter being synthesized for the first time. The prepared compounds were identified by elemental analysis, UV-Vis, IR and NMR spectroscopies. UV-Vis spectrum of DANH<sub>2</sub> contains two absorption bands at 205 and 260 nm belonging to the aromatic ring, whilst the corresponding UV-Vis spectrum of DSamH<sub>2</sub> is characterized by the absorption band at 281 nm.

In the IR-spectrum of DANH<sub>2</sub> the following absorption bands are present:  $\nu(OH)=3390$ ,  $\nu(NH)=3369$ ,  $\nu(C=N)=1637$ ,  $\nu(CC)_{arom.}=1596$  cm<sup>-1</sup>. The  $\nu(NO)=972$  cm<sup>-1</sup> band is characteristic for unprotonated oxime group, while  $\delta(CH)_{arom.}=752$  and  $689$  cm<sup>-1</sup> is attributed to monosubstituted aromatic ring. The presence of intensive bands:  $\nu(NO)$  and  $\delta(CH)$ , as well as disappearance of  $\nu(CCl)$  band at  $850$  cm<sup>-1</sup> demonstrates that the condensation between dichloroglyoxime and aniline has occurred. In IR-spectrum of DSamH<sub>2</sub> the absorption bands of  $\nu(NH)=3424$ ,  $3357$ ,  $3283$  cm<sup>-1</sup> are present and  $\nu(OH)=3076$  cm<sup>-1</sup> as well, which is shifted to lower values due to the formed by oxime OH molecular associates. The bands of  $\nu(C=N)=1642$  cm<sup>-1</sup>,  $\nu(CC)_{arom.}=1592$  cm<sup>-1</sup>,  $\nu(SO)=1302$ ,  $1150$  cm<sup>-1</sup>,  $\nu(NO)=935$  cm<sup>-1</sup> and  $\delta(CH)=767$ ,  $725$  cm<sup>-1</sup> are also characteristic for this spectrum.

The <sup>1</sup>H NMR spectrum of DANH<sub>2</sub> contains the multiplets in 6.79 – 7.09 ppm region that attest the presence of aromatic ring in compound, a singlet at 8.16 ppm that is characteristic for the NH group proton and a singlet at 10.43 ppm confirming the presence of oxime group. Integration of the peaks in this spectrum has shown that both chlorine atoms of initial dichloroglyoxime were substituted by aniline radicals. The presence of 5 resonances in <sup>13</sup>C NMR spectrum, including quaternary atom of oxime group ( $\delta_C$  142.66), quaternary atom ( $\delta_C$  139.70) and tertiary atoms of aromatic ring ( $\delta_C$  128.16, 121.23 and 118.92) were ascribed to DANH<sub>2</sub>.

The <sup>1</sup>H NMR spectrum of DSamH<sub>2</sub> (Figure 1) contains two doublets belonging to the aromatic ring at 7.54 ppm (2H, J=8.78 Hz) and 6.89 ppm (2H, J=8.78 Hz), a singlet at 7.16 ppm (NH<sub>2</sub> protons) and a singlet at 8.77 ppm (NH proton). Oxime group protons give a peak at 10.89 ppm. In <sup>13</sup>C NMR spectrum the presence of tertiary carbon resonances ( $\delta_C$  117.82 and 126.47), quaternary atoms of aromatic ring ( $\delta_C$  136.14 and 143.37) and oxime carbon atom ( $\delta_C$  141.73) has been attested. It was found that protons and carbons signals appear downfield in disulfanilamidoglyoxime, as compared to the sulfanilamide (Figure 2). Only quaternary carbon of aromatic ring close to NH group is upfield shifted by condensation. Both proton and carbon signals of oxime group are shifted to higher field as compared to the dichloroglyoxime. The attribution of the peaks for the carbon atoms has been performed on the basis of 2D NMR techniques: HSQC and HMBC (Figure 3). Also, in 2D HMBC experiment, the protons of NH and OH groups have a cross peaks at the shift of C<sup>2</sup>, that proves the condensation of sulfanilamide with dichloroglyoxime. As it can be concluded from these spectra, sulfanilamide condenses *via* amino group of aromatic ring: it suffers the biggest downfield shift and integration of the peaks confirms the loss of one proton from this group.



**Fig. 1.** Disulfanilamidoglyoxime with its <sup>1</sup>H and <sup>13</sup>C values.

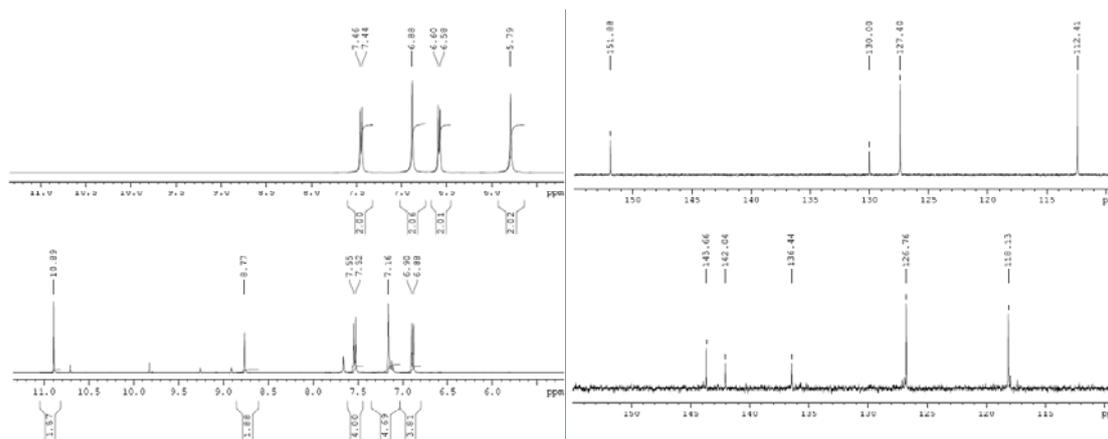


Fig. 2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of sulfanilamide (a, b) and disulfanilamidoglyoxime (c, d).

On interaction of a Co(II), Ni(II) or Cu(II) salt with the described dioximes in a 1:2 molar ratio, *bis*-dioximates or *tris*-dioximines of the corresponding metals were obtained, depending on the conditions of synthesis. The pH~2 is more favourable for the obtaining of *tris*-dioximines, while at pH~5-6 *bis*-dioximates of the respective metals are preferentially formed. Variation of the pH value was achieved by adding 1-2 drops of ammonia solution or hydrochloric acid. Methanol, water and dimethylformamide were used as solvents. A part of obtained complexes are unstable at air.

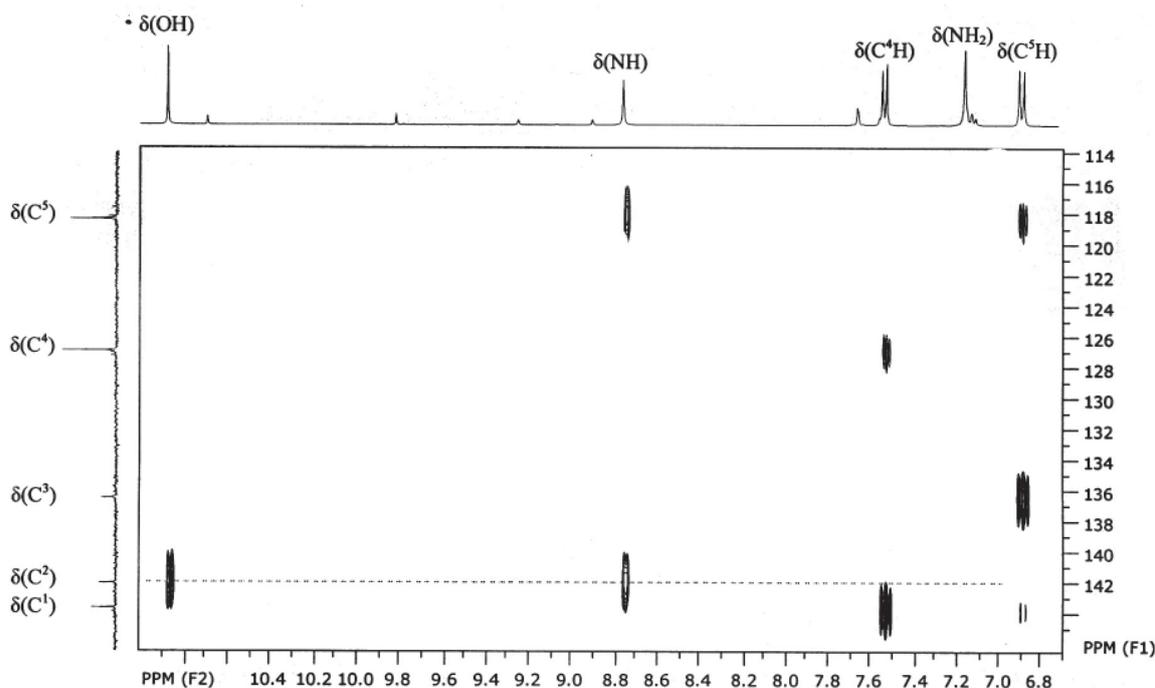
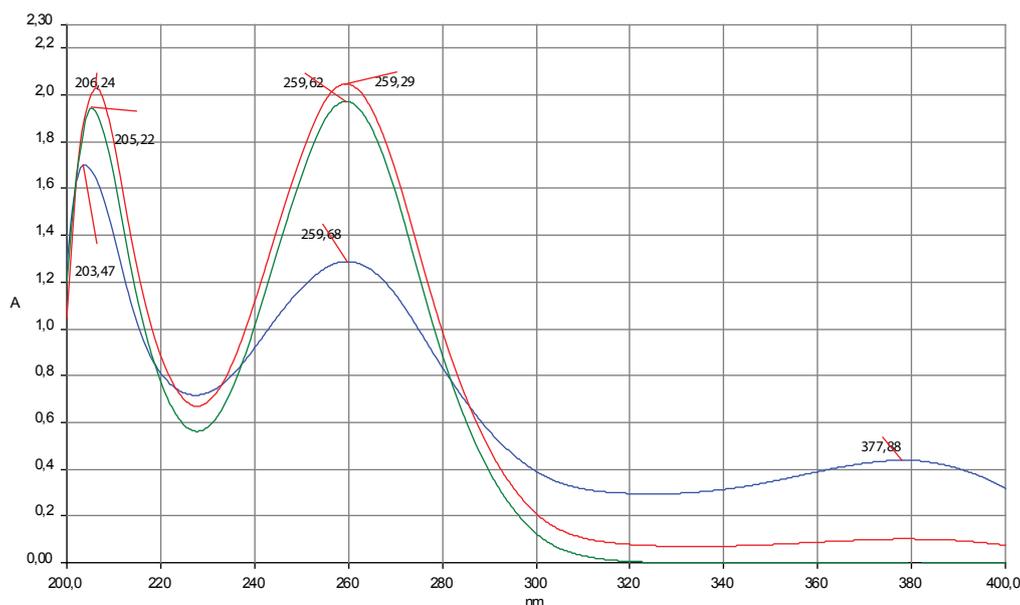


Fig. 3. 2D HMBC experiment of disulfanilamidoglyoxime.

In UV-Vis spectra of Ni(II) and Cu(II) complexes containing  $\text{DAnH}_2$  characteristic bands of aromatic ring are noted at ~205 and 260 nm, which certify the presence of this ligand in complex. In the case of *bis*-dianilineglyoximate of Ni(II) it has been observed that the corresponding absorption band at 260 nm is less intensive than the band at 205 nm, as compared to *tris*-dianilineglyoximine. Furthermore, a new band appeared at 378 nm (Figure 4). The following explanation seems plausible: the composed band at 260 nm reflects two electronic transitions and the formation of *trans*-dioximates is accompanied by the disappearance of one transition as a result of an electron shift. In the case of complex  $[\text{Co}(\text{DAnH})_2\text{Thio}]_2[\text{TiF}_6]$  three absorption bands were recorded: at 202 nm, characteristic for aromatic ring; at 243 nm probably distinguishing  $\pi$ - $\pi^*$  transitions in chelate ring and a band at 321 nm that is attributed to the molecules of coordinated thiocarbamide.



**Fig. 4.** UV-Vis spectra of compounds  
 $\text{DAnH}_2$  (1),  $[\text{Ni}(\text{DAnH}_2)_3]\text{Cl}_2$  (2),  $[\text{Ni}(\text{DAnH}_2)_2]$  (3)

In the case of Ni(II) and Co(II) dioximates containing DSamH<sub>2</sub> the presence of this ligand in the corresponding complexes has been certified by the absorption bands at 202 and 275–282 nm. Also in the case of these compounds it has been noted that the addition of one drop of ammonia, which favors the formation of *bis*-dioximates, causes the decrease in intensity of absorption band at 280 nm. The generation of intramolecular hydrogen bonds contributes to the electron density shift from the aromatic ring towards metal-cycle, which could cause intensity diminution of the respective band.

In IR-spectra of DANH<sub>2</sub>-containing *tris*-dioximines the absorption bands  $\nu(\text{NH})+\nu(\text{OH})=3331\text{--}3380$ ,  $\nu(\text{C}=\text{N})=1647\text{--}1655$  and  $\nu(\text{CC})_{\text{arom.}}=1596\text{ cm}^{-1}$  are present. The presence of  $\nu(\text{NO})=970\text{--}998\text{ cm}^{-1}$  band, as well as the lack of characteristic ionized  $\nu(\text{NO})$  at  $\sim 1240$  and  $\sim 1080\text{ cm}^{-1}$  demonstrates the absence of O–H $\cdots$ O intramolecular hydrogen bonds, proving the *tris*- character of these dioximines of 3d-metals. The absorption bands of vibrations  $\delta(\text{CH})$  that characterizes the aromatic monosubstituted ring are found at 752–755 and 691–695  $\text{cm}^{-1}$  region. In *bis*-dioximates of Co(III), Cu(II) and Ni(II) with dianilineglyoxime the bands of valence vibrations  $\nu(\text{NH})+\nu(\text{OH})=3209\text{--}3312\text{ cm}^{-1}$  are shifted to lower fields than in the free DANH<sub>2</sub> molecule. The bands  $\nu(\text{C}=\text{N})$  at 1647–1652 and  $\nu(\text{CC})_{\text{arom.}}$  at 1592–1594  $\text{cm}^{-1}$  regions are present. Decrease in intensity of 972  $\text{cm}^{-1}$  band, as well as appearance of the bands belonging to the ionized N–OH group at 1234–1241  $\text{cm}^{-1}$  and 1075–1093  $\text{cm}^{-1}$  regions implies the formation of O–H $\cdots$ O intramolecular hydrogen bonds. Bands  $\delta(\text{CH})$  are present at 747–753 and 689–694  $\text{cm}^{-1}$  regions, characterizing the aromatic monosubstituted ring.

In IR-spectra of *tris*-dioximines containing DSamH<sub>2</sub> the bands  $\nu(\text{NH})=3469\text{--}3208$ ,  $\nu(\text{OH})=3071\text{--}3075$ ,  $\nu(\text{C}=\text{N})=1643\text{--}1646$ ,  $\nu(\text{C}-\text{C})_{\text{arom.}}=1588\text{--}1595$ ,  $\nu(\text{NO})=900\text{--}913$  and  $\delta(\text{CH})=741\text{--}747\text{ cm}^{-1}$  are found. In IR-spectra of *bis*-disulfanilamideglyoximates of Co(III) and Ni(II), as in the similar complexes with DANH<sub>2</sub>, the majority of the aforementioned bands are present. Decrease in intensity of the band from 935  $\text{cm}^{-1}$  region has been established and the bands of oxime N–OH ionized group at 1255–1258 and 1093–1096  $\text{cm}^{-1}$  appeared, which prove the formation of O–H $\cdots$ O intramolecular hydrogen bonds.

In the case of Co(III) dioximates containing on axial coordinate the molecules of thiocarbamide the presence of ligand in complex is ascertained by the pronounced band  $\nu(\text{C}=\text{S})=1396\text{--}1408\text{ cm}^{-1}$ .

In <sup>1</sup>H NMR spectrum of complex  $[\text{Co}(\text{DAnH}_2)_3]_2[\text{TiF}_6]_3 \cdot 4\text{DMF}$  the peak of oxime proton is more shielded (9.10 ppm), as compared with the free ligand peak at 10.43 ppm. The peak of NH group does not suffer any chemical shift with respect to the case of free ligand, being found at 8.15 ppm. The peaks of aromatic ring of DANH<sub>2</sub>, a doublet and two triplets are found in 6.70–7.16 ppm region, as in the spectrum of free ligand. The only upfield chemical shift of the oxime proton peak is probably caused by an electronic density migration from metal to chelate ring. The peaks at 2.73 and 2.89 ppm characterize the methyl groups and at 7.95 ppm the methine group of dimethylformamide molecules from complex.

In <sup>13</sup>C NMR spectrum of this complex the peak of oxime carbon atom is upfield too, being found at 142.37 ppm, thus confirming the supposition on an electronic density migration from metal to chelate ring. The chemical shifts of aromatic carbon atoms at 118–140 ppm do not essentially vary from the corresponding values in the spectrum of the free

ligand. Despite the introduction of the Thio ligand in the reaction medium, neither IR nor NMR spectra could certify its presence. The upfield shift of the oxime proton peak, as well as integration of the peaks in  $^1\text{H}$  NMR spectrum, rule out the supposition on deprotonation of oxime group, thus constituting a further evidence (along with the elemental analysis, UV-Vis and IR- data) about Co(III) *tris*-dianilineglyoximine formation. The *tris*-dioximines of Ni(II) and Cu(II) were also obtained when the reactions were performed in the absence of ammonia or sodium acetate, according to the IR, UV-Vis and elemental analysis data. When an ammonia solution is added to the reaction medium, the formation of respective *bis*-dioximates occurred that has been ascertained by the chemical shift of oxime proton at  $\sim 17$ -18 ppm in  $^1\text{H}$  NMR spectrum, proving the intramolecular hydrogen bond formation.

In the case of  $^1\text{H}$  NMR spectrum of Co(III) *tris*-disulfanilamideglyoximine the oxime proton peak is also upfield with  $\sim 1$  ppm (from 10.89 ppm in the free ligand to 9.79-9.69 ppm). The chemical shift assigned to NH group is slightly upfield (8.36-8.25 ppm) with respect to the peak of free oxime at 8.76 ppm. These upfield shifts are attributed to an electron density migration from metal to the chelate ring, similarly to the afore-mentioned case of *tris*-form of dianilineglyoxime complexes. The two doublets assigned to the aromatic ring protons at 7.64 and 6.81 ppm are placed approximately in the same region, as compared with the free disulfanilamideglyoxime. The peak of  $\text{NH}_2$  group does not essentially move in the spectrum, being found at 7.16 ppm, as well.

Considering the  $^1\text{H}$  NMR spectrum of  $[\text{Ni}(\text{DSamH}_2)_2] \cdot 2\text{H}_2\text{O}$  complex, the peak of oxime proton is downfield at 17.32 ppm, which confirms the intramolecular hydrogen bond formation between dioxime monoanions. The proton peaks of NH (9.84 ppm) and vicinal to it CH (7.84 ppm) groups are also downfield, being shifted with  $\sim 1$  ppm, as compared with the free ligand (8.77 and 6.89 ppm, respectively). The other peaks (CH remote from oxime group at 7.69 ppm and  $\text{NH}_2$  at 7.27 ppm) do not markedly differentiate as compared with the free ligand. In  $^{13}\text{C}$  NMR spectrum the most downfield chemical shift belongs to the peak of the quaternary oxime carbon at 146.11 ppm (141.73 ppm in the free ligand). Since  $^1\text{H}$  NMR operates in a through-bond as well as through-space manner but  $^{13}\text{C}$  NMR operates mainly through-bond, any shift in  $^{13}\text{C}$   $\delta(\text{C}=\text{N})$  will be due to cobalt anisotropy or Sam fragment (if is considered as an acceptor group of electron density). The peaks of quaternary carbon atom and methine close to  $\text{SO}_2$  group are slightly downfield with 1.0-1.2 ppm, the corresponding nuclei resonating at 136.81 and 127.39 ppm. The chemical shift of the other methine group is upfield, as compared with the free ligand (116.57 ppm versus 117.82 ppm, respectively).

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the other synthesized *bis*-disulfanilamideglyoximates do not essentially differ from the spectra of  $[\text{Ni}(\text{DSamH}_2)_2] \cdot 2\text{H}_2\text{O}$  complex.

To summarize,  $\text{DAnH}_2$  and  $\text{DSamH}_2$  behave differently from the dimethylglyoxime, diphenylglyoxime or 1,2-cilcohexandiondioxime. In reaction with Co(II), Ni(II) and Cu(II) salt,  $\text{DAnH}_2$  and  $\text{DSamH}_2$  are prone to form *tris*-dioximines and not *bis*-dioximates like traditional dioximes. The *tris*-dioximine complexes with  $\text{DSamH}_2$  are most stable than those with  $\text{DAnH}_2$  due to a larger number of functional group that can participate to a hydrogen bond linkage. The new complexes may be effective as stimulators in biosynthetic processes of enzymes in some fungi strains.

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