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THE FORMATION OF COPPER(II) COMPLEXES WITH WATER SOLUBLE N-(FURAN-2-YLMETHYLIDENE)HYDROXYLAMINE*

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*The paper is devoted to the interaction of copper(II) chloride with water soluble β-furfuraldoxime (N-(furan-2-ylmethyliden)hydroxylamine) in hydrochloric solutions. It was been revealed that the degree of copper(II) precipitation from aqueous solutions and hydrochloric solutions with the pH of 4 M HCl by this reagent is not higher than 52% even when the precipitant is used in abundance. These dependencies has been compared to the similar results of palladium(II) precipitation obtained when all other conditions were equal. It has been discovered that various complexes are formed when Cu(II) reacts with a β-furfuraldoxime and that it depends on the acidity of the solution. In weak acid solutions (0.01−0.1 M HCl) the «green» complex of composition [Cu**L**4Cl2] was obtained and in this complex the oxime is coordinated with the central atom by an oxygen atom of the oxime group. The so-called «red» complex of composition [Cu**L**2Cl2] is formed in the pH range of 1−4 M HCl and in ethanol. In this complex the coordination of ligand molecules is realized by the oxygen atom of the furan ring and by the oxygen of the oxime group. Reagent N-(furan-2-ylmethyliden)hydroxylamine can be used for practical quantitative release of palladium from hydrochloric solutions. However, it does not provide the separation of copper and palladium in their joint presence.*

Keywords: *copper(II), β-furfuraldoxime, complexation, the palladium(II) complexes, hydrochloricc solution, bidentate coordination, thermal stability.*

Introduction

The complexing properties of reagents of the oxime class with respect to transitional metals drew wide attention of researchers after the publication of works by L.A. Chugayev [1, 2] at the beginning of the 20th century. These reagents found special application in analytical chemistry due to high selectivity towards nickel(II), palladium(II) and copper(II) ions [3–5]. Various β-oxyoximes are a widely known class of the cation-exchange extraction agents applied in copper hydrometallurgy [6–8]. The oxime fragment is a pharmacophore group [2] determining the biological activity of compounds containing it. Cu(II), Ni(II), Co(II) and Pd(II) complexes with oximes were found to have cytologic and catalytic activity [2, 9, 10]. Using the interaction of cationic, oxime-containing and anionic metal complexes it is possible to obtain bimetallic complexes, for example, $[Cu\mathbf{L}_2][Cr(SCN)_2A]$ (where L is β-furfural oxime, and A is a nitrogen-containing ligand) [11]. Bimetallic complexes containing atoms of two metals with dimethylglyoxime (DMG) – $[NiPd(DMG)_4]$, $[NiPt(DMG)_4]$, $[PdPt(DMG)_4]$ [12] are known and can be of interest as precursors of bimetallic powders.

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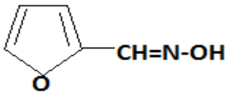
The purpose of this work is to detect the features of the interaction of copper(II) ions with N-(furan-2-ylmethyliden)hydroxylamine in HCl solutions, to determine the composition, structure and thermal stability of the formed complexes, and to compare the obtained results to similar data for chlorine complexes of palladium(II). Such comparison will allow to estimate the possibility (or impossibility) of separating copper(II) and palladium(II) ions in HCl solutions which are formed when processing different types of secondary raw materials, in particular, of bimetallic catalysts for CO to CO_2 conversion [13], acetylene hydrogenation [14] and other processes.

Experimental

Analytically pure copper dichloride hydrate $CuCl_2{\cdot}2H_2O$ produced by Acros Organics BVBA and pure palladium dichloride $PdCl_2$ TU-6-09-2025-84 produced by JSC Aurat were used in the work.

N-(Furan-2-ylmethyliden) hydroxylamine (β-furfural oxime)[1] (L)



Yellow-white needles. Melting temperature: 82–85 °C. IR spectrum, cm^{-1}: 3418, 3221, (OH), 3086, 3045, 2924, 2855 (CH), 1647 (C=N), 1570, 1478, 1378 (S=S, ring vibrations), 1325 (OH), 1239 ($\delta C–H_{oxim}$), 1188, 1147, 1084, 1020 (C–O–C), 973 (N–O), 923, 894, 824, 754 (C–O–C, =C–N), 595, 523 (=C–N). Found, %: C 54.4; N 12.4; H 4.50. $C_5H_5O_2N$. Calculated, %: C 54.1; N 12.6; H 4.50.

The interaction of Cu(II) and Pd(II) with the reagent was carried out at room temperature in aqueous and/or HCl solutions (HCl concentration was varied from pH 2 to 4). The concentration of the metals in the initial solutions was varied from $2{\cdot}10^{-2}$ to 0.1 mol/l. The molar ratio M:reagent was 1:1÷1:6.

The experiments on the isolation of copper and palladium from solutions containing both these metals were carried out by introducing a ligand into the solution (10 ml) obtained by the dissolution of the corresponding amounts of $CuCl_2{\cdot}2H_2O$ and $PdCl_2$ in 1 M HCl ($C^{init}_{Cu} = C^{init}_{Pd}$ = 0.01 mol/l). The molar ratio metal (the sum of moles of palladium and copper):ligand was varied in the range 1:2÷1:6. The solutions were kept for 2 days. Then the precipitates were separated, and the mother solution was analyzed for the presence of the metals ions.

*Synthesis of Cu(II) complex ("**green**" **complex**).* $CuCl_2{\cdot}2H_2O$ (0.426 g) was dissolved in 0.1 M HCl (25 ml). The solution was gradually added at room temperature to β-furfural oxime. The molar ratio Cu:L was 1:6. This resulted in the formation of a precipitate. After 1 h the latter was

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[1] Reagent kindly provided by I.N. Boiko.

filtered off, washed on the filter with distilled water and dried to the constant weight in a dessicator to give dark green large needles. Yield: 41.5%.

Found, %: N 9.70; C 40.9; H 3.28; Cl 12.1; Cu 11.0. Calculated for $Cu(C_5H_5O_2N)_4Cl_2$, %: N 9.68; C 41.50; H 3.46; Cl 12.3; Cu 11.0.

*Synthesis of the Cu(II) complex ("**red**" **complex**).* $CuCl_2 \cdot 2H_2O$ (0.426 g) was dissolved in 0.1 M HCl (25 ml). The solution was gradually added at room temperature to β-furfural oxime. The molar ratio Cu:L was 1:6. The formed precipitate was filtered off, washed on the filter with distilled water and dried to the constant weight in a dessicator to give dark green large needles. Yield: 51.9%.

Found, %: N 7.80; C 34.5; H 2.70; Cl 19.3; Cu 17.2. Calculated for $Cu(C_5H_5O_2N)_2Cl_2$, %: N 7.86; C 33.7; H 2.81; Cl 19.9; Cu 17.8.

The obtained substances are insoluble in water, acetone and 2 M HCl. Note that the green precipitate becomes red-brown when treated with 2 M HCl or dimethyl ether. Both substances are slowly dissolved in ethanol and are very soluble in ammonia. The resulting ammonia solutions are bright blue in color, which is typical of copper(II) ammoniates.

Synthesis of Pd(II) complex. Solid β-furfural oxime (m_L=0.044 g) was added under stirring to 10 ml of a solution of $PdCl_2$ (m_{PdCl2}=0.035 g) in 1 M HCl at room temperature. The molar ratio was 1:2. This resulted in the immediate formation of a precipitate. After 24 h the formed precipitate was filtered off, washed on the filter with distilled water and dried to the constant weight in a dessicator. The precipitate crystallizes in the form of thin yellow needles.

Found, %: N 7.00; C 30.2; H 2.30; Pd 27.4. Calculated for $[Pd(C_5H_5O_2N)_2Cl_2]$, %: N 7.01; C 30.0; H 2.50; Pd 26.6.

The palladium complex is insoluble in water and concentrated HCl, soluble in ethanol.

Analysis of the complexes and solutions for the presence of metal ions was carried out by known spectrophotometric techniques: for copper − with sodium diethyldithiocarbamate [4], for palladium – with tin dichloride [5]. Before the analysis the isolated complexes and solutions were boiled with *aqua regia* and subjected 2–3 times to coevaporation with concentrated hydrochloric acid.

The degree of extraction of the metals into the precipitate (%) by the interaction with the oxime was calculated as the ratio of the metal weight in the precipitate to the initial weight.

The elemental analysis of the complexes for C, H, N, Cl was carried out with the use of an element analyzer produced by TermoFinigan (Italy). (The analytical error was 0.2–0.5% abs.).

The electronic absorption spectra of the solutions were registered with the use of a SPECORD UV-Visible "Heλios" spectrophotometer in the range of wavelengths 200–1000 nanometers in quartz cells with the absorbing layer thickness of 1 cm. IR absorption spectra were recorded with the use of a Bruker IR Fourier-spectrometer Eq.55 in the range of frequencies 400–4000 cm^{-1}. Thermogravigrams were recorded on a Q-1500 D derivatograph at a heating rate of 10 deg/min at simultaneous recording of heating curves (T and DTA) and loss in weight (TG) in quartz crucibles in the air. The weight of samples was 30–70 mg (weighing error of ±0.4 mg). Temperature was measured by a platinum-rhodium/platinum thermocouple (PP-1) with an error of ±2 °C in the temperature range from 20 to 1000 °C.

Results and Discussion

We found that the interaction of an aqueous copper-containing solution (C^{init}_{Cu} = 0.1 mol/l) with the reagent immediately results in the formation of a precipitate in the form of dark-green large needles. If C^{init}_{Cu} < 0.1 mol/l, the formation of the precipitate does not occur. It was established that copper(II) extraction degree increases as the Cu:L molar ratio increases from 1:1 to 1:4. Further increase in the molar ratio does not lead to essential growth of copper(II) extraction degree (Fig. 1). This can indicate that 4 ligand molecules participate in the interaction with Cu(II) ions.

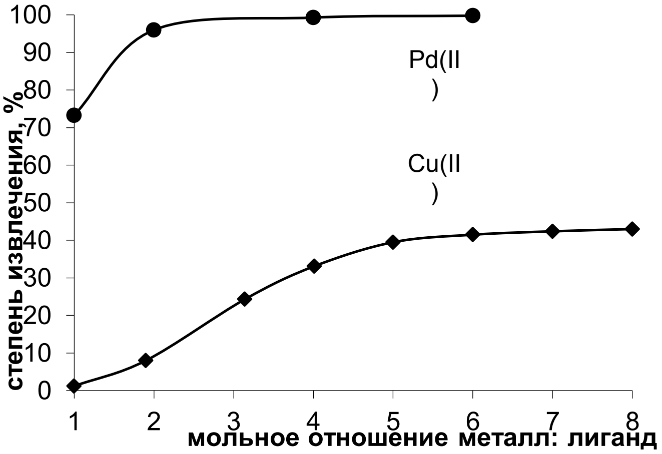

Figure 1. Dependence of the degree (%) of Cu(II) and Pd(II) extraction into the solid phase on the M:L molar ratio at 20°C
(C^{init}_{Cu} = 0.1 mol/l, aqueous solution; $C^{init}_{Pd} = 2\cdot10^{-2}$ mol/l, 1 M HCl).
[Степень извлечения, % means Extraction degree, %;
мольное отношение металл:лиганд means molar ratio metal:ligand]

It was shown that the degree of copper(II) extraction from the water solution is at the level of 30–33% (Tab. 1) up to pH 1. However, further increase of acidity leads to extraction growth. The degree of extraction from solutions with hydrochloric acid concentration of 2−4 M is at the level of 48–52%. Besides, an interesting fact was found: the green needle precipitate is formed in weakly acidic solutions (0.01–0.1 M HCl), and, as hydrochloric acid concentration increases (C_{HCl} = 1–4 M), a brick-red precipitate is formed. Thus, it is possible to conclude that the nature of the interaction of copper(II) chlorine complexes with β-furfural oxime depends on HCl concentration.

Table 1. Degree (%) of copper(II) and palladium(II) extraction into the solid phase as a function of the initial solution acidity

Precipitation conditions	Acid concentration					
	pH 7	pH 2	pH 1	1 M HCl	2 M HCl	4 M HCl
(C^{init}_{Cu}=0.1 mol/l; Cu:**L** ratio is 1:4)	32.2	30.3	32.3	37.6	48.6	51.9
(C^{init}_{Pd}=$2\cdot10^{-2}$ mol/l; Pd:**L** ratio is 1:2)	–	–	97.5	99.9	>99.9	>99.9

Interaction of Pd (II) with the same organic reagent in acidic solutions results in the formation of a yellow precipitate. Quantitative sedimentation of palladium(II) ions from HCl solutions occurs until the acidity of 4 M is achieved. Thus, even when Pd:**L** molar ratio is 1:2, Pd(II) sedimentation degree ($C^{init}_{Pd} = 2\cdot10^{-2}$ mol/l) from acidic solutions is 97.5–99.9% (Tab. 1, Fig. 1).

Note that when both Pd(II) and Cu(II) ions are present in the solution, introduction of β-furfural oxime is followed by the formation of yellow precipitates, and the degree of sedimentation of Cu(II) ions depends on the ligand quantity. However, the sedimentation degree does not exceed 42% even in case of its surplus, while Pd(II) sedimentation is quantitative (Tab. 2).

Table 2. Degree (%) of Cu(II) and Pd(II) extraction into the solid phase at their mutual presence as a function of the initial metal:ligand molar ratio ($C^{init}_{Cu} = C^{init}_{Pd}$ = 0.01 mol/l; C_{HCl} = 1 M)

Extraction degree, %	Molar ratio ∑M:**L**		
	1:2	1:4	1:6
Cu	25.8	38.2	42.0
Pd	99.5	> 99.9	> 99.9

Electronic absorption spectra of the solutions. The spectrum of an aqueous solution of the ligand shows strong absorption in the far UV region (220–245 nm) caused by π-π* transitions in the conjugated double bonds of the furan ring [15]. An absorption band at 307 nanometers is associated with the existence of the chromophoric C=N group. No absorption bands are present in the visible region.

The electronic absorption spectra of solutions of the isolated Cu(II) complexes in ethanol in the near IR region show a broad absorption band at 820–857 nanometers due to the d-d transition, which is typical of the distorted octahedral environment of the Cu(II) ion formed by the ligand and solvent molecules [16, 17]. The spectra of the solutions obtained by the dissolution of the substances in 6 M HCl are identical. The spectra show absorption bands are at $\lambda = 380$ nm ($\varepsilon = 26$ $mol^{-1}\cdot cm^{-1}$), 567 nm ($\varepsilon = 41$ $mol^{-1}\cdot cm^{-1}$) and 800 nm ($\varepsilon = 40$ $mol^{-1}\cdot cm^{-1}$). It is known [17] that the copper(II) ion in d^9 configuration is a typical stereochemically mobile ion. Therefore, the nature of the ligand and environment has a very profound impact on the position of the absorption bands. This fact makes the determination of the ion geometry by the position of the bands extremely difficult and ambiguous. The spectrum of the obtained solution differs from that of $[CuCl_4]^{2-}$ solution in 6 M HCl. The latter spectrum shows absorption bands at 440 nm ($\varepsilon = 51$ $mol^{-1}\cdot cm^{-1}$) and 880 ($\varepsilon = 66$ $mol^{-1}\cdot cm^{-1}$) in the visible region. This fact indicates the presence of complex forms of copper(II) with β-furfural oxime in the solution.

IR spectra of the isolated complexes. The participation of functional groups of the ligand in the complex formation with copper(II) ions was judged on the basis of the analysis of IR spectra (Tab. 3). The complex-forming properties of β-furfural oxime (N-(furan-2-ylmethyliden)hydroxylamine **L**) are caused by three electron-donating atoms: the oxygen atom of the furan ring, the nitrogen atoms and the oxygen of the oxime group. So, it is expected that the main changes will be related to the absorption bands responsible for fluctuations of OH, C=N and N–OH groups.

The IR spectra of the "green" complex retain the absorption bands caused by vibrations of the oxime hydroxyl groups in the range 3230–3100 cm^{-1} (ν_{OH}) and 1329–1320 cm^{-1} (δ_{OH}). The broad bands of the valence vibrations of the OH groups indicate the existence of hydrogen bonds [15]. The band of $\nu_{C=N}$ valence vibration in the IR spectrum of the "green" complex undergoes a shift to shorter wavelengths by 13 cm^{-1} (1660 cm^{-1}) as a result of complex formation. If the oxime nitrogen atom is coordinated to the central atom, a shift to longer wave-lengths is observed as a rule due to lengthening of the C=N bond [18–20]. For example, in case of palladium(II) complex with β-furfural oxime the $\nu_{C=N}$ band is shifted by 85 cm^{-1} to the long-wave region (Tab. 3) [21]. A shift of the absorption band attributed to the valence vibration of the N–O group from 973 to 988 cm^{-1} (+15 cm^{-1}) is observed. Essential changes occur in the IR spectrum of the complex in the range 500–750 cm^{-1}. In this area deformation vibrations of =C–H bonds (610 cm^{-1}, shoulder and a strong band at 595 cm^{-1}) are shown. There are no essential changes in the skeletal vibrations of the furan ring (1570–1378 cm^{-1}) and the vibrations of the C–O–C bond (1190–990 cm^{-1}). The spectrum of the "green" complex shows two pairs of bands: at 707, 670 and 629, 594 cm^{-1}. In our opinion, they are due to the valence vibrations of the metal-oxygen bond of the oxime group [22–24].

The total of the obtained data indicates the coordination of the ligand in the Cu(II) complexes via the oxygen atom of the oxime group. There are no absorption bands in the range from 400 to 500 cm^{-1}, although the vibrations of the Cu–N bond are shown as a rule in this region [22–24]. According to the elemental analysis data the Cu:**L** molar ratio in the isolated compound is equal to 1:4. It is noteworthy that complexes with the M:reagent molar ratio equal to 1:4 of the composition [M**L**$_4$X$_2$] (where M are Co(II) or Ni(II) ions, X = Cl$^-$, Br$^-$) obtained by the interaction of stoichiometrical quantities of β-furfural oxime with metal salts in ethanol or methanol at 4 °C [11] show monodentate coordination of the ligand. The coordination occurs via the oxygen atom of the oxime group.

The IR spectrum of the "red" complex retains the absorption bands of the valence and deformation vibrations of the OH groups of the oxime fragment. However, in contrast to the IR spectrum of the "green" compound, a strong narrow band at 3246 cm^{-1} corresponds to the valence vibration. Bands of valence vibrations with $\nu_{C=N}$ = 1653 cm^{-1} and $\nu_{N\text{-}O}$ = 986 cm^{-1} (ligand) in the IR spectrum of the "red" complex, as well as in the spectrum of the "green" one, are shifted to the short-wave region by 6 and 12 cm^{-1}, respectively. Splitting of the ligand band at 1019 cm^{-1} into a doublet (1035 and 1020 cm^{-1}) is observed in the region of the C−O−C bond vibrations (1190–990 cm^{-1}) of the furan ring. Perhaps this is due to the involvement of the furan oxygen into the interaction with the copper(II) ion. Changes in the IR spectrum of the complex in comparison with the ligand are observed, and new absorption bands at 656, 638 cm^{-1} appear in the range 750–500 cm^{-1} ($\delta_{=C\text{-}H}$). We attributed them to the valence vibrations of the Cu−O bond of the oxime. A broad absorption band of average intensity at 561 cm^{-1} can be attributed to the valence vibrations of the Cu−O bond of the furan ring [17].

The obtained data indicate the bidentate coordination of the ligand molecules to the central copper atom in the "red" complex via the oxygen atoms of the oxime group and of the furan ring. According to the elemental analysis data this complex contains 2 oxime molecules.

In order to compare the composition of the formed Cu(II) precipitates in HCl solutions with the Cu(II) complexes with β-furfural oxime described in the literature [11] obtained in ethanol, we reproduced the syntheses of copper(II) complexes with β-furfural oxime in ethanol at different temperatures: 4 °C and 80 °C. It is specified in [11] that the interaction of stoichiometric quantities of β-furfural oxime with metal salts in ethanol or methanol leads to the formation of complexes of composition [M(**L**)$_n$X$_m$], where M are cations of Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Ag(II), Pt(II); X is a halide ion; n = 1, 2, 3, 4; m = 1 or 2. According to the literature data the composition of the complexes considerably depends on the synthesis temperature. Thus, two ligand molecules are included in the internal sphere of the complexes at 80 °C, and four, at 4 °C.

The compounds of Cu(II) obtained at different synthesis temperatures are red-brown. According to the elemental analysis data it is found, %:

– for the compound isolated at 4 °C: N 7.45; C 33.9; H 2.87;

– for the compound isolated at 80 °C: N 7.80; C 33.9; H 2.17.

Calculated for gross formula $Cu(C_5H_5O_2N)_2Cl_2$, %: N 7.86; C 33.7; H 2.81; Cu 17.8. This corresponds to the molar ratio of Cu:**L** in the isolated compounds equal to 1:2 irrespectively of the synthesis temperature.

Comparison of the IR spectra of the "red" complex obtained by the synthesis in 4 M HCl and the complexes of copper(II) isolated from ethanol at different temperatures showed that they are identical. This indicates the identical structure of these substances.

Thus, we showed that the copper compound of composition [Cu**L**$_2$Cl$_2$] is obtained in ethanol irrespectively of the synthesis temperature or in hydrochloric acid solution in the range 1–4 M of HCl.

Thermal stability of the complexes. The thermal stability of the obtained complexes of copper and palladium with β-furfural oxime was studied[2].

According to the thermogravimetric analysis (Fig. 2) the "green" complex is stable up to 86 °C. The complex decomposition is described by a number of stages that are difficult to separate. The main weight loss of a sample (49.1%) occurs at 86–156 °C. The process is followed by an exothermal effect with a maximum at 145 °C. It should be noted that the IR spectrum of the sample obtained by isothermal keeping at 150 °C for 20 h has a weak absorption band at 2220 cm^{-1}. We attributed it to the $\nu_{C\equiv N}$ valence vibration, and it indicates that copper nitriles are intermediate decomposition products. Further temperature increase to 488 °C led to slow weight loss by 27.0%. The total weight loss was 76.1%. The calculated weight loss in the case if 4 ligand molecules and a water molecule are removed is 76.8%. An exothermal effect with a maximum at 506 °C on the DTA curve is observed in the temperature range 473−523 °C. Apparently, it is caused by burning out of the carbon residue − the product of decomposition of the organic part of the complex.

Further heating of the sample to 600 °C is followed by 12.4% weight loss, which can be due to the chloride ions removal (theoretical weight loss is 12.3%). The total weight loss of the sample was 88.7%. The weight of the residue was 11.3% (calculated for copper oxide: 13.8%). It should be noted that the compound is volatile, which is indicated by the blue coloring of the top layer of the reference substance (aluminum oxide).

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[2] Note that the thermal decomposition of N-(furan-2-ylmethyliden)hydroxylamine itself occurs in one stage. The decomposition starts at 65°C and ceases at 196°C. The reagent is completely decomposed with the formation of volatile products. The process is accompanied by two endothermal effects with narrow bands: at 75–105°C (maximum at 87°C) due to the substance melting and at 157–206°C (maximum at 186°C) with the substance decomposition.

Table 3. Positions of absorption bands in the IR spectra of the oxime (**L**), copper(II) and palladium(II) complexes (cm^{-1}) and their attribution

Attribution	Oxime	“Green” Cu(II) complex	“Red” Cu(II) complex	$[PdL_2]Cl_2$ complex
ν_{O-H}	3423 sh., 3287, 3221, 3086, 3045 br. unresolved band with several maxima	3440 sh., 3231, 3154, 3086 br. unresolved band with several maxima	3254 v.s.br., 3169, 3141, 3119, 3057 unresolved band with several maxima	3205 [21]
ν_{C-H}	2925 s., 2855 s.	2922 w., 2871 w.	2963 – 2857 w. bands	2853 w., 2810 w.
$\nu_{C=N,}$ δ_{H2O}	1647 s.	1660 m.	1653 m., 1608 br.w.	1562 [21]
$\nu_{C=C,}$ vibrations of the furan ring skeleton	1570 m., 1478 s., 1448 sh., 1379 s.	1569 m., 1475 s., 1448 sh., 1384 s.	1570 m., 1477 v.s., 1441 s., 1385 s.	1564 m., 1472 v.s., 1433 s., 1382 s.
δ_{O-H}	1325 m.	1329 m.	1320 m.	1329 m.
ν_{C-O-C}	1239 s., 1188 s., 1147 s., 1087 s., 1020 v.s.	1289 br.w., 1243 br.m., 1194 br.w., 1147 br.w., 1089 m., 1023 m.	1291 w., 1257 w., 1192 w., 1155 w., 1089 m., 1035 and 1021 br.s. band with two maxima	1254 m., 1199, m., 1154 m., 1088 m., 1031 m.
ν_{N-O}	973 v.s.	988 v.s.	986 v.s.	1008 s.
γ_{C-O-C}, $\delta_{=C-H}$	923 s., 895 s., 879 sh., 824 br.v.s., 754 v.s., 595 s., 523 m.	939 br.w., 916 br.w., 886 br.w., 829 s., 761 br.s., 707 br.w., 707 br.w., 594	942 m., 911 m., 887 m., 830 s., 801 w., 761 s., 593 s., 506 w.	943 w., 905 m., 889 m., 831 s., 766 v.s., 593 s.
$\nu_{Cu-O(ox)}$		670 br.m., 629 br.m.	656 br.m., 638 br.m.	
ν_{Pd-N}				566 [21]
$\nu_{M-O(ring)}$			561 br.c	512 [21]

sh. – shoulder;
br.s. – broad strong;
s. – strong; m. – medium;
w. – weak; v.s. – very strong;
$\nu_{Cu-O(ox)}$ – bond with the oxime oxygen;
$\nu_{Cu-O(ring)}$ – bond with the furan ring oxygen

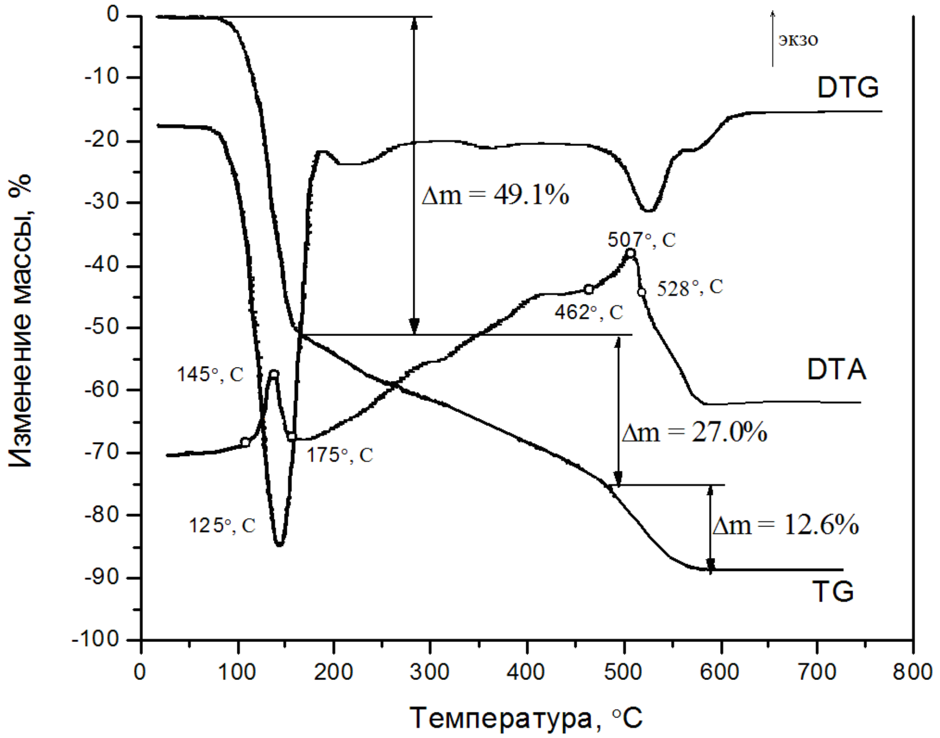

Figure 2. Thermogram of the “green” Cu(II) complex in the air.
[Изменение массы, % means Weight change, %;
Температура, °C means Temperature, °C]

The "red" complex, in contrast to the "green" one, is thermally stable up to 140 °C. Then a sharp weight loss (by 37.8%) occurs up to 164 °C. The process is followed by an exothermal effect in a wide temperature range (143–180 °C) with a maximum at 156 °C. Apparently, thermal decomposition of two coordinate oximes occurs at this stage to form nitrile complexes as intermediate compounds. This assumption is confirmed by the emergence of a valent vibration of the C≡N bond at 2236 cm^{-1} in the IR spectrum of the sample subjected to isothermal keeping at 150 °C within a day. Further decomposition occurs without pronounced thermal effects, although a broad weak band corresponding to an exothermal effect is present in the temperature range 594–648 °C. Apparently, this is due to burning out of the carbon residue. The obtained weight of the residue was 19.2% of the total weight of the sample, which is less than the expected weight calculated for copper(II) oxide (24.0%). This is also caused by some volatility of the intermediate copper-containing thermolysis products.

Thermal decomposition of the Pd(II) complex also proceeds as a series of stages that are difficult to separate. The decomposition starts at 170 °C. The process is followed by two strong exothermal effects at 200–225 °C (with a maximum at 210 °C) and 331–436 °C (with a maximum at 380 °C) caused by the destruction of the complex and oxidation of the organic part of the ligand. The decomposition ceases at 404 °C. The final weight of palladium is 26.7%

(calculated for [$Pd(C_5H_5O_2N)_2Cl_2$]: 26.6%). According to X-ray phase analysis the obtained black residue is metallic Pd.

Palladium(II) and copper(II) compounds form the following row according to their thermal stability: the Pd(II) complex > the "red" Cu(II) complex > the "green" Cu(II) complex. This can indicate that the metal–ligand bond becomes weaker in this series. The closeness of the decomposition temperatures of the "red" copper(II) complex and the palladium(II) complex confirms the conclusion about the bidentate coordination of the ligand.

Conclusion

The results obtained in the work indicate that various complexes are formed upon the interaction of Cu(II) with β-furfural oxime (N-(furan-2-ylmethyliden) hydroxylamine) depending on the solution acidity. In weakly acidic solutions (0.01–0.1 M of HCl) the "green" complex of composition [$Cu\mathbf{L}_4Cl_2$] was obtained, in which the oxime is coordinated to the central atom via the oxygen atom of the oxime group. In 1–4 M HCl, as well as in ethanol the so-called "red" complex of composition [$Cu\mathbf{L}_2Cl_2$] is formed, in which the ligand molecules are coordinated via the oxygen atom of the furan ring and the oxygen of the oxime group.

N-(Furan-2-ylmethyliden) hydroxylamine can be used as a reagent for almost quantitative isolation of palladium from HCl solutions. However, it does not provide separation of copper and palladium in case of their mutual presence.

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