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# Magnetic, thermal and spectral behaviour of 3-chloro-2-nitrobenzoates of Co(II), Ni(II), and Cu(II)

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**Abstract:** Physico-chemical properties of 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were synthesized and studied. The complexes were obtained as mono- and dihydrates with a metal ion to ligand ratio of 1 : 2. All analysed 3-chloro-2-nitrobenzoates are polycrystalline compounds with colours depending on the central ions: pink for Co(II), green for Ni(II) and blue for Cu(II) complexes. Their thermal decomposition was studied in the range of 293 – 523 K, because it was found that on heating in air above 523 K 3-chloro-2-nitrobenzoates decompose explosively. Hydrated complexes lose crystallization water molecules in one step and anhydrous compounds are formed. The final products of their decomposition are the oxides of the respective transition metals. From the results it appears that during dehydration process no transformation of nitro group to nitrite takes place. The solubilities of analysed complexes in water at 293 K are of the order of $10^{-4}$ – $10^{-2}$ mol / $dm^3$. The magnetic moment values of $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$ ions in 3-chloro-2-nitrobenzoates experimentally determined at 76 – 303 K change from $3.67\mu_B$ to $4.61\mu_B$ for Co(II) complex, from $2.15\mu_B$ to $2.87\mu_B$ for Ni(II) 3-chloro-2-nitrobenzoate and from $0.26\mu_B$ to $1.39\mu_B$ for Cu(II) complex. 3-Chloro-2-nitrobenzoates of Co(II) and Ni(II) follow the Curie-Weiss law. Complex of Cu(II) forms dimer.

*Keywords*: 3-chloro-2-nitrobenzoates; complexes of Co(II), Ni(II) and Cu(II); IR spectra; magnetic moments; thermal stability.

## Introduction

3-Chloro-2-nitrobenzoic acid is a light-yellow crystalline solid sparingly soluble in water. Its electrolytic dissociation constant is equal to $4.4 \cdot 10^{-3}$ (25°C) [1]. The compounds of 3-chloro-2-nitrobenzoic acid anion are very little known. A survey of the literature shows that it is possible to find papers on the complexes of various ligands with some of d block elements [1-4], and also on their salts with 3-chloro-2-nitrobenzoic acid anion. The salts of 3-chloro-2-nitrobenzoic acid anion were obtained in the solid state only with the cations: $Ca^{2+}$ and $Ba^{2+}$ [4]. 3-Chloro-2-nitrobenzoate of Ca(II) was obtained as trihydrate while that of Ba(II) as tetrahydrate.

Moreover some complexes of transition element cations with various isomers of chloronitro- and chloromethoxybenzoic acid anions were also prepared as solids and investigated [5-12]. The 3-chloro-2-nitrobenzoates of Co(II), Ni(II), and Cu(II) have not been obtained so far. Therefore the aim of this work was to prepare them in the solid state and to examine some of their physico-chemical properties including thermal stability in air during heating to 523 K, IR

spectral characterization, X-ray powder investigations, solubility in water at room temperature and magnetic behaviour at 76 – 303 K. Thermal stability investigations give informations about the process of dehydration. The magnetic susceptibility measurements let study the kinds of the way of coordination of the central ions and the nature of the bonding between central ions and ligands. If the magnetic moment is known, the number of unpaired electrons can be calculated. This may also give information on the oxidation state of the central metal ion of a complex. When the number of unpaired electrons on the ion of complex is known the spin-only moment can be calculated. The deviation of the measured magnetic moment from the spin-only permits the drawing of conclusions on the symmetry of the complex in certain cases. The determination of the number of unpaired electrons on the central atom establishes whether the complex investigated is of low or high spin or the ligand form the strong or weak fields.

## Experimental details

The 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were prepared by adding the equivalent quantities of 0.1 M ammonium 3-chloro-2-nitrobenzoate (pH ~ 5) to a hot solution containing the Co(II), Ni(II) and Cu(II) chlorides and crystallizing at 293 K. The solids formed were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303 K to a constant mass.

The contents of carbon, hydrogen and nitrogen were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser. The content of chlorine was determined by the Schöniger method. The contents of metals were established by ASA method with the use of ASA 880 spectrophotometer (Varian).

The IR spectra of complexes were recorded over the range of 4000 – 400 $cm^{-1}$ using M – 80 spectrophotometer (Carl Zeiss Jena).

**Table 1.** Elemental analysis data of Co(II), Ni(II) and Cu(II) 3-chloro-2-nitrobenzoates

| Complex | C / % | | H / % | | Cl / % | | N / % | | M / % | |
|---|---|---|---|---|---|---|---|---|---|---|
| $L^-$ = $C_7H_3O_4NCl$ | calcd. | found | calcd. | found | calcd. | found | calcd. | found | calcd. | found |
| $CoL_2 \cdot 2H_2O$ | 33.87 | 33.67 | 2.01 | 2.00 | 14.31 | 14.30 | 5.64 | 5.62 | 11.88 | 11.80 |
| $NiL_2 \cdot 2H_2O$ | 33.87 | 33.58 | 2.01 | 2.01 | 14.37 | 14.35 | 5.64 | 5.63 | 11.87 | 11.85 |
| $Cu_2L_4 \cdot 2H_2O$ | 33.60 | 33.70 | 1.60 | 1.58 | 14.20 | 14.21 | 5.60 | 5.60 | 12.68 | 12.64 |

**Table 2.** Wavenumbers ($cm^{-1}$) of $COO^-$ bands in 3-chloro-2-nitrobenzoates of Co(II), Ni(II), Cu(II) and Na and of the COOH

| Complex $L^-$ = $C_7H_3O_4NCl$ | $\nu_{C=O}$ | $\nu_{asOCO}$ | $\nu_{sOCO}$ | $\Delta\nu_{OCO}$ | $\nu_{C-Cl}$ | $\nu_{M-O}$ |
|---|---|---|---|---|---|---|
| $CoL_2 \cdot 2H_2O$ | – | 1590 | 1400 | 190 | 740 | 500 |
| $NiL_2 \cdot 2H_2O$ | – | 1590 | 1410 | 180 | 740 | 480 |
| $Cu_2L_4 \cdot 2H_2O$ | | 1610 | 1410 | 200 | 750 | 530 |
| HL | 1710 | – | – | – | – | – |
| NaL | – | 1625 | 1400 | 225 | 760 | 440 |

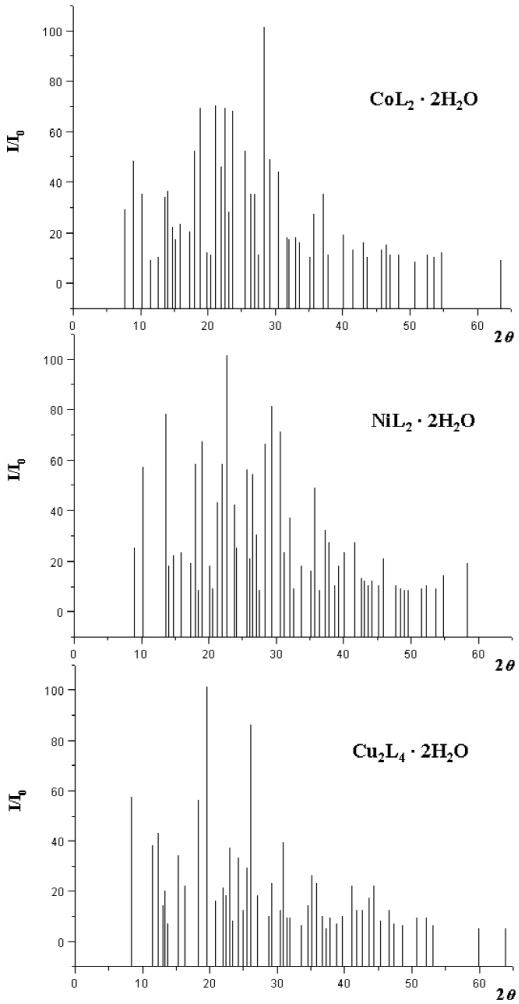


**Figure 1.** Dependence of $I/I^0$ *vs* 2θ for Co(II), Ni(II), and Cu(II) 3-chloro-2-nitrobenzoates.

Samples for IR spectra measurements were prepared as KBr discs.

The thermal stability and decomposition of the complexes were studied in air using a Setsys 16/18 (Setaram) TG, DTG and DSC instrument. The experiments were carried out under air flow in the temperature range of 293 – 523 K. Samples ranging from 5.20 mg (Co), 5.19 mg (Cu) to 5.05 mg (Ni) were heated in $Al_2O_3$ crucibles.

The thermal stability and decomposition of the prepared chloronitrobenzoates were determined by Paulik-Paulik-Erday Q-1500D derivatograph with Derill converter, recording TG, DTG and DTA curves. The measurements were made at a heating rate of 10 $K \cdot min^{-1}$ with a full scale. The samples (100 mg) were heated in platinum crucibles in static air to 523 K with a TG

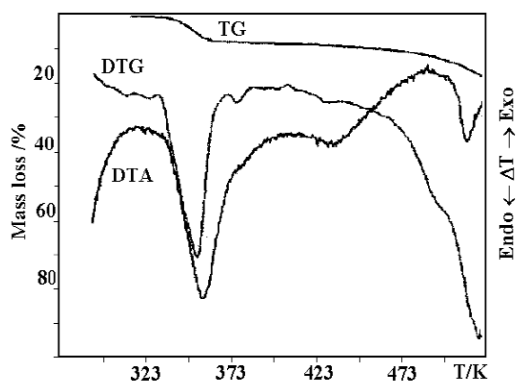


**Figure 2.** TG, DTG and DTA curves for Co(II) 3-chloro-2-nitrobenzoate.

**Table 3.** Temperature range of the dehydration process of Co(II), Ni(II) and Cu(II) 3-chloro-2-nitrobenzoates in air and their solubility in water at 293 K

| Complex $L^- = C_7H_3O_4NCl$ | $\Delta T^a$ / K | Calcd. | Found | $n^b$ | $\Delta H^c$ / $kJ \cdot mol^{-1}$ | Solubility/ $mol \cdot dm^{-3}$ |
|---|---|---|---|---|---|---|
| $CoL_2 \cdot 2H_2O$ | 360-390 | 7.25 | 7.20 | 2 | 130.80 | $1.30 \cdot 10^{-2}$ |
| $NiL_2 \cdot 2H_2O$ | 364-395 | 7.25 | 7.20 | 2 | 128.80 | $6.60 \cdot 10^{-4}$ |
| $Cu_2L_4 \cdot 2H_2O$ | 345-364 | 3.59 | 3.60 | 1 | 60.01 | $4.20 \cdot 10^{-4}$ |

$\Delta T^a$ = temperature range of dehydration process, $n^b$ = the number of loss of water molecules, $\Delta H^c$ = enthalpy of dehydration process

sensitivity equals to 100 mg, DTG and DTA sensitivities were regulated by computer Derill programme. The products of decomposition were calculated from TG curves and verified by the X-ray diffraction pattern.

The solubilities of 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) in water were measured at 293 K. Saturated solutions of the obtained compounds were prepared under isothermal conditions. The contents of Co(II), Ni(II) and Cu(II) were determined using ASA 880 spectrophotometer (Varian).

Magnetic susceptibilities of polycrystalline samples of 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were investigated at 76 – 303 K. The measurements were carried out using the Gouy method with magnetic field strength of 9.9 kOe. Mass changes were obtained from Cahn RM-2 electrobalance. The calibrant employed was $Hg[Co(SCN)_4]$ for which the magnetic susceptibility was assumed to be $1.644 \cdot 10^{-5}$ $cm^3 \cdot g^{-1}$. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [13, 14]. Magnetic moments were calculated according to Eq. (1):

$$\mu_{eff} = 2.83(\chi_M T)^{1/2} \quad (1)$$

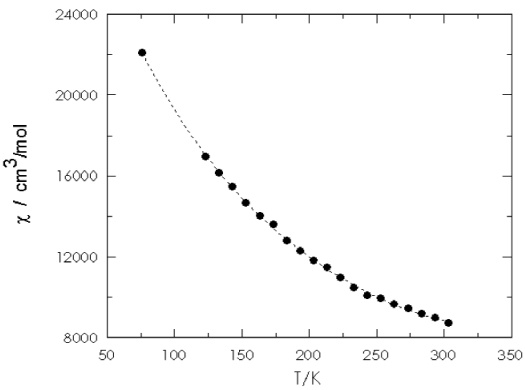


**Figure 3.** Dependence between magnetic susceptibility values *vs* temperatures for Co(II) complex.

**Table 4.** Values of magnetic data for 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II)

| $CoL_2 \cdot 2H_2O$ $L^- = C_7H_3O_4NCl$ | | | $NiL_2 \cdot 2H_2O$ | | | $Cu_2L_4 \cdot 2H_2O$ | | |
|---|---|---|---|---|---|---|---|---|
| T / K | $\chi_M \cdot 10^6$ | $\mu_{eff}$ /$\mu_B$ | T / K | $\chi_M \cdot 10^6$ | $\mu_{eff}$ /$\mu_B$ | T / K | $\chi_M \cdot 10^6$ | $\mu_{eff}$ /$\mu_B$ |
| 76 | 22095 | 3.67 | 76 | 7604 | 2.15 | 76 | 110 | 0.26 |
| 123 | 16969 | 4.09 | 123 | 6193 | 2.47 | 123 | 340 | 0.58 |
| 133 | 16142 | 4.15 | 133 | 5909 | 2.51 | 133 | 419 | 0.67 |
| 143 | 15466 | 4.21 | 143 | 5633 | 2.54 | 143 | 481 | 0.74 |
| 153 | 14684 | 4.24 | 153 | 5431 | 2.58 | 153 | 530 | 0.81 |
| 163 | 14036 | 4.28 | 163 | 5221 | 2.61 | 163 | 583 | 0.87 |
| 173 | 13595 | 4.34 | 173 | 5015 | 2.64 | 173 | 645 | 0.96 |
| 183 | 12799 | 4.33 | 183 | 4810 | 2.65 | 183 | 667 | 0.99 |
| 193 | 12312 | 4.36 | 193 | 4654 | 2.68 | 193 | 698 | 1.04 |
| 203 | 11834 | 4.39 | 203 | 4499 | 2.70 | 203 | 716 | 1.08 |
| 213 | 11484 | 4.43 | 213 | 4335 | 2.72 | 213 | 751 | 1.13 |
| 223 | 10988 | 4.43 | 223 | 4180 | 2.73 | 223 | 742 | 1.15 |
| 233 | 10468 | 4.42 | 233 | 4036 | 2.74 | 233 | 764 | 1.19 |
| 243 | 10082 | 4.43 | 243 | 3912 | 2.76 | 243 | 773 | 1.23 |
| 253 | 9949 | 4.49 | 253 | 3811 | 2.78 | 253 | 782 | 1.26 |
| 263 | 9687 | 4.52 | 263 | 3690 | 2.79 | 263 | 773 | 1.28 |
| 273 | 9452 | 4.55 | 273 | 3753 | 2.86 | 273 | 791 | 1.31 |
| 283 | 9218 | 4.57 | 283 | 3566 | 2.84 | 283 | 791 | 1.34 |
| 293 | 8983 | 4.59 | 293 | 3480 | 2.86 | 293 | 791 | 1.36 |
| 303 | 8740 | 4.61 | 303 | 3387 | 2.87 | 303 | 791 | 1.39 |

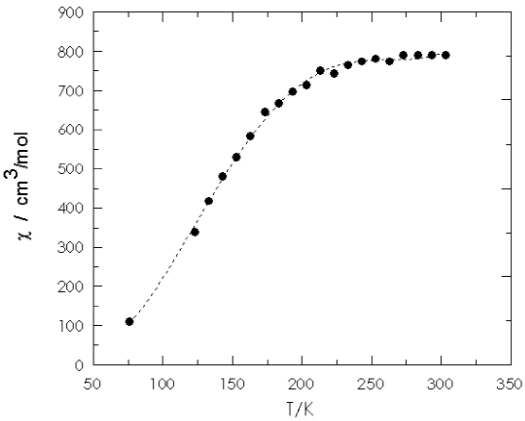


**Figure 4.** Dependence between magnetic susceptibility values *vs* temperatures for Cu(II) 3-chloro-2-nitrobenzoate.

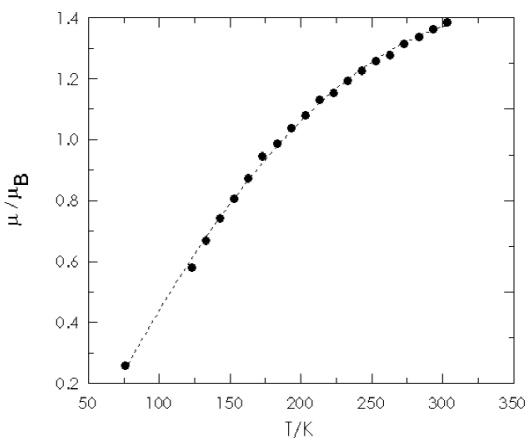


**Figure 5.** Relationship between magnetic moment values *vs* temperatures for Cu(II) 3-chloro-2-nitrobenzoate.

## Results and Discussion

3-Chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were obtained as polycrystalline solids with a metal ion to ligand mole ratio of 1 : 2 and a general formula $M(C_7H_3O_4NCl)_2 \cdot nH_2O$ (where M = Co, Ni, Cu and n = 2 for Co and Ni, and n = 1 for Cu), and colours: pink for Co(II), green for Ni(II) and blue for Cu(II) complexes (Table 1).

Some of the results of IR spectra analysis are in Table 2. The infrared spectrum of 3-chloro-2-nitrobenzoic acid shows the following absorption bands [15-18]; a strong band of COOH at 1710 $cm^{-1}$, the bands assigned to asymmetric and symmetric vibrations of $NO_2$ group at 1530 $cm^{-1}$ and 1350 $cm^{-1}$, the bands of ν(C–C) vibrations at 1610, 1425, 1150 and 1110 $cm^{-1}$, the bands of ν(C–H) vibrations at 3100, 900 and 810 $cm^{-1}$, and the bands of ν(C–Cl) stretching vibrations at 730 $cm^{-1}$. The bands of skeleton vibrations occur at 610 and 560 $cm^{-1}$ [15-18].

In the IR spectra of 3-chloro-2-nitrobenzoates the band at 1710 $cm^{-1}$ disappears, which confirms that no COOH is present in the complexes. In these spectra the intense broad absorption bands at 3570 – 3400 $cm^{-1}$ confirm the presence of crystallization water. The bands arising from asymmetric and symmetric vibrations of $COO^-$ group occur at 1610 –1590 $cm^{-1}$ and 1410 – 1400 $cm^{-1}$, respectively. The bands at 1540 – 1530 $cm^{-1}$ and 1360 –1350 $cm^{-1}$ are assigned to asymmetric and symmetric vibrations of the $NO_2$ group. They are not significantly shifted with respect to those of the parent acid, and thus one must conclude that the $NO_2$ group is not coordinated to the metal ions. The ν(C–Cl) stretching vibration occurs at 750 – 740 $cm^{-1}$, and the bands at 530 – 480 $cm^{-1}$ are assigned to the metal-oxygen ionic bond. The bands of skeleton vibrations are shifted to lower frequencies (600 and 540 $cm^{-1}$) compared to those in the acid IR spectrum. The changes in their positions are caused by the interaction between aromatic ring vibrations and the groups of atoms and ions. In the IR spectra of the complexes the bands of $\nu_{as}(OCO^-)$ are shifted to the lower frequencies whereas the bands of $\nu_s(OCO^-)$ are moved to higher or stay at the same frequencies compared to those of the sodium salt (Table 2). Therefore it is possible to assume that the carboxylate ion is a bidentate, chelating group [15, 19, 20]. The magnitudes of separation, $\Delta\nu(OCO^-)$, between the frequencies due to $\nu_{as}(OCO^-)$ and $\nu_s(OCO^-)$ in the analysed complexes indicate a lower degree of ionic bond in these compounds compared to sodium salt. Having a greater ionic potential than a sodium ion, $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$ ions have a stronger deforming effect on the ligand.

In order to verify that the prepared complexes are not converted to the nitrite isomers (during precipitation or on heating to 523 K), the IR spectra of the hydrates of 3-chloro-2-nitrobenzoates, and of dehydrated complexes, and also of sodium nitrite were recorded. A survey of the literature shows that under the influence of sunlight or with rising the temperature the nitro complexes may be transformed to the nitrite analogues in the endothermic process [21]. It was found that the isomerization of the nitro group may accompany the dehydration process of the complex or be connected with the transformation process in its inner sphere [22]. As a monodentate ligand, nitrite ion may be bounded either through a nitrogen atom forming the nitro complex or through one of the oxygen atoms yielding a nitrite complex. The general effect of coordination via nitrogen is a rise in the frequencies of both $\nu_{as}NO_2$ and $\nu_sNO_2$ compared to the values for free ion ~1328 $cm^{-1}$ and ~1260 $cm^{-1}$, respectively [23]. The IR spectra recorded for the hydrated and dehydrated 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) show that the nitro group is not transformed to the nitrite group with rising temperature. No bands confirming the isomerization of the nitro group through the oxygen atom are observed [22, 23].

From the X-ray diffraction patterns recorded for the 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) it appears that they are crystalline of low symmetry and large size of the unit cells. They have different crystal structures [24], which have not been determined, because their single crystals have not been obtained so far.

It follows from earlier studies on the thermal stability of 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) that on heating these complexes are explosively decomposed above 523 K [25, 26]. The thermal stability of 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) was studied in the range of 293 – 523 K. The results reveal that the analysed compounds lose the crystallization water in one step at 345 – 395 K. The process is connected with an endothermic effect as shown by the DTA curves [27-29]. The anhydrous 3-chloro-2-nitrobenzoates are formed above 400 K. The loss in mass calculated from TG curves is about 7.20 % in the case of dihydrates and 3.60 % in the case of monohydrate of Cu(II) 3-chloro-2-nitrobenzoate (Table 3). Their theoretical values are 7.25 % and 3.59 %, respectively. Considering the temperatures at which the dehydration takes place and the way by which it proceeds it is possible to assume that the water molecules form outer sphere water [29]. The anhydrous complexes of Co(II), Ni(II) and Cu(II) are finally decomposed to the oxides of respective metals: CoO, NiO and CuO, which were identified by IR spectra and X-ray powder diffractograms. The products of the final decompositions of chloronitrobenzoates were obtained by roasting the analysed complexes of Co(II), Ni(II) and Cu(II).

The thermogravimetric studies of 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were carried out with DSC/TG technique at 293 – 523 K (Table 3). The obtained results reveal the complexes to be hydrates containing two or one molecules of water of crystallization depending on the central ion. As example, the TG, DTG and DTA curves of Ni(II) 3-chloro-2-nitrobenzoate are presented in Fig. 2.

The complexes are stable up to 345 – 360 K. Next in the range of 345 – 395 K they dehydrate in one step. The mass losses estimated from TG curves (3.6 – 7.2 %) correspond to the loss from 1 to 2 molecules of water (the theoretical values are equal to 3.59 – 7.25 %) and the energetic effects ($\Delta H$ = 60.01 – 130.80 $kJ \cdot mol^{-1}$) accompanying these transformation processes confirm the losses of definite numbers of water molecules. The products of dehydration process were also characterized by elemental analysis, IR spectra and X-ray powder diffractograms.

The solubilities of 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) in water at 293 K were measured ( Table 3). They are in the order of $10^{-4}$ – $10^{-2}$ $mol \cdot dm^{-3}$. The Co(II) 3-chloro-2-nitrobenzoate is the most soluble, while those of Ni(II) and Cu(II) the least soluble salts. From the obtained results it appears that 3-chloro-2-nitrobenzoic acid may be used as an eluent for the separation of transition metal ions by ion-exchange chromatography.

The magnetic susceptibility of 3-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) was measured over the range of 76 – 303 K (Table 4).

The measured values for Co(II) and Ni(II) complexes obey the Curie-Weiss law suggesting a weak ferromagnetic interaction (Fig. 3). The magnetic moment values experimentally determined at 76 – 303 K for Co(II) and Ni(II) compounds change from 3.67 $\mu_B$ (at 76 K) to 4.61 $\mu_B$ (at 303 K) for Co(II) complex and from 2.15 $\mu_B$ (at 76 K) to 2.87 $\mu_B$ (at 303 K) for Ni(II) 3-chloro-2-nitrobenzoate. These magnetic moment data are very close to the spin – only values for the respective ions calculated from equation $\mu_{eff} = [4S (S + 1)]^{1/2}$ in the absence of the magnetic interactions for present spin-system. The magnetic moment values calculated at room temperature for Co(II), Ni(II) and Cu(II) ions are equal to 3.88 $\mu_B$, 2.83 $\mu_B$ and 1.73 $\mu_B$, respectively. For Co(II), Ni(II), and Cu(II) ions the magnetic moment values may be diffrent, than the spin-only worth. In the case of Co(II) compound they are higher than the spin-only value. This difference between measured and calculated data results from a spin-orbital coupling [30]. For Ni(II) and Cu(II) complexes these values are lower. This is due to the fact that the vectors L and S are aligned by the strong field of the heavy atom in opposite directions and this diminishes the resultant magnetic moment. The experimental data suggest that compounds of Co(II) and Ni(II) seem high-spin complexes with probably weak ligand fields [31].

The magnetic susceptibility values of 3-chloro-2-nitrobenzaote of Cu(II) increase with rising temperatures suggesting a weak antiferromagnetic interaction (Fig. 4). The magnetic moment values experimentally determined change from 0.26 $\mu_B$ (at 76 K) to 1.39 $\mu_B$ (at 303 K). These values are lower than the $d^9$ spin-only magnetic moment $\mu_{eff} = 1.73\ \mu_B$. Such dependence is a typical behaviour for copper dimer (Table 4, Fig. 5) [31-34]. The magnetic moment values of the Cu(II) complex decrease from 1.39 $\mu_B$ at 303 K to 0.26 $\mu_B$ at 76 K, as a consequence of depopulation of the excited triplet ($S = 1$) state. It is well-known that the interaction between two $S = 1/2$ metal atoms in a dimer leads to two molecular states: a spin singlet ($S = 0$), and a triplet ($S = 1$) separated by $2J$. The interaction will be antiferromagnetic ($J < 0$) if $S = 0$ is the ground state; on the contrary if $S = 1$ the interaction will be ferromagnetic ($J > 0$) [35-39].

## Conclusion

3-Chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were characterized by elemental analysis, thermal stability in air, IR spectral data, X-ray powder analysis, solubility in water at 293 K and magnetic properties. The obtained results indicate them to be mono-or dihydrates. Their thermal stability was studied at 293 – 523 K. I twas found that on heating in air above 523 K, they decompose explosively. When heated they dehydrate to form anhydrous salts which next are decomposed to the oxides of the respective metals. The solubility of the analysed compounds in water (at 293 K) is of the order of $10^{-4}$ – $10^{-2}$ mol·dm$^{-3}$. The measured values of magnetic susceptibilities for Co(II) and Ni(II) complexes obey the Curie-Weiss law, since they decrease with rising temperatures. The obtained $\mu_{eff}$ values of Co(II) and Ni(II) compounds may suggest that they are high-spin complexes with octahedral coordination and the ligands from the weak electrostatic field in coordination sphere of central ion. The magnetic susceptibility of 3-chloro-2-nitrobenzoate of Cu(II) increases with rising temperatures and the magnetic moment values suggest it to be dimer.

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