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Thermal and magnetic behaviour of 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II)

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Abstact 5-Chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) having formulae $Co(C_7H_3O_4NCl)_2{\cdot}3H_2O$, $Ni(C_7H_3O_4NCl)_2{\cdot}3H_2O$ and $Cu(C_7H_3O_4NCl)_2{\cdot}2H_2O$, were obtained as polycrystalline compounds. From the IR spectra analysis of complexes, sodium salt and according to the spectroscopic criteria the carboxylate ions seem bidentate groups. The complexes of Co(II) and Cu(II) lose the water of crystallization in one step at 363–523 K. The Ni(II) complex loses it in two stages in the ranges of 323–378 and 378–523 K, respectively. The compounds follow the Curie–Weiss law. The magnetic moment values experimentally determined change from 4.53 to 4.55 μ_B for Co(II) complex, from 2.34 to 2.97 μ_B for Ni(II) 5-chloro-2-nitrobenzoate and from 1.80 to 1.90 μ_B for Cu(II) complex.

Keywords 5-Chloro-2-nitrobenzoates · Thermal stability · Magnetic moments · Co(II) · Ni(II) Cu(II) complexes

Introduction

5-Chloro-2-nitrobenzoic acid having formula $C_7H_4O_4NCl$ is a crystalline solid sparingly soluble in cold water but readily soluble in the hot one and also in ethanol and benzene. Its electrolytic dissociation constant is 1.52×10^{-2} (25 °C) and melting point 139 °C [1]. 5-Chloro-2-nitrobenozic acid was used as component of 5,5′-dithiobis-2-nitrobenzoic acid which found application to the determination of the acid-soluble disulphide content of blood [2]. Benzene and some of its derivaties (e.g. chloronitrobenzoic acids) have shown to cause alterations in heme and globin synthesis. Chloronitrobenzoic acids inhibited activity of δ-aminolevulinic acid (δ-ALA) and enhanced ferrochelatase (FC) activity. These information may prove useful for assessing toxicity of pollutants in animal species [3]. 5-Chloro-2-nitrobenzoic acid was also used as component of synthesis of 2-aryl 4(3H)-quinazolinones [4] and 6-pyrrolidinyl-2-(2-substituted phenyl)-4-quinazolinones [5], which are potential anticancer candidates.

The 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) in the powder forms have not been obtained so far. However, in the literature there is article only about the synthesis and crystal structure determination of copper(II) 5-chloro-2-nitrobenzoate dimer, obtained as monocrystal, but there is no the information on its various property investigations [6]**.** The aim of this study was to obtain the complexes of Co(II), Ni(II) and Cu(II) with the 5-chloro-2-nitrobenzoic acid anion as solids in the powder form and to examine some of their physico-chemical properties including thermal stability in air during heating. The complexes were synthesized and characterized by elemental analysis. Their IR spectra were recorded in order to verify their compositions and to estimate the dentates of carboxylate groups in ligands. Their thermal stability was also investigated for evaluating the assumed position of crystallization water molecules in outer or inner spheres of coordination and for determining the thermal effects connected with such processes as: dehydration, melting,

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oxidation, or reduction that take place during heating in the analysed complexes. It was very important to estimate also the character of bonding between atoms or groups of atoms and ions in the molecules of compounds. The magnetic susceptibility of complexes were measured and the magnetic moments calculated in order to study the nature of coordination of the central ions and ligands to get information whether the analysed complexes are of low or high spin or if the ligands form the strong or weak fields and if the analysed compounds are monomers or dimers.

Experimental

Materials

The 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were prepared by adding the equivalent quantities of 0.1 M ammonium 5-chloro-2-nitrobenzoate (pH $\sim$ 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. For the preparation of the complexes, the following chlorides of *d*-block elements were used: $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ (REAGENTS—Chemical Enterprise in Lublin (Poland)). The 5-chloro-2-nitrobenzoic acid used for the preparation of complexes was produced by Aldrich Chemical Company. In the experiments, the solution of NH_3aq (25%) produced by Polish Chemical Reagents in Gliwice (Poland) was also used.

Methods

The contents of carbon, hydrogen and nitrogen were determined by elemental analysis using a CHN 2400 Perkin-Elmer analyser. The content of chloride was determined by the Schöniger method. The contents of M^{2+} metals were established by using ED XRF spectrophotometer (Canberra-Packard) (Table 1).

The IR spectra of complexes were recorded over the range of 4000–400 cm^{-1} using M–80 spectrophotometer (Carl Zeiss, Jena). 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 297–523 K at a heating rate of 5 $K \cdot min^{-1}$. The initial mass of samples of 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) used for measurements are following: Co(II)—5.05 mg; Ni(II)—5.36 mg and Cu(II)—5.40 mg. Samples of the compounds were heated in Al_2O_3 crucibles.

The thermogravimetric analysis of DSC was performed at 293–523 K in nitrogen using a differential thermoanalyser Netzsch STA 4009C 3F at a heating rate of 5 K min^{-1}. The initial mass of samples of 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) used for measurements are following: Co(II)—9.57 mg; Ni(II)—10.71 mg and Cu(II)—10.57 mg.

Magnetic susceptibilities of polycrystalline samples of 5-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. Weight 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 1.644×10^{-5} cm^{-3} g^{-1}. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [7].

Results and discussion

5-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 $n = 3$ for Co(II) and Ni(II) and $n = 2$ for Cu(II). Their colours depend on the kind of central ion: pink for Co(II), green for Ni(II) and blue for Cu(II) complexes. The IR spectra of 5-chloro-2-nitrobenozates of Co(II), Ni(II) and Cu(II) were recorded. Some results of IR spectra analysis are presented in Table 2. The infrared spectrum of 5-chloro-2-nitrobenzoic acid shows the following absorption bands: a strong band of COOH at 1716 cm^{-1}, the bands assigned to asymmetric and symmetric vibrations of NO_2 group at 1520 and 1344 cm^{-1}, the bands of ν(C–C) vibrations at 1608, 1568, 1420 and 1120 cm^{-1}, the bands of ν(C–H) vibrations at 2856, 1288

Table 1 Elemental analysis data of Co(II), Ni(II) and Cu(II) 5-chloro-2-nitrobenzoates

Complex	C/%		H/%		N/%		M/%	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Co(C_7H_3O_4NCl)_2 \cdot 3H_2O$	32.68	32.59	2.33	2.20	5.45	5.57	11.45	11.05
$Ni(C_7H_3O_4NCl)_2 \cdot 3H_2O$	32.70	32.05	2.34	2.24	5.45	5.20	11.42	11.12
$Cu(C_7H_3O_4NCl)_2 \cdot 2H_2O$	33.56	33.44	1.99	1.78	5.59	5.40	12.69	12.34

Table 2 Spectroscopic data (cm^{-1}) of 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) and 5-chloro-2-nitrobenzoic acid

Frequencies/cm^{-1}				Assignment
$C_7H_4O_4NCl$	$Co(C_7H_3O_4NCl)_2 \cdot 3H_2O$	$Ni(C_7H_3O_4NCl)_2 \cdot 3H_2O$	$Cu(C_7H_3O_4NCl)_2 \cdot 2H_2O$	
–	3402 *s*	3496 *s*	3456 *s*	ν (O–H) + ν (C–H)
2856 *m*	3104 *w*	–	–	ν (C–H)
1716*vs*	–	–	–	ν (C=O)
1608 *s*	1588 *vs*	1608 *vs*	1584–1556 *s*	ν_{as}(OCO) + ν(C=C) + δ(O–H)
1568 *s*	–	–	–	ν (C=C)
1520 *vs*	1532 *vs*	1524 *vs*	1524 *vs*	$\nu_{as}(NO_2)$
1420 *s*	1428 *vs*	1424 *vs*	1416 *vs*	ν (C=C)
–	1384 *vs*	1390 *vs*	1380 *vs*	ν_s(OCO)
1344 *s*	1352 *s*	1348 *vs*	1368 *vs*	$\nu_s(NO_2)$
1288 *m*	–	–	–	δ (C–H)
1152 *m*	1168 *m*	–	1168 *m*	δ (C–H)
1104 *m*	–	1104*w*	–	
1072 *m*	–	1118 *m*	1124 *m*	
–	1048 *s*	1048 *s*	1052 *s*	ν (C=C)
–	1011 *s*	1020 *s*	1020 *m*	ring
–	944 *w*	966 *w*	-	γ (C–H)
–	910 *w*	900 *w*	900 *w*	γ (O–H) + γ (C–H)
880 *s*	892 *m*	878 *m*	889 *m*	γ (C–H) + δ (OCO)
840 *m*	840 *s*	832 *s*	840 *s*	γ (C–H)
722 *s*	744 *s*	744 *s*	744 *s*	ν(CCl) + δ_s(CO) + δ_r(OCO)
688 *m*	704 *m*	704 *m*	704 *m*	ν(CCl) + γ(CH) + φ(CC)
616 *m*	620 *m*	608 *m*	616 *m*	α (CCC)
560 *m*	592 *w*	–	–	γ (C–H)
528 *m*	544 *m*	540 *m*	540 *m*	γ (C–H) + γ_w (OCO)
448 *m*	472 *m*	448 *m*	448 *m*	ν (M–O) + φ (CC)

s strong, *m* medium, *w* weak, *v* very

and 900–800 cm^{-1}, and the bands of ν(C–Cl) stretching vibrations at 722 and 688 cm^{-1}, the bands of skeleton vibrations occur at 616 and 570 cm^{-1}. In the IR spectra of 5-chloro-2-nitrobenzoates, the band at 1716 cm^{-1} disappears, which confirms that no COOH is present in the complexes. In these spectra, the intense broad absorption bands at 3496–3402 cm^{-1} confirm the presence of water of crystallization. The bands arising from asymmetric and symmetric vibrations of COO$^-$ group occur at 1608–1556 cm^{-1} and 1390–1380 cm^{-1}, respectively. The bands at 1532–1524 cm^{-1} and 1368–1348 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 744–704 cm^{-1} and the bands at 448 cm^{-1} are assigned to the metal–oxygen ionic bond [8–21]. The bands at 448 cm^{-1} in the spectra of ligand and analysed complexes of Ni(II) and Cu(II) have the same value of frequency but their shapes are not identical. The bands in the spectra of complexes are simultaneously assigned to M–O stretching vibrations and vibrations of φ (CC) while that in the ligand spectrum only to φ (CC) vibration. The magnitudes of separation,

$\Delta\nu$, between the frequencies of ν_{as}OCO and ν_sOCO in the complexes are lower ($\Delta\nu = 218$–204 cm^{-1}) than the sodium salt ($\Delta\nu = 240$ cm^{-1}) which indicates a smaller degree of ionic bond in the 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II). In the case of 5-chloro-2-nitrobenzoates of analysed elements the shifts of the frequencies ν_{as}OCO and ν_sOCO are lower and higher, respectively, than those for sodium 5-chloro-2-nitrobenzoate (ν_{as}OCO = 1600 cm^{-1} and ν_sOCO = 1360 cm^{-1}). Therefore, the carboxylate ion in the obtained complexes appears to be a symmetrical, bidentate chelating ligand [20, 22].

The thermal properties of 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were investigated by thermogravimetric (TG) analysis, differential thermogravimetric (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The thermal analysis was

Table 3 Decomposition data for 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) in air atmosphere

Compound	ΔT/K	Mass loss/%		n	ΔH/kJ/mol^{-1}
		Calcd.	Found		
$Co(C_7H_3O_4NCl)_2 \cdot 3H_2O$	363–523	10.50	10.60	3	196.60
$Ni(C_7H_3O_4NCl)_2 \cdot 3H_2O$	323–378	3.50	4.20	1	180.60
	378–523	7.50	7.40	2	
$Cu(C_7H_3O_4NCl)_2 \cdot 2H_2O$	383–448	7.20	7.30	2	121.40

ΔT temperature range of dehydration process, n number of crystallization water molecules, ΔH enthalpy of the dehydration process

studied in the temperature range of 293–523 K because these compounds are explosively decomposed when hated above 523 K. Some results are presented in Table 3 and Figs. 1, 2. Figure 1 presents the recorded TG/DTG/DTA curves of three metal(II) complexes in air atmosphere while Fig. 2 shows only their DSC curves in nitrogen atmosphere. The thermal analysis results reveal them to be hydrated compounds. It can be seen that the TG curves of complexes show mass losses about 323 K, indicating the presence of water molecules. It was also confirmed by the elemental analysis and IR spectra. The complexes of Co(II) and Ni(II) were found to be trihydrates while that of Cu(II) dihydrate.

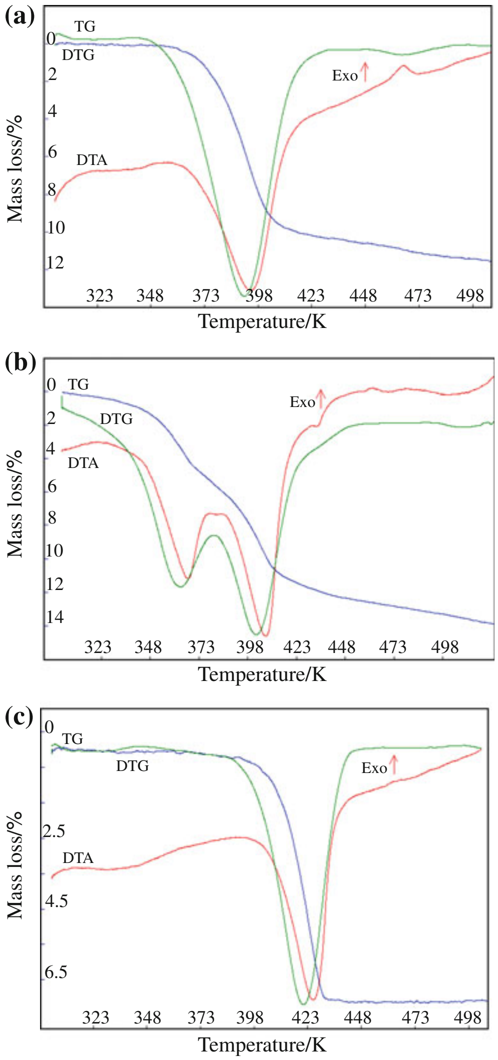

Fig. 1 TG, DTG and DTA curves of the metal(II) complexes: **a** $Co(L)_2 \cdot 3H_2O$, **b** $Ni(L)_2 \cdot 2H_2O$, **c** $Cu(L)_2 \cdot 2H_2O$

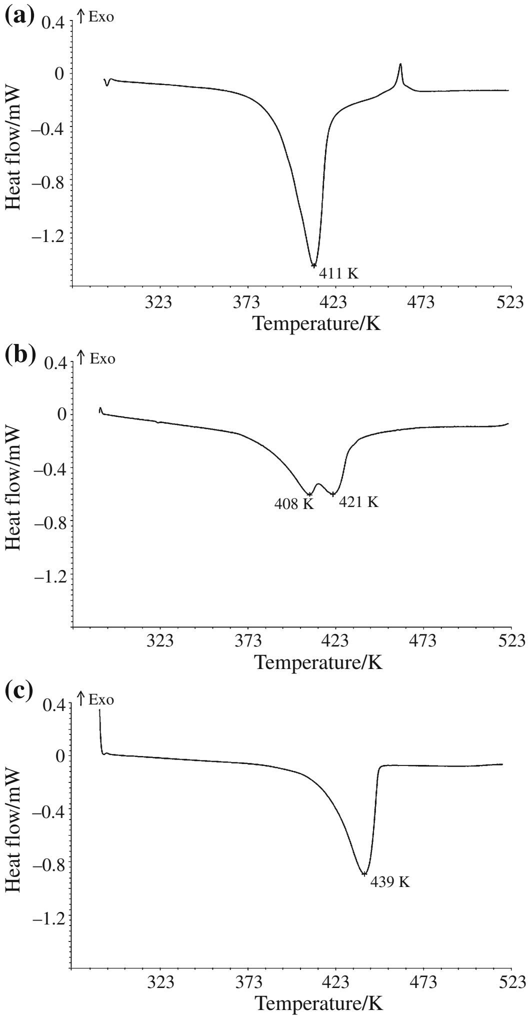

Fig. 2 DSC curves of the metal(II) complexes: **a** $Co(L)_2 \cdot 3H_2O$, **b** $Ni(L)_2 \cdot 3H_2O$, **c** $Cu(L)_2 \cdot 2H_2O$

The $Co(C_7H_3O_4NCl)_2{\cdot}3H_2O$ shows only one-step dehydration (Fig. 1a). The TG curve reveals drastic mass loss of 10.60% within a wide temperature range of 363–523 K. This may be attributed to the loss of the two molecules of water (calcd. 10.50%). The DTG peak corresponding to this stage is observed at 393 K. The recorded DTA and DSC curves reveal sharp endothermic peak at 398 and 411 K, respectively (Figs. 1a, 2a). The value of dehydration process enthalpy, ΔH, is equal to 196.60 kJ mol^{-1} (65.53 kJ mol^{-1} per one molecule of water).

The thermal dehydration of the $Ni(C_7H_3O_4NCl)_2{\cdot}3H_2O$ complex occurred in two-steps (Fig. 1b) by giving two endothermic DTA and DSC peaks. The first step displays a gradual mass loss of 4.20% within the temperature range of 323–378 K with a DTG peak at 363 K, which may be attributed to the loss of the one water molecule (calcd. 3.50%). The recorded DTA curve reveals endothermic peaks at 363 K. The water elimination process occurs at low temperature. This may indicate the crystallization nature of the water molecules. Such type of behaviour was observed for other complexes having this kind of water in composition [9, 19]. After the first mass loss of the Ni(II) complex, the second step exhibits also gradual loss in mass within the higher temperature range of 378–523 K with a DTG peak at 403 K, which results from the loss of the two water molecules coordinated to metal ion (found 7.40%, calcd. 7.50%) [13]. The recorded DTA and DSC curves reveal endothermic peak at 413 and 421 K, respectively (Figs. 1b, 2b). The value of dehydration process enthalpy, ΔH, is equal to 180.60 kJ mol^{-1} (60.20 kJ mol^{-1} per one molecule of water).

The $Cu(C_7H_3O_4NCl)_2{\cdot}2H_2O$ complex displays one-step dehydration (Fig. 1c). This step shows clear mass loss of 7.30% within a wide temperature range of 383–448 K with the DTG peak at 423 K, also giving rise to a sharp endothermic peak at 428 and 439 K in DTA and DSC curves, respectively (Figs. 1c, 2c). This process can be readily interpreted as loss of two water molecules (calcd. 7.20%). The value of dehydration process enthalpy, ΔH, is equal to 121.40 kJ mol^{-1} (60.67 kJ mol^{-1} per one molecule of water).

The above TG and DTG data reveal that the dehydration patterns of the Co(II), Ni(II) and Cu(II) are different. The $Co(L)_2{\cdot}3H_2O$ and $Cu(L)_2{\cdot}2H_2O$ complexes exhibit only one-step dehydration, whereas a two-stage dehydration is observed in the case of $Ni(L)_2{\cdot}3H_2O$. According to the beginning temperature of the dehydration of the metal(II) complexes, the following order of thermal stability may be proposed: $Cu(C_7H_3O_4NCl)_2{\cdot}2H_2O > Co(C_7H_3O_4NCl)_2{\cdot}3H_2O > Ni(C_7H_3O_4NCl)_2{\cdot}3H_2O$. The difference in thermal properties of the metal(II) complexes reveals that the metal(II) ion may have some marked influence on the thermal stability of complexes. The values of dehydration process enthalpy are proportional to the energy of the bonding of respective water molecules in the appropriate compounds.

Considering the temperature at which the dehydration process takes place and the way by which it proceeds it may be assumed that the molecules of water are differently bounded in the obtained complexes. According to Nikolaev et al. [23] water eliminated below 413–423 K can be considered as lattice water while that eliminated above 423 K may be coordinated to the central ion. The anhydrous 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) are formed above 413, 448 and 433 K, respectively. The products of dehydration process were characterized by elemental analysis and IR spectra registrations. The final products of complex decompositions obtained by roasting 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) to 1173 K were identified roentgenographically as CoO, NiO and CuO.

The magnetic susceptibility of the 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) was measured in the temperature range of 76–303 K (Table 4). The complexes of Co(II), Ni(II) and Cu(II) follow the Curie–Weiss law, since the values of the magnetic susceptibility decrease with increasing temperature. The paramagnetic dependences of magnetic susceptibility values of the complexes as a function of temperatures are presented in Table 3 and those only for Ni(II) 5-chloro-2-nitrobenzoate in Fig. 3. The effective magnetic moment values were calculated from the equation:

$$\mu_{\mathrm{eff}} = 2.83(c_{\mathrm{M}}T)^{1/2}$$

where: μ_{eff}—effective magnetic moment, χ_{M}—magnetic susceptibility per molecule and T absolute temperature.

The effective magnetic moment values experimentally determined for 5-chloro-2-nitrobenzoate Ni(II) change from 2.34 μ_{B} (at 76 K) to 2.97 μ_{B} (at 303 K). The experimental data reveal that the magnetic moment of Ni^{2+} ion in the complex is connected with spin-only moment. Its theoretical value at room temperature is equal to 2.83 μ_{B}. The obtained magnetic moment values of Ni(II) 5-chloro-2-nitrobenzoate are in agreement with literature values obtained for similar Ni(II) octahedral complexes [13, 19].

In the case of 5-chloro-2-nitrobenzoate of Co(II), the effective magnetic moments of cobalt ion change from 4.53 μ_{B} (at 76 K) to 4.55 μ_{B} (at 303 K) (Table 4). This value differs from that of the spin-only moment which amounts to 3.88 μ_{B}. The relatively large difference between measured and calculated values results from a spin-orbital coupling [24, 25]. The obtained magnetic moment values of Co(II) 5-chloro-2-nitrobenzoate are consistent with the reported value for the octahedral Co(II) complex [13, 19, 26].

The experimental data suggest that the compounds of Co(II) and Ni(II) seem high-spin complexes with probably weak ligand fields and octahedral coordination. In the

Table 4 Values of μ_{eff} for 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II)

$Co(C_7H_3O_4NCl)_2 \cdot 3H_2O$			$Ni(C_7H_3O_4NCl)_2 \cdot 3H_2O$			$Cu(C_7H_3O_4NCl)_2 \cdot 2H_2O$		
T/K	$\chi_M^{\mathrm{corr}} \times 10^6$	μ_{eff}/μ_B	T/K	$\chi_M^{\mathrm{corr}} \times 10^6$	μ_{eff}/μ_B	T/K	$\chi_M^{corr} \times 10^6$	μ_{eff}/μ_B
76	33741	4.53	76	8974	2.34	76	5312	1.80
123	20940	4.54	123	6863	2.60	123	3296	1.80
133	18835	4.48	133	6436	2.62	133	3020	1.79
143	17610	4.49	143	6193	2.66	143	2792	1.79
153	16491	4.50	153	5951	2.70	153	2637	1.80
163	15534	4.50	163	5699	2.73	163	2490	1.80
173	14721	4.52	173	5412	2.74	173	2348	1.80
183	13974	4.53	183	5174	2.75	183	2254	1.82
193	13352	4.54	193	5005	2.78	193	2147	1.82
203	12730	4.55	203	4849	2.81	203	2039	1.82
213	12242	4.57	213	4670	2.82	213	1972	1.83
223	11697	4.57	223	4485	2.83	223	1885	1.83
233	11190	4.57	233	4379	2.86	233	1811	1.84
243	10759	4.58	243	4209	2.86	243	1737	1.84
253	9870	4.47	253	4097	2.88	253	1683	1.85
263	9544	4.48	263	3932	2.88	263	1616	1.84
273	9305	4.51	273	3879	2.91	273	1616	1.88
283	9018	4.52	283	3796	2.93	283	1555	1.88
293	8712	4.52	293	3714	2.95	293	1515	1.89
303	8549	4.55	303	3627	2.97	303	1481	1.90

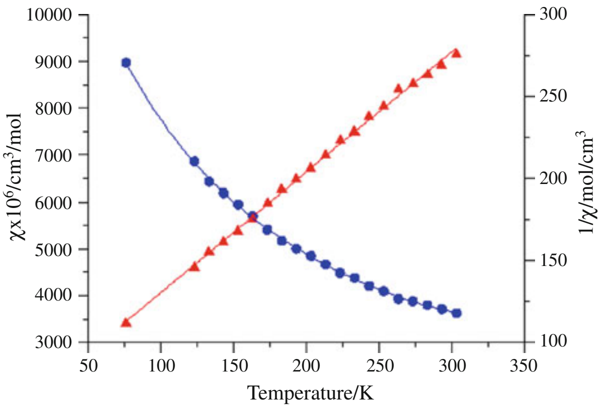

Fig. 3 Dependence between magnetic susceptibility values vs. temperatures for $Ni(L)_2 \cdot 3H_2O$

5-chloro-2-nitrobenzoates of Co(II) and Ni(II), the cations are presumably in octahedral coordination in which there are four oxygen atoms of two carboxylate groups and two oxygen atoms of water molecules. The coordination numbers of Cu(II), Co(II) and Ni(II) ions could be established on the basis of the complete crystal structure determination of monocrystals but they have not been obtained. As it was indicated by thermal analysis data, the water molecules in analysed complexes were supposed to be lattice water because they were released below 423 K [23] but their position in the complex coordination sphere was not precisely determined. However, taking into account the dentates of carboxylate groups and coordination numbers of central ions, we can suggest them to be coordination water that is released at the temperature typical generally for lattice water. From the obtained results it appears that in the 5-chloro-2-nitrobenzoates of Co(II) and Ni(II), the coordination numbers may be equal to 6 depending on the dentates of the carboxylate group and the position of water molecules in the complexes.

The magnetic susceptibility of Cu(II) complex changes with rising temperature according to the Curie–Weiss law and the observed effective moment at 76 K is 1.80 μ_B, while that at room temperature is 1.90 μ_B. Copper in +2 oxidation state has only the spin magnetic moment of 1.73 μ_B but due to spin orbit coupling, its higher values are often observed [13, 27]. The results of μ_{eff} obtained for the Cu(II) complexes may also suggest it to be monomeric. The experimentally determined room temperature magnetic moment per Cu(II) in the analysed complex is similar to those observed for other monomeric Cu(II) compounds and is higher than the d^9 spin-only magnetic moment $\mu_{\mathrm{eff}} = 1.73\ \mu_B$. This discrepancy may be due to spin-orbital coupling in the ion can mix the ground state representing no orbital momentum, with higher levels of identical multiplicity. The participation of those higher levels results in a small orbital contribution in those cases where it is not to be expected. It may also indicate the operation of ferromagnetic interaction.

In the 5-chloro-2-nitrobenzoates Co(II), Ni(II) and Cu(II), the presence of the NO_2 group in the *ortho* position does not stabilize system because of the steric effects but the inductive effect caused by the Cl substituent is the most important. In the complexes in which the Cl is in the *meta* position in the benzene ring, its inductive effect mainly influences the electron density, whereas the NO_2 group in the *ortho* position causes a noncoplanar arrangement of the substituents with the benzene because of the steric effects. Thus, the NO_2 group electrons are not conjugated with the ring Π electrons and mesomeric effect is partially eliminated.

Conclusions

5-Chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were characterized by elemental analysis, thermal stability in air, IR spectral data and magnetic properties. The obtained results indicate them to be di- or trihydrates. Their thermal stability was studied at 293–523 K. It was 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 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 μ_{eff} values of Co(II) and Ni(II) compounds may suggest that they are high-spin complexes and the ligands from the weak electrostatic field in coordination sphere of central ion.

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