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

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Abstract 5-Chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) having formulae Co(C_7H_3O_4NCl)_2•3H_2O, Ni(C_7H_3O_4NCl)_2•3H_2O and Cu(C_7H_3O_4NCl)_2•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-nitrobenzoic 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 derivatives (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 monocystal, 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,
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 mag-
netic moments calculated in order to study the nature of
co-ordination of the central ions and ligands to get infor-
mation 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 ~ 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: CoCl₂·6H₂O, NiCl₂·6H₂O
and CuCl₂·2H₂O (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
NH₃aq (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 Per-
kin-Elmer analyser. The content of chloride was deter-
mined by the Schöninger method. The contents of M²⁺
metals were established by using ED XRF spectropho-
tometer (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.

| Complex                  | C/%   | H/%   | N/%   | M/%   |
|--------------------------|-------|-------|-------|-------|
|                          | Calcd.| Found | Calcd.| Found | Calcd.| Found | Calcd.| Found |
| Co(C₇H₃O₄NCl)₂·3H₂O       | 32.68 | 32.59 | 2.33  | 2.20  | 5.45  | 5.57  | 11.45 | 11.05 |
| Ni(C₇H₃O₄NCl)₂·3H₂O       | 32.70 | 32.05 | 2.34  | 2.24  | 5.45  | 5.20  | 11.42 | 11.12 |
| Cu(C₇H₃O₄NCl)₂·2H₂O       | 33.56 | 33.44 | 1.99  | 1.78  | 5.59  | 5.40  | 12.69 | 12.34 |

The thermal stability and decomposition of the com-
plexes 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 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 Al₂O₃ crucibles.

The thermogravimetric analysis of DSC was performed
at 293–523 K in nitrogen using a differential thermoana-
lyser 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 fol-
lowing: 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 cm³ 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(C₇H₃O₄NCl)₂
· nH₂O (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-nitrobenzo-
ates 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 fol-
lowing absorption bands: a strong band of COOH at
1716 cm⁻¹, the bands assigned to asymmetric and sym-
metric vibrations of NO₂ group at 1520 and 1344 cm⁻¹, the
bands of m(C–C) vibrations at 1608, 1568, 1420 and
1120 cm⁻¹, the bands of m(C–H) vibrations at 2856, 1288
The thermal and magnetic behaviour

The spectra of complexes are simultaneously assigned to M–O stretching vibrations and vibrations of \( \varphi \) (CC) while that in the ligand spectrum only to \( \varphi \) (CC) vibration. The magnitudes of separation, \( \Delta \nu \), between the frequencies of \( \nu_{\text{as}}\text{OCO} \) and \( \nu_{\text{s}}\text{OCO} \) in the complexes are lower (\( \Delta \nu = 218–204 \text{ cm}^{-1} \)) than the sodium salt (\( \Delta \nu = 240 \text{ cm}^{-1} \)) 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 \( \nu_{\text{as}}\text{OCO} \) and \( \nu_{\text{s}}\text{OCO} \) are lower and higher, respectively, than those for sodium 5-chloro-2-nitrobenzoate (\( \nu_{\text{as}}\text{OCO} = 1600 \text{ cm}^{-1} \) and \( \nu_{\text{s}}\text{OCO} = 1360 \text{ cm}^{-1} \)). 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 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\(_2\)H\(_4\)O\(_2\)NCl |  | |
| Co(C\(_2\)H\(_4\)O\(_2\)NCl)\(_2\):3H\(_2\)O |  | |
| Ni(C\(_2\)H\(_4\)O\(_2\)NCl)\(_2\):3H\(_2\)O |  | |
| Cu(C\(_2\)H\(_4\)O\(_2\)NCl)\(_2\):2H\(_2\)O |  | |
| 3402 \textit{s} | 3496 \textit{s} | 3456 \textit{s} | \( \nu \) (O–H) + \( \nu \) (C–H) |
| 2856 \textit{m} | 3104 \textit{w} | – | – | \( \nu \) (C–H) |
| 1608 \textit{s} | 1588 \textit{vs} | 1608 \textit{vs} | 1584–1556 \textit{s} | \( \nu_{\text{as}}\text{OCO} \) + \( \nu \) (C=C) + \( \delta \) (O–H) |
| 1568 \textit{s} | – | – | – | \( \nu \) (C=C) |
| 1520 \textit{vs} | 1532 \textit{vs} | 1524 \textit{vs} | 1524 \textit{vs} | \( \nu_{\text{as}}\text{NO}_2 \) |
| 1420 \textit{s} | 1428 \textit{vs} | 1424 \textit{vs} | 1416 \textit{vs} | \( \nu \) (C=C) |
| – | 1384 \textit{vs} | 1390 \textit{vs} | 1380 \textit{vs} | \( \nu_{\text{s}}\text{OCO} \) |
| 1344 \textit{s} | 1352 \textit{s} | 1348 \textit{vs} | 1368 \textit{vs} | \( \nu_{\text{s}}\text{NO}_2 \) |
| 1288 \textit{m} | – | – | – | \( \delta \) (C–H) |
| 1152 \textit{m} | 1168 \textit{m} | – | 1168 \textit{m} | \( \delta \) (C–H) |
| 1072 \textit{m} | – | 1118 \textit{m} | 1124 \textit{m} |  |
| – | 1048 \textit{s} | 1048 \textit{s} | 1052 \textit{s} | \( \nu \) (C=C) |
| – | 1011 \textit{s} | 1020 \textit{s} | 1020 \textit{m} | ring |
| – | 944 \textit{w} | 966 \textit{w} | – | \( \gamma \) (C–H) |
| – | 910 \textit{w} | 900 \textit{w} | 900 \textit{w} | \( \gamma \) (O–H) + \( \gamma \) (C–H) |
| 880 \textit{s} | 892 \textit{m} | 878 \textit{m} | 889 \textit{m} | \( \gamma \) (C–H) + \( \delta \) (OCO) |
| 840 \textit{m} | 840 \textit{s} | 832 \textit{s} | 840 \textit{s} | \( \gamma \) (C–H) |
| 722 \textit{s} | 744 \textit{s} | 744 \textit{s} | 744 \textit{s} | \( \nu \) (CCl) + \( \delta \) (CO) + \( \delta \) (OCO) |
| 688 \textit{m} | 704 \textit{m} | 704 \textit{m} | 704 \textit{m} | \( \nu \) (CCl) + \( \gamma \) (CH) + \( \varphi \) (CC) |
| 616 \textit{m} | 620 \textit{m} | 608 \textit{m} | 616 \textit{m} | \( \pi \) (CCC) |
| 560 \textit{m} | 592 \textit{w} | – | – | \( \gamma \) (C–H) |
| 528 \textit{m} | 544 \textit{m} | 540 \textit{m} | 540 \textit{m} | \( \gamma \) (C–H) + \( \gamma \) \textit{w} (OCO) |
| 448 \textit{m} | 472 \textit{m} | 448 \textit{m} | 448 \textit{m} | \( \nu \) (M–O) + \( \varphi \) (CC) |

\( s \) strong, \( m \) medium, \( w \) weak, \( \nu \) very

and 900–800 cm\(^{-1}\), and the bands of \( \nu \) (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 \( \nu \) (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
studied in the temperature range of 293–523 K because these compounds are explosively decomposed when heated 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.

| Compound | $\Delta T$/K | Mass loss/% | $n$ | $\Delta H$/kJ/mol$^{-1}$ |
|----------|--------------|-------------|-----|-------------------------|
| Co(C$_7$H$_3$O$_4$NCl)$_2$·3H$_2$O | 363–523 | 10.50 | 3 | 196.60 |
| Ni(C$_7$H$_3$O$_4$NCl)$_2$·3H$_2$O | 323–378 | 7.50 | 2 | 180.60 |
| Cu(C$_7$H$_3$O$_4$NCl)$_2$·2H$_2$O | 383–448 | 7.20 | 2 | 121.40 |

$\Delta T$ temperature range of dehydration process, $n$ number of crystallization water molecules, $\Delta H$ enthalpy of the dehydration process
The Co(C$_7$H$_3$O$_4$NCl)$_2$·3H$_2$O 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. 1b, 2b). The value of dehydration process enthalpy, $\Delta H$, 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$_7$H$_3$O$_4$NCl)$_2$·3H$_2$O 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 molecules of water (calcd. 7.20%). The DTG peak corresponding to this stage may be attributed to the loss of the two molecules of water.

The Cu(C$_7$H$_3$O$_4$NCl)$_2$·2H$_2$O 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, $\Delta H$, 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)$_2$·3H$_2$O and Cu(L)$_2$·2H$_2$O complexes exhibit only one-step dehydration, whereas a two-stage dehydration is observed in the case of Ni(L)$_2$·3H$_2$O. According to the beginning temperature of the dehydration of the metal(II) complexes, the following order of thermal stability may be proposed: Cu(C$_7$H$_3$O$_4$NCl)$_2$·2H$_2$O $>$ Co(C$_7$H$_3$O$_4$NCl)$_2$·3H$_2$O $>$ Ni(C$_7$H$_3$O$_4$NCl)$_2$·3H$_2$O. 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 differentially 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:

$$\mu_{\text{eff}} = 2.83(\gamma_M T)^{1/2}$$

where: $\mu_{\text{eff}}$—effective magnetic moment, $\gamma_M$—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 $\mu_B$ (at 76 K) to 2.97 $\mu_B$ (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 $\mu_B$. 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 $\mu_B$ (at 76 K) to 4.55 $\mu_B$ (at 303 K) (Table 4). This value differs from that of the spin-only moment which amounts to 3.88 $\mu_B$. 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
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 \(\mu_B\), while that at room temperature is 1.90 \(\mu_B\). Copper in +2 oxidation state has only the spin magnetic moment of 1.73 \(\mu_B\) but due to spin orbit coupling, its higher values are often observed \[13, 27\]. The results of \(\mu_{\text{eff}}\) 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 \(\mu_{\text{eff}} = 1.73\ \mu_B\). 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

### Table 4

| \(T/K\) | \(\chi M_{\text{eff}} \times 10^6\) | \(\mu_{\text{eff}}/\mu_B\) | \(T/K\) | \(\chi M_{\text{eff}} \times 10^6\) | \(\mu_{\text{eff}}/\mu_B\) | \(T/K\) | \(\chi M_{\text{eff}} \times 10^6\) | \(\mu_{\text{eff}}/\mu_B\) |
|-------|----------------|----------------|-------|----------------|----------------|-------|----------------|----------------|
| 76    | 33741          | 4.53           | 76    | 3974           | 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           |
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 NO₂ 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 NO₂ group in the ortho position causes a noncoplanar arrangement of the substituents with the benzene because of the steric effects. Thus, the NO₂ 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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