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The physico-chemical properties of 4-chlorophenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II)

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Abstract: The complexes of 4-chlorophenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) have been synthesized as polycrystalline solids, and characterized by elemental analysis, spectroscopy, magnetic studies and also by X-ray diffraction and thermogravimetric measurements. The analysed complexes have the following colours: pink for Co(II), green for Ni(II), blue for Cu(II) and a pale pink for Mn(II) compounds. The carboxylate group binds as monodentate and bidentate ligands. On heating to 1173K in air the complexes decompose in several steps. At first, they dehydrate in one step to anhydrous salts, that next decompose to the oxides of respective metals. Their magnetic moments were determined in the range of 76-303K. The results reveal them to be high-spin complexes of weak ligand fields.

Keywords: 4-chlorophenoxyacetates; thermal stability; magnetic properties of Mn(II), Co(II), Ni(II), Cu(II).

Introduction

4-Chlorophenoxyacetic acid is a white solid hardly soluble in water ($K=7,9 \cdot 10^{-4}$) and easily soluble in ether and ethanol [1]. It is used as growth hormone for plants and is known as herbicide [2]. In some papers the details of its molecular structure was presented [3-5]. From the survey of literature it appears that its complexes with Li(I) and Cu(II) ions were synthesized and their properties were studied [6, 7].

The carboxylates play an important role in inorganic and bioinorganic chemistry. Many metal cations in a great number of various biological processes are a component of several vitamins and drugs [8, 9]. The carboxylates of d- and 4f- ion elements may be used as electric materials in the modern branches of techniques and technology or they may have applications as pre-

cursors in superconducting ceramic and magnetic field productions. These compounds are used as catalysts, pigments, solvents, food preservatives and plastics productions.

Metal carboxylates are applied for the productions of high degree purity of metal oxides and polycarboxylic acids are used for supermolecular compound synthesis, which in many cases, form with metal ions the molecular polymers containing in their structures, pores and channels owing to them they appear catalytic and adsorption properties. Therefore they may be used for the adsorption of inorganic gases such as: argon, nitrogen and hydrocarbons or small molecules of another inorganic compounds. Polycarboxylic acid may also form the molecules with two- and three-dimensional structures, yielding special magnetic and luminescence properties which let them be used in optical and electronic industries [10-16].

As a continuation of our studies on carboxylates we decided to synthesize 4-chlorophenoxyacetates with Mn(II), Co(II), Ni(II) and Cu(II) and to study some of their properties not to be investigated so far, such as magnetic properties in the range of 77-300K thermal stability in air at 293-1173K, solubility in water at 293K and to record their FTIR spectra.

Thermal stability investigations give informations about the process of dehydration and the ways of decompositions, and the magnetic susceptibility measurements let study the kinds of the way of coordination of the central ions and ligands. The determination of the solubility is valuable because it informs about the practical use of acid for separation of transition metal ions by extraction or ion-exchange chromatographic methods.

Experimental details

The 4-chlorophenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) were prepared by the addition of the equivalent quantities of 0,1 mol/dm³ ammonium 4-chlorophenoxyacetate

(pH≈5) to a hot solutions containing the 0,1 mol/dm³ Mn(II), Co(II), Ni(II) and Cu(II) nitrates (V) and crystallizing at 293K (1h). The solid formed were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303K to a constant mass.

The contents of carbon and hydrogen in the complexes and in the intermediate and final products obtained from their thermal decompositions were determined by elemental analysis using a CHN 2500 Perkin-Elmer analyzer and the content of chlorine by the Schöniger method. The contents of M²⁺ metals were established gravimetrically and by XRF method using spectrometer of X-ray fluorescence with energy dispersion EDXRF-1510 (CANBERRA firm).

The IR and FIR spectra of complexes were recorded over the ranges 4000-400cm⁻¹ and 600-100cm⁻¹, respectively, using M-80 and Perkin-Elmer 180 spectrometers. Samples for IR spectra measurements were prepared as KBr discs. FIR spectra were obtained in Nujol mulls sandwiched between polyethylene plates (Table 2). The FTIR spectra of the intermediate and final products obtained from the complex thermal decompositions were also registered.

Table 1. Elemental analysis data of Mn(II), Co(II), Ni(II) and Cu(II) 4-chlorophenoxyacetates and their solubility in water at 293K.

Complex L ⁻ = C ₆ H ₄ ClO ₂	H/%		C/%		Cl/%		M/%		Solubility mol/dm ³
	calcd	found	calcd	found	calcd	found	calcd	found	
MnL ₂ ·2H ₂ O	3.46	3.32	41.57	41.47	15.37	15.40	11.89	10.45	2,7 · 10 ⁻³
CoL ₂ ·4H ₂ O	3.98	3.22	38.25	40.96	14.15	14.20	11.74	11.32	2,8 · 10 ⁻³
NiL ₂ ·4H ₂ O	3.98	3.82	38.27	38.36	14.15	14.25	11.70	11.53	1,2 · 10 ⁻³
CuL ₂ ·2H ₂ O	3.40	3.26	40.81	40.97	15.09	15.12	13.49	12.06	2,6 · 10 ⁻⁴

Table 2. Wavenumbers (cm⁻¹) of COO⁻ bands in the analysed complexes of Mn(II), Co(II), Ni(II), Cu(II), and Na(I), and of the COOH band in 4-chlorophenoxyacetic acid.

Complex L ⁻ =C ₆ H ₄ ClO ₂	ν C=O	ν as OCO	ν sym OCO	Δν OCO	ν C-Cl	ν M-O
MnL ₂ ·2H ₂ O	-	1569, 1608	1335	234, 273	699 - 722	439
CoL ₂ ·4H ₂ O	-	1607	1334	273	699 - 728	441
NiL ₂ ·4H ₂ O	-	1598	1337	260	697 - 729	450
CuL ₂ ·2H ₂ O	-	1599	1346	252	739	458
HL	1708	-	-	-	722	-
NaL	-	1615	1344	271	722	449

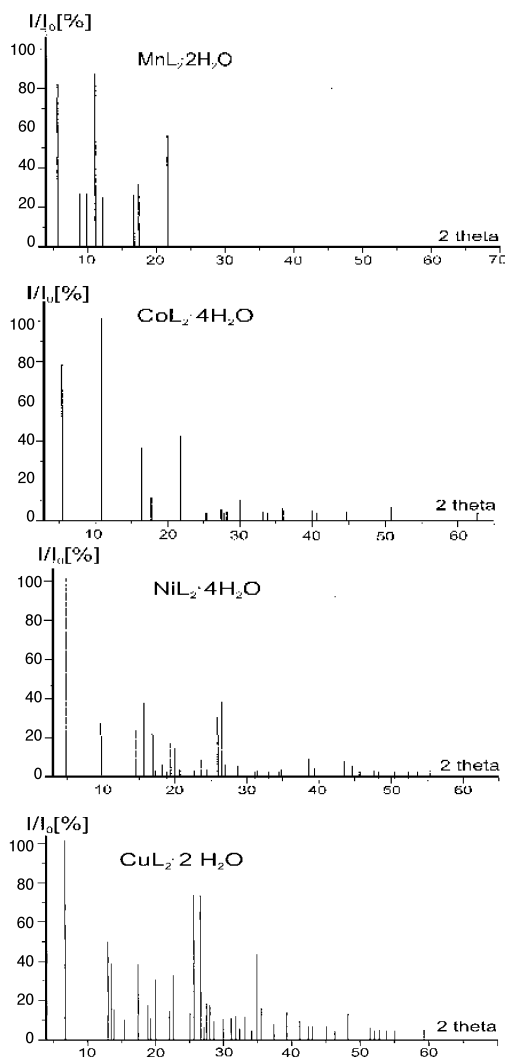


Figure 1. Dependence of I/I_0 vs 2θ for Mn(II), Co(II), Ni(II) and Cu(II) complexes.

The X-ray diffraction patterns of hydrated and dehydrated complexes, the intermediate and final products of complex thermal decompositions were taken on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered Cu $K\alpha$ radiation. The measurements were made within the range $2\theta=4-80^\circ$ by means of the Debye-Scherrer-Hull method. The relationships between I/I_0 and 2θ for these complexes are presented in Fig. 1.

The thermal stability and decomposition of the prepared complexes were determined by Paulik-Paulik-Erdy Q-1500D derivatograph with Derill converter, recording TG, DTG, and DTA curves (Fig. 2). The measurements were made at a heating rate of 10K min^{-1} with a full scale. The samples (100mg) were heated in platinum crucibles in static air to 1173K with a sensitivity of TG-100mg. DTG and DTA sensitivities were regulated by a Derill computer program. The products of decomposition were calculated from TG curves and verified by the diffraction pattern registration and IR spectra. The thermogravimetric analysis of DSC/TG was performed at temperature 323-723K using a differential thermoanalyzer Netzsch STA 409C 3F. The measurements were carried out under nitrogen flow (99,995% purity) and temperature increase rates of $1-12\text{K min}^{-1}$.

Magnetic susceptibilities of polycrystalline samples of 4-chlorophenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) were measured by the Gouy method using a sensitive Cahn RM-2 balance. The samples were placed in a long cylindrical tube which was suspended from an analytical balance. The sample tube was positioned between the poles of the magnet such

Table 3. Temperature ranges of thermal stability of Mn(II), Co(II), Ni(II) and Cu(II) 4-chlorophenoxyacetates in air.

Complex $L^- = \text{C}_6\text{H}_4\text{ClO}_2$	$\Delta T_1 / \text{K}$	Mass loss / %		n	$\Delta T_2 / \text{K}$	Mass loss / %		$\Delta H / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_{1H_2O} / \text{kJ}\cdot\text{mol}^{-1}$	T_K / K	Mass of residue / %	
		calcd.	found			calcd.	found				calcd.	found
$\text{MnL}_2\cdot 2\text{H}_2\text{O}$	350-385	7,79	8,16	2	497-868	83,48	84,60	151,99	75,99	938	16,52	15,40
$\text{CoL}_2\cdot 4\text{H}_2\text{O}$	371-406	7,17	7,98	2	518-910	85,29	84,00	138,77	34,69	938	15,98	14,71
$\text{NiL}_2\cdot 4\text{H}_2\text{O}$	347-406	14,35	14,12	4	583-833	85,11	84,61	243,83	60,95	903	14,80	15,40
$\text{CuL}_2\cdot 2\text{H}_2\text{O}$	357-385	7,65	7,59	2	490-896	84,00	79,50	129,06	32,00	938	16,00	20,50

ΔT_1 – temperature range of dehydration process, ΔT_2 – temperature range of decomposition process, n – number of water molecules lost in the dehydration process, ΔH – enthalpy of dehydration process, ΔH_{1H_2O} – enthalpy value for one molecule of water, T_K – final temperature of decomposition process

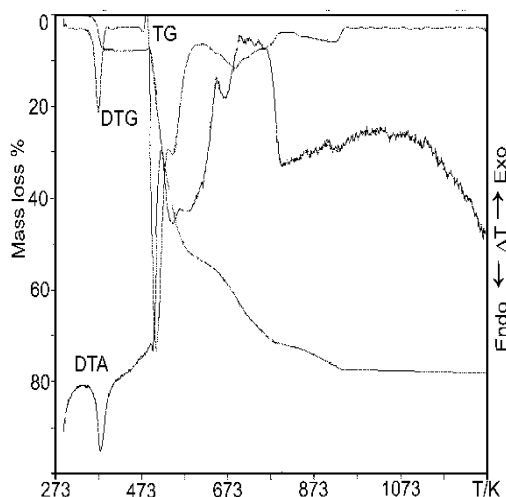


Figure 2. TG, DTG and DTA curves for Cu(II) 4-chlorophenoxyacetate in air.

that one its end was in the region of homogeneous field and the other end was in the region of zero field. The force exerted on the sample was a function of the volume occupied by the sample in the region of the field gradient. This force may be written in scalar form as a function of the isotropic volume susceptibility. Measurements were carried out at a magnetic field strength of 9,9 kOe. The calibrant employed was $\text{Hg}[\text{Co}(\text{SCN})_4]$ for which the magnetic susceptibility was assumed to be

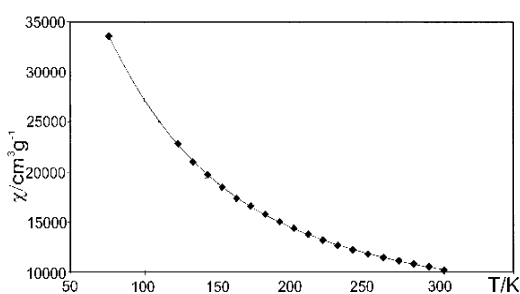


Figure 3. Dependence between magnetic susceptibility values vs temperatures for 4-chlorophenoxyacetate of Co(II).

$1,644 \cdot 10^{-5} \text{cm}^3 \text{g}^{-1}$. Correction for diamagnetism of the calibrant atoms was calculated by the use of Pascal's constants [17, 18]. Magnetic moments were calculated from Eq. (1):

$$\mu_{\text{eff}} = 2,83 (\chi_M \cdot T)^{1/2} \quad (1)$$

The solubilities of 4-chlorophenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) in water were measured at 293K. Saturated solutions of the obtained compounds were prepared under isothermal conditions. The contents of Mn(II), Co(II), Ni(II) and Cu(II) were determined using ASA 880 spectrofotometer (Varian). The values of solubilities are presented in Table 1.

Table 4. Magnetic data for the studied complexes of Mn(II), Co(II), Ni(II) and Cu(II).

MnL ₂ ·2H ₂ O L' = C ₆ H ₆ ClO ₂			CoL ₂ ·4H ₂ O			NiL ₂ ·4H ₂ O			CuL ₂ ·2H ₂ O		
T/K	χ _M ·10 ³	μ _{eff} /μ _B	T/K	χ _M ·10 ³	μ _{eff} /μ _B	T/K	χ _M ·10 ³	μ _{eff} /μ _B	T/K	χ _M ·10 ³	μ _{eff} /μ _B
76	52351	5,64	76	33580	4.52	76	15658	3.09	76	4780	1.71
123	32723	5,68	123	22822	4.74	123	9520	3.06	123	2408	1.54
133	30295	5,68	133	21008	4.73	133	8690	3.04	133	2447	1.61
143	26978	5,56	143	19757	4.76	143	8094	3.04	143	2408	1.66
153	25239	5,56	153	18490	4.76	153	7546	3.04	153	2109	1.61
163	23877	5,58	163	17378	4.76	163	7061	3.04	163	2226	1.70
173	22603	5,60	173	16602	4.80	173	6663	3.04	173	2148	1.73
183	21209	5,58	183	15792	4.81	183	6305	3.04	183	2291	1.83
193	20692	5,66	193	15057	4.82	193	6014	3.05	193	2265	1.87
203	19718	5,66	203	14411	4.84	203	5701	3.04	203	2161	1.87
213	18685	5,65	213	13798	4.85	213	5449	3.05	213	2174	1.93
223	18060	5,68	223	13177	4.85	223	5197	3.05	223	1824	1.81
233	16642	5,57	233	12637	4.86	233	4954	3.04	233	2135	2.00
243	16137	5,60	243	12179	4.87	243	4764	3.05	243	2045	1.99
253	15716	5,64	253	11787	4.89	253	4597	3.05	253	1746	1.88
263	15404	5,70	263	11419	4.90	263	4486	3.07	263	1669	1.87
273	14935	5,71	273	11100	4.93	273	4323	3.07	273	1733	1.95
283	14562	5,75	283	10782	4.94	283	4182	3.08	283	1500	1.84
293	14130	5,76	293	10479	4.96	293	4045	3.08	293	1500	1.88
303	13649	5,76	303	10136	4.96	303	3930	3.09	303	1435	1.87

Results and discussion

The complexes of 4-chlorophenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) were obtained as polycrystalline products with a metal ion to ligand ratio of 1:2 and the general formula $M(C_8H_6ClO_3)_2 \cdot nH_2O$, where M(II)=Mn, Co, Ni, Cu and $n=2$ for Mn(II) and Cu(II) complexes and $n=4$ for Co(II) and Ni(II).

Their colours are following: pinkish for Mn(II), pink for Co(II), green for Ni(II), and blue for Cu(II) complexes. In these compounds the $d \rightarrow d$ electron transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wave lengths that depends on the nature of the metal ion [19, 20].

The compounds were characterized by elemental analysis (Table 1), FTIR and FIR spectra (Table 2).

The 4-chlorophenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) exhibit similar solid state IR spectra. The band at 1708 cm^{-1} originating from the RCOOH group, presented in the acid spectrum, is replaced in the spectra of complexes by two bands at $1608\text{--}1569\text{ cm}^{-1}$ and $1346\text{--}1334\text{ cm}^{-1}$, which can be ascribed to the asymmetric and symmetric vibrations of COO⁻ group, respectively [21-24]. The bands with the maxima at $3494\text{--}3074\text{ cm}^{-1}$ characteristic for ν_{OH} vibrations [21-26] confirm the presence of crystallization water molecules in the complexes. The bands of C-H vibrations are observed at $2989\text{--}2009\text{ cm}^{-1}$. The bands of $\nu(C=C)$ ring vibrations appear at $1651\text{--}1623\text{ cm}^{-1}$, 1493 cm^{-1} , $1174\text{--}1172\text{ cm}^{-1}$, 1094 cm^{-1} and $670\text{--}630\text{ cm}^{-1}$. The valency $\nu(C-Cl)$ vibration bands occur at $740\text{--}720\text{ cm}^{-1}$ and those of the asymmetric and symmetric $\nu(C-O-C)$ at $1260\text{--}1217\text{ cm}^{-1}$ and $1060\text{--}1058\text{ cm}^{-1}$, respectively. The bands at $458\text{--}330\text{ cm}^{-1}$ confirm the ionic metal-oxygen bond [27-36]. In the range of $458\text{--}439\text{ cm}^{-1}$ they increase in the following way: Mn(II) < Co(II) < Ni(II) < Cu(II), which suggests the stronger M-O bond in the case of Cu(II) complex.

The bands in the range of $117\text{--}104\text{ cm}^{-1}$ are connected with the O-H...O stretching vibrations and they change their shapes according to the rise of atomic number of elements and the degree of hydration, in 4-chlorophenoxyacetates. The bands at $137\text{--}135\text{ cm}^{-1}$ confirm the internal C-C torsion vibrations and the bands at $267\text{--}216\text{ cm}^{-1}$

arising from the aromatic ring vibrations also change their shapes.

Table 2 presents the values of the two band frequencies of asymmetrical and symmetrical vibrations for carboxylate group of analyzed complexes. The separations of the $\nu_{as}(OCO^-)$, and $\nu_s(OCO^-)$ modes in the compounds $\Delta\nu(OCO^-)$ are greater or smaller than that of the sodium salt ($\Delta\nu_{OCO^-} = 271\text{ cm}^{-1}$) indicating a various degree of M-O ionic bonds in 4-chlorophenoxyacetates compared to that of the sodium salt. For the complexes the shifts of the frequencies of bands of $\nu_{as}(OCO^-)$, and $\nu_s(OCO^-)$ are lower, lower and higher, respectively, than those for sodium 4-chlorophenoxyacetate. Accordingly, taking into account the spectroscopic criteria [22, 24, 37] the carboxylate ions appear to be monodentate and bidentate groups.

In order to estimate the crystalline forms of the 4-chlorophenoxyacetates the X-ray powder diffraction measurements were done. The diffractogram values suggest them to be polycrystalline compounds with various degree of crystallinity [38] (Fig. 1)

The thermal stability of Mn(II), Co(II), Ni(II), and Cu(II) 4-chlorophenoxyacetates was studied in air at $293\text{--}1173\text{ K}$ (Table 3, Fig. 2). When heated to 1173 K the Mn(II) complex is dehydrated in one step. In the temperature range of $350\text{--}385\text{ K}$ it losses two water molecules in one step and forms anhydrous salt. The loss of mass calculated from TG curve is equal to $8,16\%$ (theoretical value is $7,79\%$). The anhydrous salt at $497\text{--}868\text{ K}$ is gradually decomposed to Mn_3O_4 that is a final product of complex decomposition. The intermediate compounds formed in this range of temperature is Mn_2OCl_2 . The found mass loss is equal to $84,6\%$ and the calculated value $83,48\%$. The residue mass estimated from TG curve is equal to $15,4\%$ while that theoretically calculated $16,52\%$. The dehydration process is connected with endothermic effect whereas the combustion of the organic ligand is accompanied by exothermic one. The final product of complex decomposition was confirmed by IR spectra and X-ray powder diffractogram.

The tetrahydrate of 4-chlorophenoxyacetate of Co (II) during heating in air losses the water molecules in two steps. At first in the range of $371\text{--}406\text{ K}$ it releases two of them and the rest ones are

expelled during the ligand decompositions at 518-910K. The final product of complex decomposition was identified by elemental analysis and X-ray powder diffractogram as Co_3O_4 and the Co and Co_2O_3 were estimated to be the intermediate products of its decomposition. The found weight loss is equal to 85,28 and calculated one 84,0 %. The residue mass estimated from TG curve is 14,71% and theoretically determined 15,98%. The dehydration process is connected with the endoeffect while that of oxidation with exothermic one.

When heated in air to 1173K the tetrahydrate of 4-chlorophenoxyacetate of Ni(II) dehydrates in one step at 347-406K and forms anhydrous complex. The mass loss calculated from TG curve being equal to 14,12% corresponds to the loss of four molecules of water (theoretical value is equal to 14,35%). The anhydrous 4-chlorophenoxyacetate of Ni(II) at 583-833K is decomposed to NiO, which is the final product of thermal decomposition. The mass loss calculates from TG curve is equal to 84,6% that corresponds to the NiO formation (calculated value is 85,1%). The dehydration process is connected with an endothermic effect seen in DTA curve, while the combustion of the organic ligand is accompanied by exothermic one. Considering the temperature at which the dehydration process of the complex takes place, and the way by which it proceeds it is possible to assume that the water molecules may be also in the outer sphere of complex coordination [27, 39-41].

During heating in air to 1173K the Cu (II) complex dehydrates in one step (Fig. 2). In the temperature range of 357-385K it losses two water molecules and forms anhydrous compound. The loss of mass calculated from TG curve is equal to 7,59% (the theoretical value is 7,65%). The anhydrous complex at 490-896K is decomposed to CuO that is a final product of complex decomposition. The intermediate compounds formed in this range of temperature may contain Cu_2OCl , Cu and Cu_2O that being next oxidized to CuO. The residue mass calculated from TG curve is equal to 20,5% while that theoretically calculated 16,00%. This discrepancy probably appears from the rest of Cu_2O in the final mass of complex decomposition, which was indicated by elemental analysis, IR spectra, and X-ray powder diffractogram. The mass loss calculated from TG curve is equal to

79,5% (theoretical value is 84,0%). The dehydration process, in this case, is connected with an endothermic effect seen on DTA curve, while the combustion of the organic ligand is accompanied by exothermic one. Considering the temperature of dehydration process and the way in which it proceeds it is possible to assume that the water molecules may be in the outer coordination sphere of the complex.

The values of enthalpy of dehydration process were determined with the use of DSC/TG system under nitrogen atmosphere. They are in the range of 129-243 kJ/mol and 75,9-32 kJ/mol per one molecule of water. These values indicate that the water molecule is the strongest bounded in the Mn(II) complex while that the weakest in Cu(II) compound. Taking into account the temperatures of dehydration process it appears that Co(II) complex is the most thermally stable while Ni(II) has the least thermal stability.

The solubility of analysed compounds was measured (Table 1). It is in the order of 10^{-3} - 10^{-4} mol·dm³. The Co(II) 4-chlorophenoxyacetate is the most soluble salt, while that of Cu(II) the least soluble one. These compounds are relatively hardly soluble in water and the order value is not sufficient to use 4-chlorophenoxyacetic acid for the separation of some metal ions by ion-exchange chromatography method.

The magnetic susceptibility of 4-chlorophenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) was measured over the range of 76-303K (Table 4, Fig. 3). The values of the Weiss constant, θ , for all complexes were found to have a negative sign which probably arises from the antiferromagnetic spin interaction or from a crystal field splitting of the paramagnetic spin state [42-47].

The magnetic moment values experimentally determined at 76-303K for Mn(II), Co(II), Ni(II) and Cu(II) compounds change from 5,57 μ_B (at 76K) to 5,72 μ_B (at 303K) for Mn(II) complex, from 4,52 μ_B (at 76K) to 4,96 μ_B (at 303K) for Co(II), from 3,09 μ_B (at 76K) to 3,08 μ_B (at 293K) for Ni(II) and from 1,71 μ_B (at 76K) to 1,87 μ_B (at 303K) for Cu(II) 4-chlorophenoxyacetates.

The magnetic moment data are very close to the spin only values for the respective ions calculated from the equation $\nu_{\text{eff}} = [4s(s+1)]^{1/2}$ in the absence of the magnetic interactions for present

spin-system. The magnetic moment values calculated at room temperature for Mn(II), Co(II), Ni(II) and Cu(II) ions are equal to $5,9 \mu_B$, $3,88 \mu_B$, $2,83 \mu_B$, and $1,73 \mu_B$, respectively. For Mn(II), Co(II), Ni(II) and Cu(II) ions the magnetic moment values may be different than the spin-only. In the cases of Co(II) and Cu(II) compounds they are higher than the spin-only worth which results from a spin-orbital coupling. For Ni(II) and Mn(II) ions the magnetic moment are lower than the spin-only value. 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 Mn(II) and Ni(II) seem high-spin complexes with octahedral symmetry and probably weak ligand fields [42-47].

From the obtained results it appears that in 4-chlorophenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) the coordination numbers may be equal to 5 and 6 depending on the dentates of carboxylate group and the position of water molecules in the complex. The coordination numbers of Mn(II), Co(II), Ni(II) and Cu(II) ions could be established on the basis of the complete crystal structure determination of monocrystals but they have not been obtained.

Conclusions

On the basis of the results it appears that 4-chlorophenoxyacetates of Mn (II), Co(II), Ni(II), and Cu (II) were synthesized as hydrated complexes.

Their colours are following: pinkish for Mn (II), pink for Co (II), green for Ni (II), and blue for Cu(II) compounds. The complexes are crystalline compounds and on heating in air to 1173K they decompose in two steps: at first they dehydrate to form anhydrous compounds that next are decomposed to the oxides of respective metals. The values of μ_B calculated for analysed complexes in the range of 76-303K reveal that the Mn(II), Co(II) and Ni(II) complexes are high-spins and that of Cu(II) forms monomer.

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