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THE PHYSICO-CHEMICAL PROPERTIES OF 2-METHOXYPHENOXYACETATES OF MN(II), CO(II), NI(II) AND CU(II)

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Abstract: The complexes of 2-methoxyhenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II)with the general formula: $M(C_9H_9O_4)_3 \cdot 4H_2O$, where M(II) = Mn, Co, Ni and Cu have been synthesized and characterized by elemental analysis, IR spectroscopy, magnetic and thermogravimetric studies and also X-ray diffraction measurements. The complexes have colours typical for M(II) ions (Mn(II) - a pale pink, Co(II) - pink, Ni(II) - green, and Cu(II) – blue). The carboxylate group binds as monodentate and bidentate ligands. On heating to 1273K in air the complexes decompose in the same way. At first, they dehydrate in one step to anhydrous salts, that next decompose to the oxides of respective metals with the intermediate formation of the oxycarbonates. Their solubility in water at 293K is of the order of 10^{-5} mol·dm^{-3}. The magnetic moments of analysed complexes were determined in the range of 76-303K. The results reveal them to be high-spin complexes of weak ligand fields.

Keywords: 2-methoxyphenoxyacetates, thermal stability, magnetic properties of Mn(II), Co(II), Ni(II), Cu(II).

Introduction

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 [1-3]. 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 precursors in superconducting ceramic and magnetic field productions.

These kind of compounds are often used as catalysts, pigments, solvents, food preservatives and plastics productions.

From the survey of literature it follows that metal carboxylates may be applied for the productions of high degree purity of metal oxides and polycarboxylic acids are often used for supramolecular compound synthesis, which in many cases, form with metal ions the molecular polymers containing in their structures, pores and channels owning 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 – dimentional structures, yielding special magnetic and luminescence properties which let them be used in optical and electronic industries [1,4,5].

2-Methoxyphenoxyacetic acid is a grey-white solid hardly soluble in water. A literature survey indicates that its compounds with various cations have been relatively seldom studied. The complex of Cu(II) with 2-methoxyphenoxyacetic acid was synthesized and its structure determined [6].

As a continuation of our studies on carboxylates we decided to synthesize 2-methoxyphenoxyacetates 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 77-303K thermal stability in air at 293-1273K, solubility in water at 293K and to record their FTIR spectra.

Thermal stability investigations give informations about the dehydratation process 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

The 2-methoxyphenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) were prepared by the addition of the equivalent quantities of 0,1 mol·dm^{-3} ammonium 2-metoxyphenoxyacetate (pH ≈ 5) to a hot solutions containing the 0,1 mol·dm^{-3} Mn(II), Co(II), Ni(II) and Cu(II) chlorides and crystallizing at 293K. 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 determined by elemental analysis using a CHN 2500 Perkin-Elmer analyzer. The contents of M^{2+} metals were established by XRF method using spectrometer of X-ray fluorescence with energy dispersion EDXRF-1510 (CANBERRA firm).

Table 1. Elemental analysis data of Mn(II), Co(II), Ni(II) and Cu(II) 2-methoxyphenoxyacetates and their solubility in water at 293K

Complex $L^- = C_9H_9O_4$	H/%		C/%		M/%		Solubility
	calcd	found	calcd	found	calcd	found	mol/dm^3
$MnL_2·4H_2O$	5.32	5.14	44.18	44.11	11.23	11.20	2,61 ·10^{-5}
$CoL_2·4H_2O$	5.27	5.11	43.82	43.76	12.76	12.70	9,28 ·10^{-5}
$NiL_2·4H_2O$	5.28	5.04	43.84	43.04	11.90	11.70	1,50 ·10^{-5}
$CuL_2·4H_2O$	5.23	5.27	43.42	43.58	12.76	12.70	5,11 ·10^{-5}

The FTIR and FIR spectra of complexes were recorded over the ranges of 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 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 in 2-methoxyphenoxyacetic acid

Complex $L^-=C_9H_9O_4$	$\nu_{C=O}$	$\nu_{as\ OCO}$	$\nu_{sym\ OCO}$	$\Delta\nu_{OCO}$	$\nu_{M\text{-}O}$
$MnL_2 \cdot 4H_2O$	-	1654	1425	229	465
$CoL_2 \cdot 4H_2O$	-	1619	1412	207	470
$NiL_2 \cdot 4H_2O$	-	1603	1414	189	472
$CuL_2 \cdot 4H_2O$	-	1597	1427	170	465
HL	1742	-	-	-	-
NaL	-	1615	1427	188	454

The X-ray diffraction patterns of hydrated, intermediate and final products of complex thermal decompositions were taken on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered Cu Kα radiation. The measurements were made within the range 2Θ = 4-80^o by means of the Bragg - Brentano method. The relationships between I/I_o and 2Θ for these complexes are presented in Fig.1.

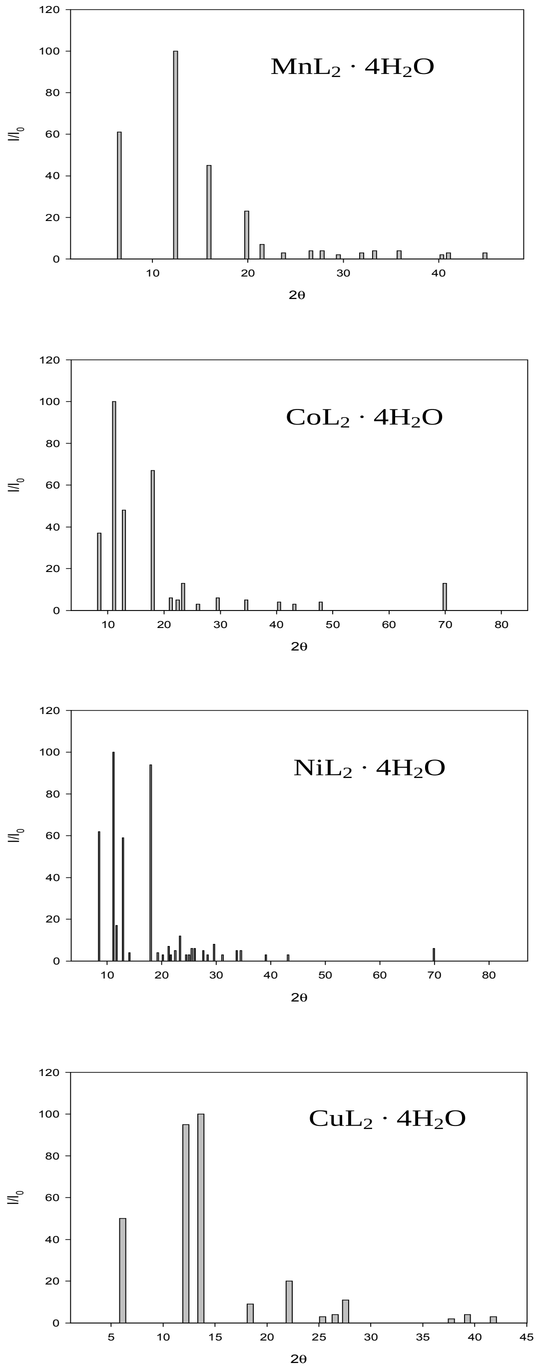

Fig.1. Dependence of I/I_0 vs 2θ for Mn(II), Co(II), Ni(II) and Cu(II) complexes

The thermal stability and decomposition of the analysed complexes were determined by Paulik-Paulik-Erday Q-1500D derivatograph with Derill converter, recording TG, DTG, and DTA curvers (Fig.2). The measurements were made at a heating rate of 10 $K\cdot min^{-1}$ with a full scale. The samples (100mg) were heated in platinum crucibles in static air to 1273K 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 $K\cdot min^{-1}$.

Table 3. Temperature ranges of thermal stability of Mn(II), Co(II), Ni(II) and Cu(II) 2-methoxyphenoxyacetates in air

Complex $L^- = C_9H_9O_4$	ΔT_1 / K	Mass loss / %		n H_2O	ΔH / kJ·mol^{-1}	ΔH_{1H_2O} / kJ·mol^{-1}	Residue
		calcd.	found				
$MnL_2 \cdot 4H_2O$	348-443	14,73	14,69	4	128,91	32,2	MnO
$CoL_2 \cdot 4H_2O$	353-433	14,61	14,70	4	113,76	28,4	CoO
$NiL_2 \cdot 4H_2O$	323-433	14,61	14,54	4	128,48	32,1	NiO
$CuL_2 \cdot 4H_2O$	318-393	14,47	14,48	4	117,47	29,4	CuO

ΔT_1 – temperature range of dehydration 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,

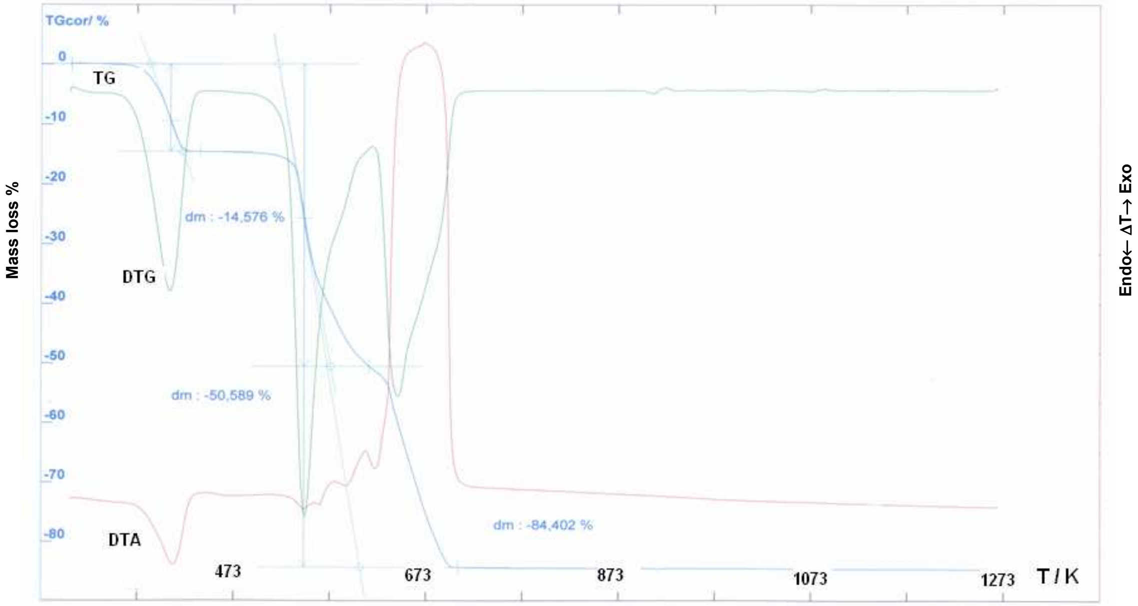

Fig.2. TG, DTG and DTA curves for Co(II) 2-methoxyphenoxyacetate

Magnetic susceptibilities of polycrystalline samples of 2-methoxyphenoxyacetates 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 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 $Hg[Co(SCN)_4]$ for which the magnetic susceptibility was assumed to be $1{,}644 \cdot 10^{-5} cm^3 g^{-1}$.

Correction for diamagnetism of the calibrant atoms was calculated by the use of Pascal's constants [8,9]. Magnetic moments were calculated from Eq.(1):

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

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

$MnL_2 \cdot 4H_2O$ $L^- = C_9H_9O_4$			$CoL_2 \cdot 4H_2O$			$NiL_2 \cdot 4H_2O$			$CuL_2 \cdot 4H_2O$		
T/K	$\chi_M \cdot 10^6$	μ_{eff}/μ_B	T/K	$\chi_M \cdot 10^6$	μ_{eff}/μ_B	T/K	$\chi_M \cdot 10^6$	μ_{eff}/μ_B	T/K	$\chi_M \cdot 10^6$	μ_{eff}/μ_B
76	60395	6.06	76	31831	4.40	76	16750	3.19	76	5747	1.87
123	38190	6.13	123	21090	4.56	123	10150	3.16	123	3483	1.85
133	34155	6.03	133	19687	4.58	133	9434	3.17	133	3317	1.88
143	31641	6.02	143	18628	4.62	143	8986	3.21	143	3059	1.87
153	29635	6.03	153	17653	4.65	153	8461	3.22	153	2875	1.88
163	27849	6.03	163	16344	4.62	163	7937	3.22	163	2709	1.88
173	26371	6.04	173	15511	4.64	173	7489	3.22	173	2581	1.89
183	24982	6.05	183	14774	4.65	183	7093	3.22	183	2433	1.89
193	23880	6.08	193	14108	4.67	193	6747	3.23	193	2341	1.90
203	22777	6.09	203	13454	4.68	203	6440	3.24	203	2212	1.90
213	21796	6.10	213	12871	4.69	213	6108	3.23	213	2139	1.91
223	20749	6.09	223	12216	4.67	223	5788	3.22	223	1991	1.89
233	19889	6.09	233	11717	4.68	233	5532	3.21	233	1936	1.90
243	19183	6.11	243	11348	4.70	243	5340	3.22	243	1863	1.90
253	18522	6.13	253	10967	4.71	253	5148	3.23	253	1826	1.92
263	17904	6.14	263	10634	4.73	263	4982	3.24	263	1789	1.94
273	17639	6.15	273	10599	4.77	273	4918	3.25	273	1734	1.99
283	16934	6.20	283	10230	4.77	283	4803	3.27	283	1697	1.94
293	16449	6.21	293	9921	4.78	293	4649	3.27	293	1660	1.96
303	15986	6.23	303	9516	4.81	303	4419	3.27	303	1586	1.96

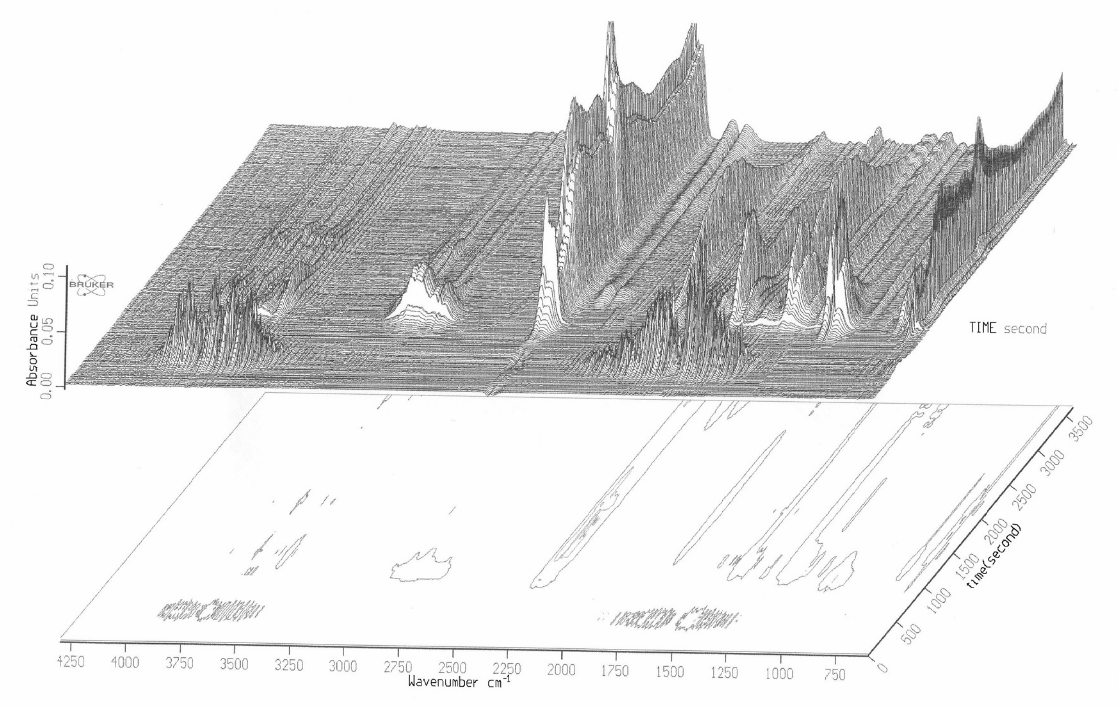

Fig.3. FTIR spectrum of gaseous products of thermal decomposition of Mn(II) 2-methoxyphenoxyacetate

The solubilities of 2-methoxyphenoxyacetates 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 spectrophotometer (Varian). The values of solubilities are presented in Table1.

Results and Discussion

2-Methoxyphenoxyacetates 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 $M(C_9H_9O_4)_3\cdot 4H_2O$, where M(II) = Mn, Co, Ni and Cu. The colours of these complexes are typical for M(II) ions: pinkish for Mn(II), pink for Co(II), green for Ni(II), and blue for Cu(II). In these compounds the d→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 [9,10].

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

The 2-methoxyphenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) exhibit similar solid state IR spectra. The band at 1742 cm^{-1} originating from the -COOH group, seen in the acid spectrum, is replaced in the spectra of complexes by two bands at 1619-1581 cm^{-1} and 1355-1341cm^{-1}, resulting from the asymmetric and symmetric vibrations of COO^- group, respectively [11-14]. The bands with the maxima at 3565-3208cm^{-1}, 1599-1505cm^{-1} and 971-908cm^{-1} confirm the presence of crystallization water molecules in the analyzed complexes. The bands of ν(C=C) ring vibrations appear at 1654-1597cm^{-1}, 1493cm^{-1}, 1290-1010cm^{-1} and 670-620cm^{-1}. The bands attributed to asymmetric and symmetric C-H stretching modes of the CH_3 groups are observed at 2969-2928cm^{-1} and 2924-2901cm^{-1}, respectively. The bands of asymmetric and symmetric valency vibrations occur at 1260-1217 and 1060-1058cm^{-1}, respectively. The bands at 472-465cm^{-1} confirm the ionic metal-oxygen bond [15-21]. In the range of 472-465cm^{-1} they increase in the following way: Mn(II) = Cu(II) < Co(II) < Ni(II), which suggests the strongest M-O bond in the case of Ni(II) complex.

The bands in the range of 336-276cm^{-1} are connected with the O-H…O streching vibrations and they change their shapes according to the rise of atomic number of elements in 2-methoxyphenoxyacetates.

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 ν_{asCOO}^{-}, and ν_{sCOO}^{-} modes in the compounds $\Delta\nu(COO^{-})$ are greater or smaller than those of the sodium salt ($\Delta\nu_{COO}^{-}$ = 188cm^{-1}) indicating a various degree of M-O ionic bonds in 2-methoxyphenoxyacetates compared to that of the sodium salt. For the complexes the shifts of the frequencies of bands of $\nu_{as}(COO^{-})$, and $\nu_{s}(COO^{-})$ are lower and higher, respectively, than those for sodium 2-methoxyphenoxyacetate. Accordingly, taking into account the spectroscopic criteria [12,14,22] the carboxylate ions appear to be monodentate (Co(II), Ni(II) and Mn(II)) or bidentate (Cu(II) complex) groups.

In order to estimate the crystalline forms of the 2-methoxyphenoxyacetates the X-ray powder diffraction measurements were done. The diffractogram values suggest them to be polycrystalline compounds with various degree of crystallinity (Fig.1) [23].

The thermal stability of Mn(II), Co(II), Ni(II), and Cu(II) 2-methoxyphenoxyacetates was studied in air at 293-1273 K (Table 3. Fig.2). When heated to 1273 K the Mn(II) complex is dehydrated in one step. In the temperature range of 348 – 443 K it losses two water molecules in one step and forms anhydrous salt. The loss of mass calculated from TG curve is equal to 14,69% (theoretical value is 14,73%). The anhydrous salt at 603–703 K is gradually decomposed to MnO that is the final product of complex decomposition. The intermediate compound formed in this range of temperature is oxycarbonate of manganium. 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 2-methoxyphenoxyacetate of Co(II) during heating in air losses the water molecules in one step at 353 – 433 K and forms the anhydrous complex. The loss of mass calculated from TG curve is equal to 14,70% and calculated one 14,61%. During heating the anhydrous salt 1183-1223 K is decomposed to CoO with the intermediate formation of oxycarbonate of cobalt. The final product of complex decomposition was identified by X-ray powder diffractogram as CoO. The dehydration process is accompanied with the endoeffect while that of oxidation by exothermic one (Fig.2).

When heated in air to 1273 K the tetrahydrate of Ni(II) 2-methoxyphenoxyacetate dehydrates in one step at 323 – 433K and forms anhydrous complex. The found mass loss being equal to 14,54% corresponds to the loss of four molecules of water (theoretical value is equal to 14,61%). The anhydrous 2-methoxyphenoxyacetate of Ni(II) at 633-713 K is decomposed to NiO, which is the final product of thermal decomposition. The dehydration process is connected with an endothermic effect seen in DTA curve, while the combustion of the organic ligand is connected with exothermic one.

During heating to 1273 K the Cu (II) complex dehydrates in one step. In the temperature range of 318 – 393 K it losses four molecules of water and forms anhydrous salt. The loss of mass calculated from TG curve is equal to 14,48% (the theoretical value is 14,47%). The anhydrous complex at 598-768 K is decomposed to CuO that is a final product of complex decomposition. The intermediate compounds formed in this range of temperature may contain oxycarbonate of Cu, Cu and Cu_2O that being next oxidized to CuO. The final product of complex decomposition was identified by X-ray powder diffractogram. 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 by which it proceeds it is possible to assume that the water molecules may be in the outer coordination sphere of the complex [24,25].

Taking into account the temperature values of the initial dehydration process it appears that Co(II) complex is the most thermally stable while Cu(II) compound has the least thermal stability because it starts to release water molecule at 318K.

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 128,9 – 113,7 kJ·mol^{-1} and 32,2 – 28,4 kJ·mol^{-1} 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 Co(II) compound.

The decomposition process with the gas product analysis was recorded for 2-methoxyphenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II). For example the FTIR spectrum of gaseous products of decomposition process of Mn(II) 2-methoxyphenoxyacetate is presented in Fig.3. FTIR spectra of the gas phase products indicate that the decomposition of complexes is connected with the release of CO_2, CO, H_2O, alcohols and hydrocarbons. The characteristic valence and deformation vibration bands of water molecules in FTIR spectra appear in the wavenumber ranges of 4000-3500cm^{-1} and 2000cm^{-1}. The bands characterictic for CO_2 molecule vibrations occur in the following ranges: 2700 – 2500 cm^{-1} and 1000 cm^{-1}. The bands of hydrocarbon vibrations are observed at 2250 cm^{-1-} and the band characteristic for CO molecule vibrations appears at 2060 cm^{-1}. The bands typical for alcohol molecule vibrations are observed at 4000 – 3500 cm^{-1} and 1700-1500 cm^{-1} [26-28].

The solubility of analyzed compounds was measured (Table 1). It is in the order of 10^{-5} mol·dm^{-3}. The Co(II) 2-methoxyphenoxyacetate is the most soluble salt, while that of Ni(II) the least soluble one. The compounds are hardly soluble in water and the order value is not sufficient to use 2-methoxyphenoxyacetic acid for the separation of some metal ions by ion-exchange chromatography method.

The magnetic susceptibility of 2-methoxyphenoxyacetates of Mn(II), Co(II), Ni(II) and Cu(II) was measured in the temperature range of 77-303K (Table 4. Fig.4).

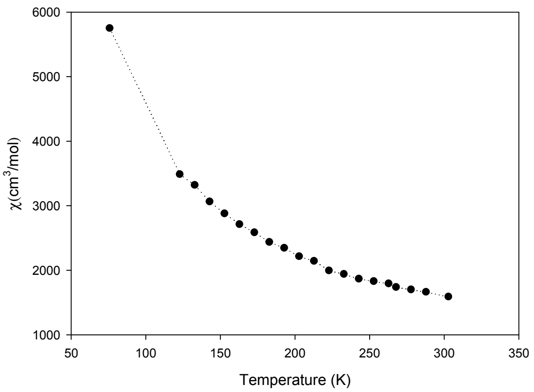

Fig.4. Dependence between magnetic susceptibility values vs temperatures for 2-methoxyphenoxyacetate of Cu(II)

The values of the Weiss constant, Θ, for all complexes were found to have a negative sign which probably arises from antiferromagnetic spin interaction or from a crystal field splitting of the paramagnetic spin state [29-34].

The magnetic moment values experimentally determined at 76-303K for Mn(II), Co(II), Ni(II) and Cu(II) compounds change from 6,06 μ_B (at 76K) to 6,23 μ_B (at 303K) for Mn(II) complex, from 4,40 μ_B (at 76K) to 4.81 μ_B (at 303K) for Co(II), from 3,19 μ_B (at 76K) to 3.27 μ_B (at 303K) for Ni(II) and from 1.87 μ_B (at 76K) to 1,96 μ_B (at 303K) for Cu(II) 2-methoxyphenoxyacetates.

The magnetic moment data are very close to the spin only values for the respective ions calculated from the 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 Mn(II), Co(II), Ni(II) and Cu(II) ions are equal to 5,9 μ_B, 3,88 μ_B, 2,83$\mu_{B,}$ and 1,73μ_B, respectively. For Mn(II), Co(II), Ni(II) and Cu(II) ions the magnetic moment values may be different than the spin-only. These values are higher than the spin-only worth which results from a spin-orbital coupling. The experimental data suggest that these compounds are high-spin complexes with weak ligand field [29-34].

From the obtained results it appears that in 2-methoxyphenoxyacetates 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 so far.

Conclusions

On the basis of the results it appears that 2-methoxyphenoxyacetates of Mn(II), Co(II), Ni(II), and Cu(II) were synthesized as tetrahydrates. Their colours are typical for M(II) ions. The complexes are crystalline compounds and on heating in air to 1273K 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 compounds reveal Mn(II), Co(II) and Ni(II) complexes to be high-spin and that of Cu(II) to be monomer.

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