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THERMAL AND SPECTRAL CHARACTERIZATION OF 5-CHLORO-2-METHOXYBENZOATES OF Mn(II), Co(II), Ni(II), Cu(II) AND Zn(II)

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Abstract

The thermal stabilities of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were studied in air and nitrogen atmospheres. The complexes were obtained as mono-, di-, tetra- and pentahydrates with a metal to ligand ratio of 1:2 and with colours typical for M^{2+} ions (Mn-slightly pink, Co-pink, Ni-green, Cu-blue and Zn-white) and as polycrystalline compounds. When heated they dehydrate to form anhydrous salts which next are decomposed to the oxides of the respective metals in air while in nitrogen to the mixtures of metal oxides and oxychlorides and carbon. The most thermally stable in air, nitrogen and argon atmospheres is 5-chloro-2-methoxybenzoate of Cu(II) while the least thermally stable is that of Co(II).

Keywords: complexes of d-electron elements, thermal investigations, thermal stability of complexes, thermal stability of compounds in air and nitrogen atmospheres

Introduction

A literature survey indicates that the compounds of 5-chloro-2-methoxybenzoic acid with various cations have been relatively seldom studied. There is no information on its salts obtained as solids. The literature informs mainly about the derivatives of chloro- and dichlorobenzoic acids and about some of their salts [1–3] including also the papers on 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and rare earth elements [4–6]. The complexes have been obtained as solids and some of their properties investigated. The thorough thermal stability of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) has not been studied so far. Therefore we decided to synthesize them as solids and to examine their thermal stability in air and nitrogen atmospheres during heating to 1273 K (air) and to 1173 K

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(nitrogen) and to compare their crystalline forms at 293 and 403 K and to study their IR spectra at above temperatures.

Experimental

The 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by the addition of equivalent quantities of 0.1 M ammonium 5-chloro-2-methoxybenzoate (pH~5) to a hot solution containing the nitrates of those elements and crystallizing at 293 K. The solids were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303 K to a constant mass.

The contents of carbon and hydrogen in complexes were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser and the content of chlorine by Schöniger method. The contents of M^{2+} metals were established by ASA method [6].

The IR and FIR spectra of hydrated complexes were recorded over the ranges 4000–400 and 600–100 cm^{-1}, respectively using M-80 and Perkin Elmer 180 spectrophotometers. The IR spectra of anhydrous complexes were also recorded over the range 4000–400 cm^{-1}. Samples for IR spectra measurements were prepared as KBr discs. FIR spectra were obtained in Nujol mulls sandwiched between poly(ethylene) plates (Figs 1 and 2).

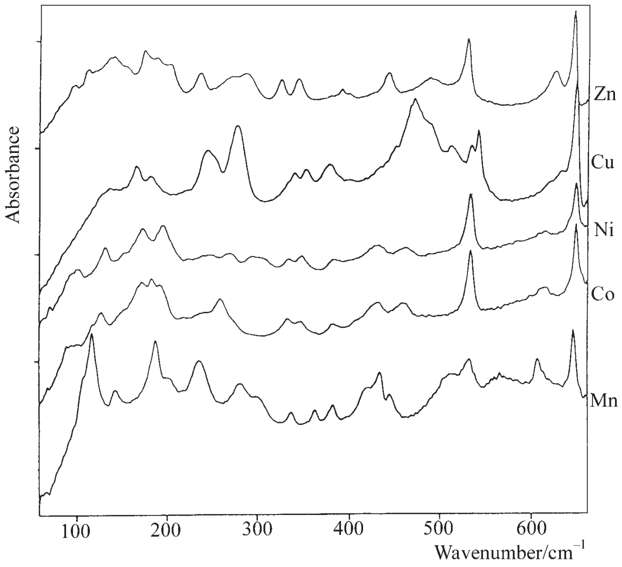

Fig. 1 Far-infrared spectra of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)

The X-ray diffraction patterns of the hydrated and dehydrated complexes were taken on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered CuK_{α} radiation. The X-ray diffraction patterns of the complexes dried at 403 and 973 K were made on

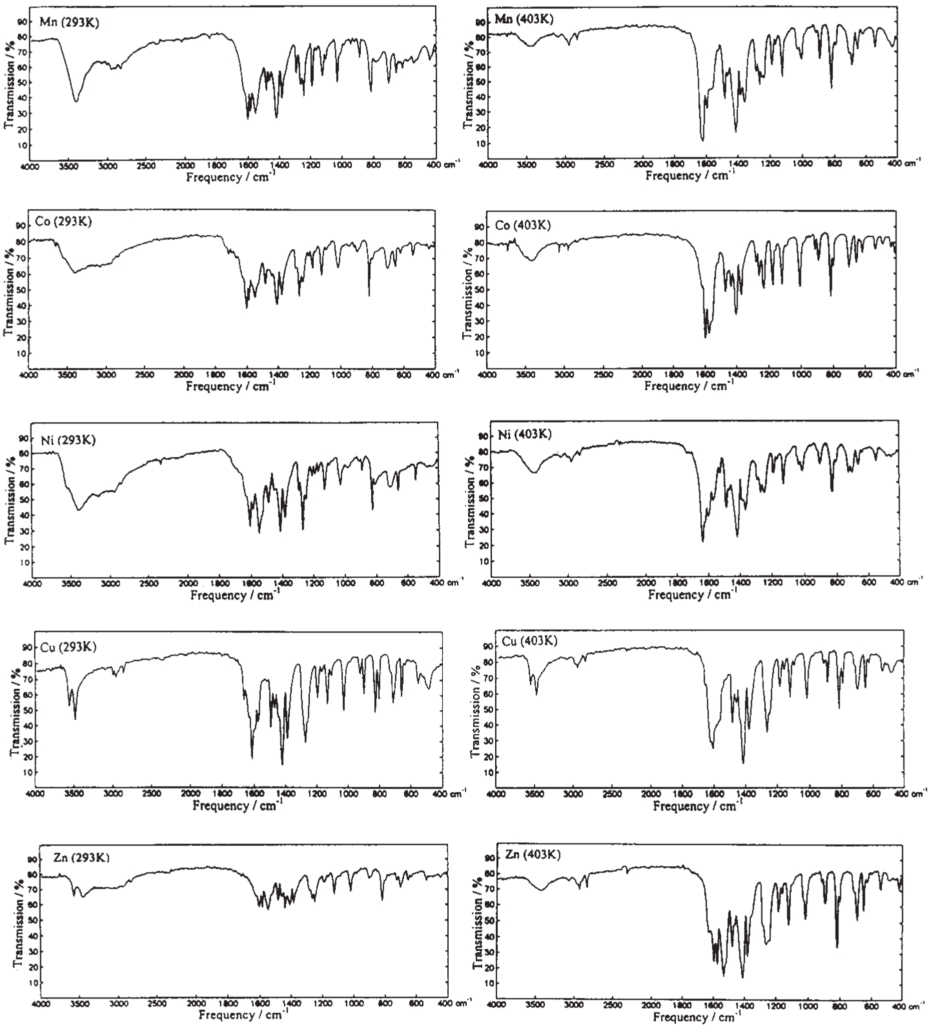

Fig. 2 Infrared spectra of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) at 293 and 403 K

a PW 1050 Philips diffractometer using Ni filtered CuK$_{\alpha}$ radiation. The measurements were made within the range 2Θ=4–80° and 2Θ=5–70° by means of the Debye–Scherrer–Hull method (Fig. 3).

The thermal stability and decomposition of the prepared complexes were determined by Paulik–Paulik–Erdey Q-1500D derivatograph with Derill converter, recording TG, DTG and DTA curves. The measurements were made at a heating rate of 10 K min^{-1} with a full scale. The samples were heated in platinum crucibles in static air to 1273 K with a sensitivity TG-100 mg. DTG and DTA sensitivities were regu-

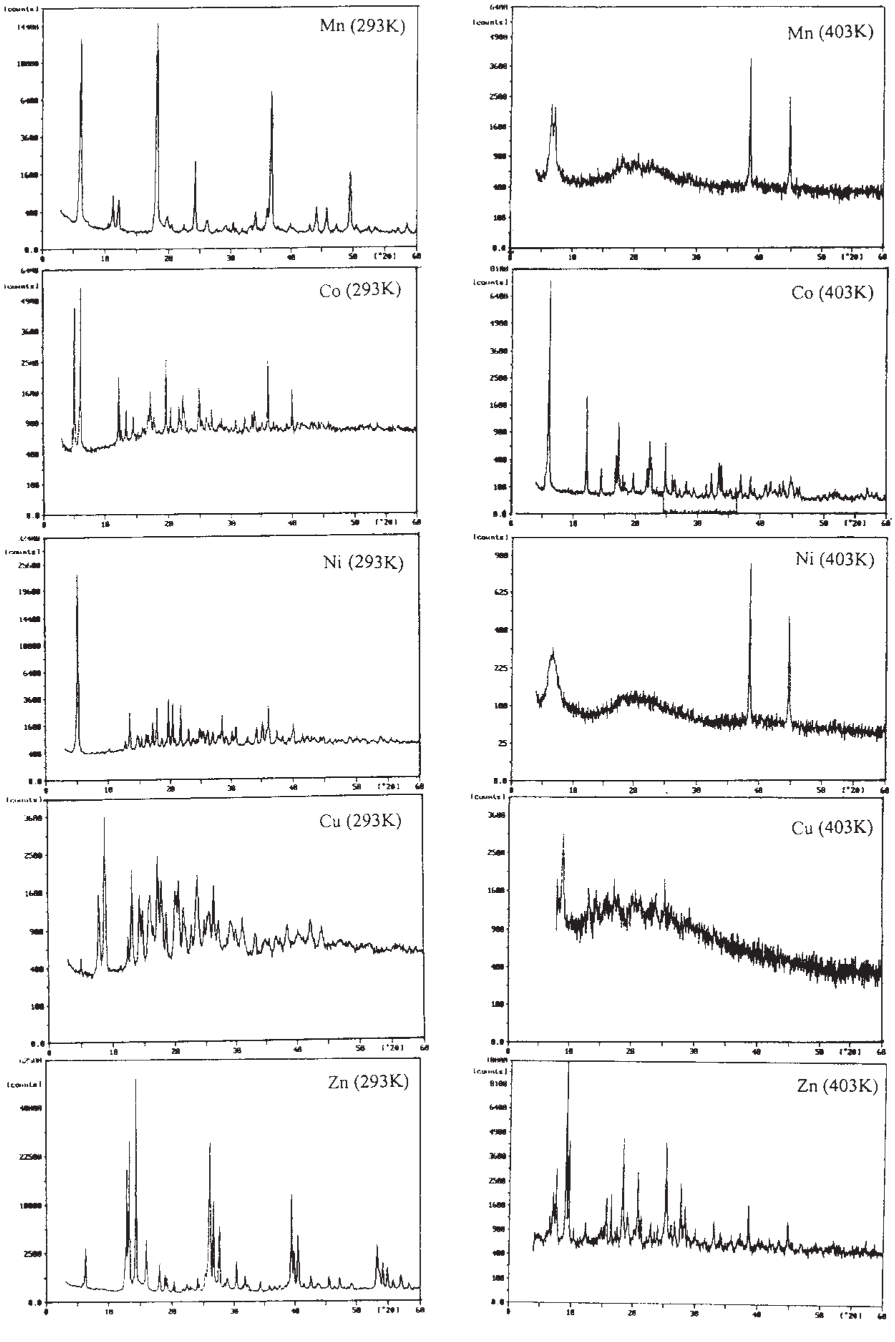

Fig. 3 Diffractograms of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) at 293 and 403 K

Table 1 Temperature range of thermal stability of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in air and nitrogen atmospheres and the values of enthalpy for dehydration process

Complex	ΔT_1/K	Mass loss/%		n	Air	ΔH/ kJ mol^{-1}	ΔT_2/K	Ln_2O_3/%		T_k/K	Residue/%
		calcd.	found					calcd.	found		
$MnL_2 \cdot 4H_2O$	353–398	14.46	14.07	4	A	246.48	533–1273	15.32	15.18	1273	
	333–393		13.70		N		533–1153				6.45
$CoL_2 \cdot 5H_2O$	338–383	17.30	17.16	5	A	220.97	543–913	15.39	15.41	892	
	333–373		17.56		N		533–928				54.05
$NiL_2 \cdot 5H_2O$	348–398	17.32	17.16	5	A	262.96	568–868	14.37	13.99	868	
	343–393		17.03		N		553–873				62.22
$CuL_2 \cdot H_2O$	403–433	3.98	3.96	1	A	74.67	483–983	15.86	12.64	963	
	393–428		4.13		N		473–973				57.93
$ZnL_2 \cdot 2H_2O$	343–378	7.62	7.26	2	A	175.26	483–913	17.23	12.92	892	
	353–383		7.82		N		493–883				52.63

L – $C_8H_6O_3Cl$; ΔT_1 – temperature range of dehydration process; n – number of crystallization water molecules being lost in one endothermic step; ΔH – enthalpy for dehydration process; ΔT_2 – temperature range of the anhydrous complex decomposition; T_k – temperature of the oxide formation

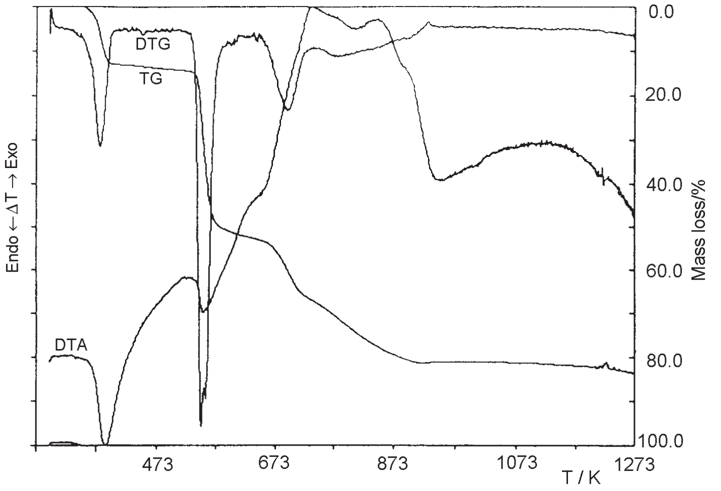

Fig. 4 TG, DTG and DTA curves of 5-chloro-2-methoxybenzoate of Mn(II) in air

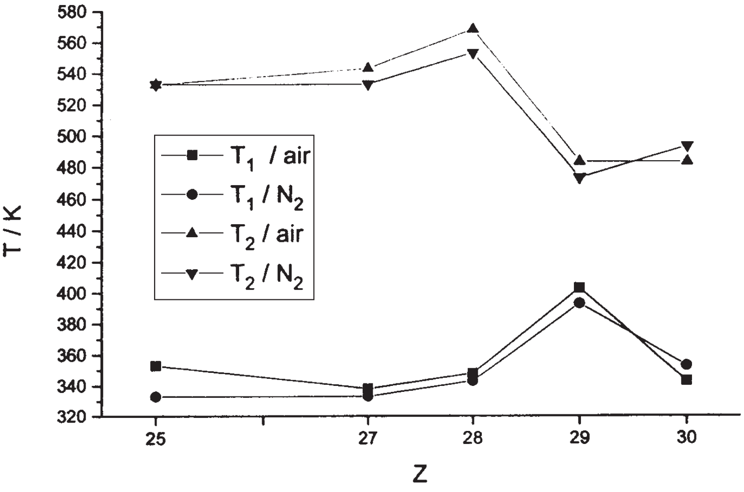

Fig. 5 Relationships between the temperatures of initial dehydration (T_1) and decomposition of anhydrous complex (T_2) and Z

lated by a Derill computer programme. The initial mass of samples used in measurements were equal to 100 mg. The products of decomposition were calculated from TG curves and verified by the diffraction pattern registration. The obtained results are presented in Figs 4 and 5.

The measurements in nitrogen were made on an OD-102 derivatograph at a heating rate of 10°C min^{-1}. The samples were heated at the following sensitivities: TG – 200–100 mg, DTA – 1/10, DTG – 1/5. The initial mass of samples used for measurements are the following: 0.145 g for complex of Cu(II); 0.152 g for that of

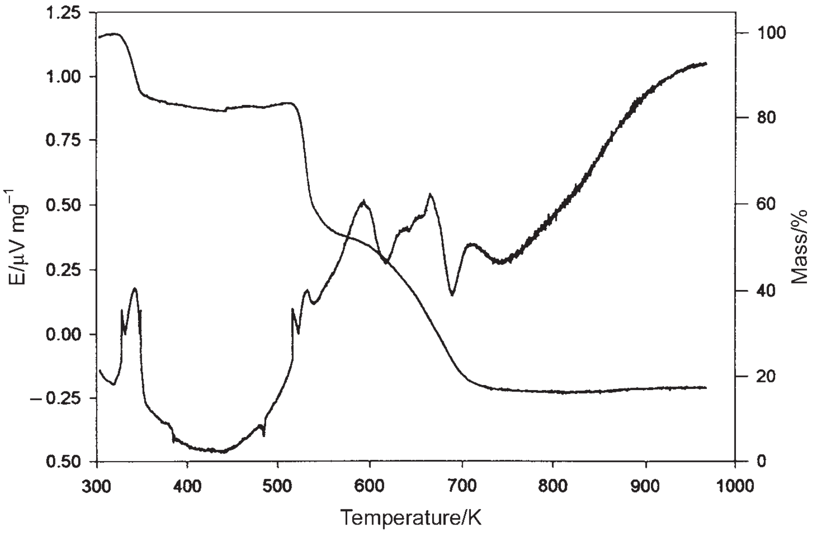

Fig. 6 TG and DSC curves of 5-chloro-2-methoxybenzoate of Mn(II)

Zn(II); 0.148 g for Co(II) complex, 0.124 g for that of Mn(II) and 0.135 g for complex of Ni(II). The nitrogen flowed through gas washers filled with pyrogallol and silica gel at a rate of 115 cm^3 min^{-1}. The results are presented in Table 1. The nature of the solid products of decomposition was established from TG curves and confirmed by IR and X-ray spectra.

The thermogravimetric analysis of DSC/TG was performed at temperatures 293–973 K using a differential thermoanalyser Netzsch STA 409C 3F at a heating rate of 1 K min^{-1}. The experiments were carried out under argon flow at a rate of 75 ml min^{-1} (Fig. 6).

The initial mass of samples of 5-chloro-2-methoxybenzoates of Cu(II), Zn(II), Co(II), Mn(II) and Ni(II) used for measurements are following: Cu(II) – 3.8 mg; Zn(II) – 5.1 mg; Co(II) – 3.5 mg; Mn(II) – 2.9 mg; Ni(II) – 3.3 mg. The samples were heated in platinum crucibles without cover. The DSC curves were used for determination of the temperature of the begining of the dehydration and of the beginning of the decomposition of anhydrous complexes.

Results and discussion

The complexes of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were obtained as crystalline products with a metal to ligand ratio of 1:2 and a general formula $M(C_8H_6ClO_3)_2{\cdot}nH_2O$, where M=Mn, Co, Ni, Cu, Zn and n=4 for Mn(II), n=5 for Co(II), Ni(II), n=1 for Cu(II) and n=2 for Zn(II). The colour of the complexes is typical of the particular divalent ion salts, i.e., is slightly pink in the case of Mn(II), pink for Co(II), green for Ni(II), blue for Cu(II) and white for Zn(II) and originates from d$\rightarrow$d electronic transitions of the central ions [7, 8].

The complexes were characterized by IR and FIR spectra (Figs 1, 2). 5-Chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) exhibit in solid state similar IR spectra. As anticipated, the characteristic wavenumbers corresponding to the carbonyl group are altered markedly when going from the acid to the complex. The band at 1728 cm^{-1} originating from COOH group, present in the IR spectrum of the acid, is replaced in the spectra of the complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) by two bands at 1608–1544 and 1424–1408 cm^{-1}, which can be ascribed to the asymmetric and symmetric vibrational modes of the $\mathrm{COO^-}$ group, respectively. The bands with the maxima at 3495–3400 cm^{-1} characteristic for ν(OH) vibrations [9, 10] and the narrow band of $\delta(\mathrm{H_2O})$ at 1608–1605 cm^{-1} confirm the presence of crystallization water molecules in the complexes. The bands attributed to asymmetric and symmetric C–H stretching modes of $\mathrm{CH_3}$ group are observed at 2980 and 2860–2840 cm^{-1}, respectively. The bands of $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ ring vibrations appear at 1590, 1390–1385, 1195–1130 and at 1040–1025 cm^{-1}. The valency ν(C–Cl) vibration bands occur at 710–700 cm^{-1}. The bands corresponding to the metal–oxygen stretching appear at 473–434 cm^{-1} for the whole series of the complexes [6, 11–21]. The values of these frequency bands stay the same for the 5-chloro-2-methoxybenzoates of Mn(II), Co(II) and Ni(II) but they are higher for those of the complexes of Cu(II) and Zn(II). The bands in the range 129–119 cm^{-1} are connected with the O–H$\cdots$O stretching vibrations and they change their shapes according to the rise of atomic number of elements and the degree of hydration in 5-chloro-2-methoxybenxoates. The bands at 137–135 cm^{-1} confirm the internal C–C torsion vibrations and the bands at 231–225 cm^{-1} arising from the aromatic ring vibrations also change their shapes. The bands of $\delta(\mathrm{H_2O})$ vibrations appear at 530 cm^{-1} and they change their shapes in the spectra of complexes depending on the numbers of molecules of crystallization water. The IR spectra of 5-chloro-2-methoxybenzoates of d-electron elements dried at 403 K were recorded. They contain bands of relatively strong intensities but the changes of their numbers and positions compared to those in the spectra recorded for hydrated complexes were not observed. Only in the case of the complexes of Mn(II), Co(II) and Ni(II) the bands of asymmetrical vibrations of $\mathrm{OCO^-}$ bond clearly disappear. Similarly the bands characteristic for asymmetrical aromatic ring vibrations at 1390, 1260 and 1190–1175 cm^{-1} vanish from the spectra of 5-chloro-2-methoxybenzoates of Ni(II) and Zn(II). The band typical of symmetrical ring vibration at 1025 cm^{-1} also decays from the spectra of 5-chloro-2-methoxybenzoate of Ni(II). In the spectra of dried complexes the new bands characteristic for aromatic ring vibrations occur at 1645–1635 cm^{-1} (complexes of Co(II), Ni(II), Zn(II)), 1590–1525 cm^{-1} (complexes of Co(II), Ni(II)), 1460–1450 cm^{-1} (complexes of Co(II), Cu(II)), 1300–1290, 1250–1245 cm^{-1} (complexes of Co(II), Ni(II)) and 1160 cm^{-1}, 1100 cm^{-1} (complexes of Ni(II), Cu(II)). The comparison of the spectra of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with those of the anhydrous complexes (dried at 403 K) let us notice the influence of the increase of temperature on the aromatic ring vibrations. Its rise causes the appearance of the new bands characteristic of aromatic ring vibration and the increase of the intensities of the bands primarily existing. The heating of the complexes to 403 K brings about the decrease of the strength of bonding and the reduction of the values of the force constants. Thus in the spectra of the complexes some bands shift to lower frequencies. The slackness of metal-ligand bonding causes the decrease of electronic cloud deformation of ligand by central ion. As a consequence the tendency for the restoration of energetic advisable distribution of electronic charge in the aromatic ring is observed. Therefore, the aromatic nature of ligand is regenerated and the bands of its vibrations occur. From the IR spectra analysis it follows that there is not a clear influence of the hydration on the aromatic system of the complexes [22].

In order to study the crystalline forms of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) their powder diffractograms were recorded (Fig. 3). They reveal them to be polycrystalline compounds with various crystalline degrees. The IR spectra and powder diffractograms of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) dried at 403 K were recorded (Figs 2, 3). All hydrated complexes of d-electron elements are crystalline compounds but 5-chloro-2-methoxybenzoates of Mn(II), Ni(II) and Cu(II) are amorphous complexes with completely destroyed crystalline structure. There are only some reflections at $2\Theta=7°$. The appearance of the reflections at $2\Theta=38$ and 45° is most probably caused by the aluminium window in the diffractometer. In the case of complex of Mn(II) there is the residual crystalline phase to be difficult for interpretation. Considering the great hygroscopicity of 5-chloro-2-methoxybenzoate of Cu(II), the difficulties resulting from the measurements (the measurements chamber is not hermetic) and the properties of sample, its XRD spectra has been generally deformed but the residual hydrated phase is simultaneously seen. The anhydrous 5-chloro-2-methoxybenzoates of Co(II) and Zn(II) dried at 403 K insignificantly change their crystalline forms. Their diffractograms are very difficult for interpretation on account of the presence of so many reflections that cover also the reflections characteristic for hydrated compounds [23, 24]. The comparison of the IR spectra of hydrated and anhydrous complexes (dried at 403 K) confirms this transformation.

The thermal stability of the 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was studied in air and nitrogen atmospheres (Table 1, Fig. 4). 5-Chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) are stable in air up to 338–403 K. Next at 338–433 K they lose the water molecules in one step and form the anhydrous compounds. The mass losses calculated from TG curves are equal to 3.96–17.16% and correspond to the release of 1–5 molecules of water (the theoretical values are 3.98–17.32%). The dehydration process is associated with endothermic effect observed in the DTA curve. The enthalpy of this process was determined for the complexes with the use of the DSC technique. Its values being equal to 74.67–262.92 kJ mol^{-1} are proportional to the energy of the bonding of respective water molecules in the appropriate complexes.

The temperatures of the thermal stability of the complexes (T_1) do not change regularly with increasing atomic number of elements (Fig. 5). Monohydrate of

5-chloro-2-methoxybenzoate of Cu(II) is the most thermally stable (T_1=403 K), which indicates that the water molecule is the most strongly bounded in this complex. The least thermally stable complex is pentahydrate of 5-chloro-2-methoxybenzoate of Co(II) (T_1=338 K). The rests of the hydrates for which the initial temperature values of dehydration are at 343–353 K have thermal stability similar to that of pentahydrate of 5-chloro-2-methoxybenzoate of Co(II). The anhydrous 5-chloro-2-methoxybenzoate of Mn(II) decomposes in air to Mn_3O_4 (533–1273 K) with the intermediate formation of Mn_2OCl_2 (908 K) which was calculated from TG curve. The mass loss estimated from TG curve is equal to 80.57, while calculated is 80.27%. The anhydrous complexes of 5-chloro-2-methoxybenzoates of Co(II), Ni(II) and Zn(II) heated further to 1273 K decompose to the respective oxides with formulae: Co_3O_4, NiO and ZnO. In air the anhydrous 5-chloro-2-methoxybenzoate of Cu(II) decomposes to Cu_2O, Cu and CuO (483–983 K) with the intermediate formation of Cu_2OCl (833 K) to be calculated from TG curve [25]. The mass loss estimated from TG curve is equal to 79.54 while calculated is 80.27%. The smaller value of ZnO mass, to be the final product of zinc 5-chloro-2-methoxybenzoate decomposition, determined from TG curve (12.92%) compared to that calculated theoretically (17.23%) results from the partial sublimation of ZnO at higher temperatures [26, 27]. In the case of Cu(II) complex the found value of the mass of the final product of its decomposition (12.64%) is also smaller compared to the theoretical value (15.86%). It is probably connected with the loss of the gaseous molecules of chlorine, or volatilization of gaseous copper products, and with the chemical transformation of copper compounds [26–28]. The final products of decomposition were identified roentgenographically by X-ray powder diffraction (with the exception of Cu_2O, Cu, CuO which were fused with the crucible).

The anhydrous 5-chloro-2-methoxybenzoate of Ni(II) is the most thermally stable (its initial temperature of decomposition, T_2, is equal to 568 K) while the least thermally stable are complexes of Cu(II) and Zn(II) (T_2=483 K). The anhydrous complexes of Co(II) and Mn(II) have values of thermal stability similar to that of Ni(II) complex. The oxidation process is associated with the strong exothermic effect reflected in the DTA curve.

The results indicate that the thermal decomposition of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in air proceeds in the following steps:

$$\mathrm{ML_2\cdot}n\mathrm{H_2O} \xrightarrow{353-398\ \mathrm{K}} \mathrm{ML_2} \xrightarrow{533-908\ \mathrm{K}} \mathrm{M_2OCl_2} \xrightarrow{908-1273\ \mathrm{K}} \mathrm{M_3O_4} \qquad M=\mathrm{Mn}$$

$$\mathrm{ML_2\cdot}n\mathrm{H_2O} \xrightarrow{338-398\ \mathrm{K}} \mathrm{ML_2} \xrightarrow{483-913\ \mathrm{K}} \mathrm{M_3O_4} \qquad M=\mathrm{Co}$$

$$\mathrm{MO} \qquad M=\mathrm{Ni,\ Zn}$$

$$\mathrm{ML_2\cdot}n\mathrm{H_2O} \xrightarrow{403-433\ \mathrm{K}} \mathrm{ML_2} \xrightarrow{483-833\ \mathrm{K}} \mathrm{M_2OCl} \xrightarrow{833-983\ \mathrm{K}} \mathrm{M_2O,\ MO,\ M} \qquad M=\mathrm{Cu}$$

where M=Mn, Co, Ni, Cu, Zn; $L=C_8H_6ClO_3$; n=1, 2, 3, 4, 5.

The temperatures of the oxide formations change from 868 (for NiO) to 1273 K (for Mn_3O_4).

The thermal stability of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was studied in nitrogen atmosphere (Table 1). The complexes were found to be hydrates; the complex of Mn(II) is tetrahydrate, those of Co(II) and Ni(II) are pentahydrates, the complex of Cu(II) is monohydrate and that of Zn(II) is dihydrate. The complexes heated to 1173 K decompose in two steps. They are stable up to 333–393 K. Next in the temperature range 333–428 K they dehydrate in one step and form the anhydrous complexes. The mass losses calculated from TG curves being equal to 4.13–17.56% correspond to the loss from 1 to 5 molecules of water (theoretical values are 3.98–17.32%). The values of thermal stability of the hydrates in nitrogen do not change regularly with the increase of atomic number of element (Fig. 5).

Monohydrate of 5-chloro-2-methoxybenzoate of Cu(II) is the most thermally stable both in air (T_1=393 K) and nitrogen atmospheres while pentahydrate of 5-chloro-2-methoxybenzoate of Co(II) and tetrahydrate 5-chloro-2-methoxybenzoate of Mn(II) are the least thermally stable (T_1=333 K). 5-Chloro-2-methoxybenzoates of Ni(II) and Zn(II) reveal the similar stability in air (T_1=343–353 K) as well as in nitrogen atmospheres. The dehydration process is accompanied by endothermic effect observed in DTA curve. During further heating the anhydrous complexes decompose in the range 473–1153 K and form the mixture of the oxides of respective metals and carbon as the final products of decomposition. The anhydrous 5-chloro-2-methoxybenzoate of Ni(II) is the most thermally stable both in nitrogen (T_2=553 K) and in air atmospheres, while the least thermally stable (T_2=473 K) is anhydrous complex of Cu(II). The hydrated complexes of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) are more thermally stable in air (T_1=338–403 K) than in nitrogen (T_1=333–393 K). Only dihydrate of 5-chloro-2-methoxybenzoate of Zn(II) is more stable in nitrogen (T_1=353 K) than in air (T_1=343 K). In the series of anhydrous complexes 5-chloro-2-methoxybenzoates of Co(II), Ni(II) and Cu(II) are more stable in air (T_2=483-568 K) than in nitrogen (T_2=473–553 K). The complex of Mn(II) reveals the same thermal stability both in air and in nitrogen. Only anhydrous 5-chloro-2-methoxybenzoate of Zn(II) is more thermally stable in nitrogen (T_2=493 K) than in air (T_2=483 K).

The thermogravimetric studies of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were carried out with DSC/TG technique in the temperature range 303–1150 K (Table 1, Fig. 6). The obtained results reveal the complexes to be hydrates containing various molecules of water of crystallization depending on the central ions. The complexes are stable up to 314.7–356.2 K. Next in the range 314.7–372.1 K they dehydrate in one step. The mass loss estimated from TG curves during heating to 403 K (4.30–17.09%) corresponds to the loss from 1 to 5 molecules of water (the theoretical value is equal to 3.98–17.32%) and the energetic effects (ΔH=74.67–262.96 kJ mol^{-1}) accompanying these transformation processes confirm the losses of definite numbers of water molecules. The products of dehydration process were characterized by elemental analysis, IR spectra and X-ray powder diffractograms and their interpretations were earlier presented in this paper. In the series of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) the most thermally stable is complex of Cu(II) (T_1=356.2 K) whereas that of Co(II) is the least thermally stable (T_1=314.7 K). The values of the initial temperature of dehydration for the rests of hydrates changing from 320.2 to 327.5 K have the stability similar to that for complex of Co(II). The anhydrous complexes are decomposed to the oxides of the appropriate metals: Mn_3O_4, Co_3O_4, NiO, ZnO or Cu_2O, Cu and CuO, which were determined roentgenographically by X-ray powder diffraction or were estimated from the calculations of the percentage contents of the final products of complex decompositions.

Conclusions

On the basis of the obtained results it appears that 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were synthesized as hydrated complexes. Their colours are typical of the particular M(II) ion, i.e. slightly pink for Mn, pink for Co, green for Ni, blue for Cu(II) and white for Zn, having their origin in the lowest energy of d–d electronic transitions of the central ions. The complexes are crystalline compounds that on heating in air, nitrogen and argon atmospheres decompose in two steps. In the first step they dehydrate to form anhydrous complexes that next decompose to the oxides of the appropriate metals in air or in nitrogen to the mixture of metal oxides, their oxychlorides and carbon. The complexes are more stable in air than in nitrogen atmosphere. The most thermally stable complex is 5-chloro-2-methoxybenzoate of Cu(II) while the least thermally stable in air, nitrogen and argon atmospheres is that of Co(II).

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