Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 3, 783–789

COMPLEXES OF Mn(II), Co(II), Ni(II), Cu(II) AND Zn(II) WITH 4-CHLORO-2-METHOXYBENZOIC ACID ANION
Physico-chemical properties

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The complexes of 4-chloro-2-methoxybenzoic acid anion with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} were obtained as polycrystalline solids with general formula $M(C_8H_6ClO_3)_2{\cdot}nH_2O$ and colours typical for *M*(II) ions (Mn – slightly pink, Co – pink, Ni – slightly green, Cu – turquoise and Zn – white). The results of elemental, thermal and spectral analyses suggest that compounds of Mn(II), Cu(II) and Zn(II) are tetrahydrates whereas those of Co(II) and Ni(II) are pentahydrates. The carboxylate groups in these complexes are monodentate. The hydrates of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) heated in air to 1273 K are dehydrated in one step in the range of 323–411 K and form anhydrous salts which next in the range of 433–1212 K are decomposed to the following oxides: Mn_3O_4, CoO, NiO and ZnO. The final products of decomposition of Cu(II) complex are CuO and Cu. The solubility value in water at 293 K for all complexes is in the order of 10^{-3} mol dm^{-3}. The plots of χ_M *vs*. temperature of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) follow the Curie–Weiss law. The magnetic moment values of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions in these complexes were determined in the range of 76–303 K and they change from: 5.88–6.04 μ_B for $Mn(C_8H_6ClO_3)_2{\cdot}4H_2O$, 3.96–4.75 μ_B for $Co(C_8H_6ClO_3)_2{\cdot}5H_2O$, 2.32–3.02 μ_B for $Ni(C_8H_6ClO_3)_2{\cdot}5H_2O$ and 1.77–1.94 μ_B for $Cu(C_8H_6ClO_3)_2{\cdot}4H_2O$.

Keywords: *4-chloro-2-methoxybenzoic acid, 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), IR spectra, magnetic moments, thermal stability*

Introduction

4-Chloro-2-methoxybenzoic acid having formula $C_8H_7ClO_3$ is a white crystalline solid, weakly soluble in water. The reaction of 4,2-$Cl(MeO)C_6H_3CO_2H$ with $H_2NCH_2CH_2NEt_2$ carried out at a temperature of 80–90°C in HCl medium and catalysed by PCl_3 gave 4,2-$Cl(MeO)C_6H_3COHNCH_2CH_2NEt_2{\cdot}HCl$, which has practical application as antiemetic [1]. The 4-chloro-2-methoxybenzoic acid was used also by other scientists to obtain compounds having antiemetic and psychotropics properties [2, 3]. From the survey of literature it follows that there are papers on various organic ligands with *d* block elements [4–7] but the compounds of 4-chloro-2-methoxybenzoic acid anion with various cations are not known. There are no papers on its properties and its salts obtained as solids. Recently, we have prepared the complexes of 5-chloro-2-methoxybenzoic acid anion with following selected cations of *d* and *f* block elements: La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III), Y(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) as solids and have examined some of their physico-chemical properties [8–15]. This time, as a continuation of our research on the compounds of methoxybenzoic [16] and chloromethoxybenzoic acids [17], we decided to synthesise and investigate the complexes of 4-chloro-2-methoxybenzoic acid anion with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). These types of compounds maybe find the application in medicine as components of drugs or they may be used in technique as magnetic materials depending on their magnetic properties. The physico-chemical properties of 4-chloro-2-methoxybenzoates of *d* block elements were determined by thermal stability in air atmosphere during heating to 1273 K, IR spectral data, X-ray powder investigations, solubility in water at room temperature and magnetic properties. Thermal stability investigations give information about the ways of complex decompositions and the endo- or exo-effects connected with such processes as: dehydration, melting, polymorphic changes, crystallization, oxidation or reduction. The magnetic properties of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) were investigated in the range of 76–303 K in order to study the kind of coordination of central ions and the nature of bonding between central ions and ligands. If the effective magnetic moment μ_{eff} is known, the number of unpaired electrons can be calculated. This may also give infor-

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1388–6150/$20.00

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mation on the oxidation state of the metal ion or the central atom of a complex, on the electron configuration and, hence, on the nature of the bonding between the metal and the ligands. The determination of the number of unpaired electrons of the central atom allows to establish whether the complex investigated is of low or high spin and whether the ligand field is strong or weak.

Experimental

The complexes of the 4-chloro-2-methoxybenzoic acid anion with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} were obtained by the addition of equivalent quantities of 0.1 M ammonium 4-chloro-2-methoxybenzoate (pH~5) to a hot solution containing the nitrates(V) of respective metal ions and crystallizing at 293 K. The solids were filtered off, washed with hot water and ethanol to remove ammonium ions and dried at 303 K.

The C, H analysis was performed using a CHN 2400 Perkin Elmer analyser.

The contents of metals were calculated from TG curves.

The IR spectra of complexes were recorded over the range 4000–400 cm^{-1} using M–80 spectrophotometer (Carl-Zeiss, Jena). Samples for IR spectra measurements were prepared as KBr discs.

The X-ray powder diffraction were taken on a HZG-4 (Carl Zeiss-Jena) diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range 2θ=4–80° by means of the Debye–Scherrer–Hull method.

The thermal stability and decomposition of Mn(II) and Co(II) complexes were studied in air using a Setsys 16/18 TG, DTA instrument. The experiments were carried out under air flow in the temperature range of 297–1273 K. Samples 5.07 mg of Mn(II) and 4.96 mg of Co(II) complexes were heated in Al_2O_3 crucibles. The thermal analysis of 4-chloro-2-methoxybenzoates of Ni(II), Cu(II) and Zn(II) 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 (100 mg) were heated in platinum crucibles in static air to 1273 K with a sensitivity of TG – 100 mg, DTG and DTA sensitivities were regulated by computer Derill programme. The products of decomposition were calculated from TG curves and verified by the diffraction pattern and IR spectra registration.

Magnetic susceptibilities of polycrystalline samples of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) were investigated in the temperature range of 76–303 K. The measurements were carried out using the Gouy method. 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 constituent atoms was calculated by the use of Pascal's constants [18].

Solubility of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in water was measured at 293 K. 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 by using ASA 880 spectrophotometer (Varian).

Results and discussion

4-Chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were obtained as polycrystalline solids with a metal ion 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), Cu(II), Zn(II) and *n*=5 for Co(II), Ni(II), respectively). Their colours are typical for the corresponding divalent ions of *d* block elements i.e. is slightly pink in the case of Mn(II), pink for Co(II), slightly green for Ni(II), turquoise for Cu(II) and white for Zn(II). The compounds were characterized by elemental analysis (Table 1) and IR spectra (Table 2). 4-Chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in solid state show similar IR spectra. As anticipated, the characteristic wavenumbers corresponding to the carbonyl group are altered markedly when going from acid to the complex. The band at 1684 cm^{-1} originating from COOH group, present in the IR spectrum of the acid, is replaced in the spectra of *d*-block element complexes

Table 1 Elemental analysis data of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)

Compound	H/%		C/%		*M*/%	
	calcd.	found	calcd.	found	calcd.	found
$Mn(C_8H_6ClO_3)_2 \cdot 4H_2O$	4.02	3.83	38.55	38.76	11.03	11.20
$Co(C_8H_6ClO_3)_2 \cdot 5H_2O$	4.23	4.04	36.92	37.05	11.33	11.40
$Ni(C_8H_6ClO_3)_2 \cdot 5H_2O$	4.23	4.08	36.93	37.19	11.30	11.50
$Cu(C_8H_6ClO_3)_2 \cdot 4H_2O$	3.95	3.76	37.90	37.90	12.53	12.40
$Zn(C_8H_6ClO_3)_2 \cdot 4H_2O$	3.93	3.79	37.75	38.01	12.86	12.50

Table 2 Wavenumbers (cm^{-1}) of COO^- bands in 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), sodium and of the COOH band in 4-chloro-2-methoxybenzoic acid

Compound	$\nu_{C=O}$	$\nu_{as(OCO)}$	$\nu_{s(OCO)}$	$\Delta\nu_{OCO}$	ν_{M-O}
$Mn(C_8H_6ClO_3)_2{\cdot}4H_2O$	–	1604	1420	184	500
$Co(C_8H_6ClO_3)_2{\cdot}5H_2O$	–	1596	1412	184	500
$Ni(C_8H_6ClO_3)_2{\cdot}5H_2O$	–	1596	1416	180	500
$Cu(C_8H_6ClO_3)_2{\cdot}4H_2O$	–	1608	1416	192	512
$Zn(C_8H_6ClO_3)_2{\cdot}4H_2O$		1604	1424	180	505
$C_6H_3ClOCH_3COOH$	1684	–	–	–	–
$NaC_8H_6ClO_3$	–	1580	1404	176	–

by two bands at 1608–1596 and 1424–1412 cm^{-1}, due to asymmetric and symmetric vibrational modes of the COO^- group, respectively. The bands with the maxima at 3488–3416 cm^{-1} characteristic for ν_{OH} vibrations, and the narrow band of δ_{OH} at 1608–1596 cm^{-1} confirm the presence of crystallization water molecules in the complexes. The bands of ν_{C-C} ring vibrations appear at 1608–1596, 1488–1456 and 1032–1024 cm^{-1}. The bands of CH_3, δ_{CH_3}, antisymmetric and symmetric vibrations are observed at 1488–1456 and 1384–1376 cm^{-1}, respectively. The bands at 1252–1248 and 1032–1024 cm^{-1} were assigned to C–O bond, ($\nu_{as(C-O-C)}$ and $\nu_{s(C-O-C)}$, respectively) in ether compounds. The valency ν_{C-Cl} vibration bands occur at 704–696 cm^{-1} and the bands at 512–500 cm^{-1} confirm the metal–oxygen bond [19, 20]. The magnitudes of separation, $\Delta\nu$, between the frequencies of $\nu_{as(OCO)}$ and $\nu_{s(OCO)}$ in the complexes are higher ($\Delta\nu_{OCO}$=192–180 cm^{-1}) than in the sodium salt ($\Delta\nu_{OCO}$=176 cm^{-1}). Accordingly, the carboxylate ion in the analysed coordination compounds appears to be a monodentate [20, 21].

In order to evaluate, if the 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) are crystalline or amorphous compounds, their X-ray powder diffraction measurements were carried out. The analysis of the diffractograms suggests that the obtained complexes are polycrystalline compounds (Fig. 1). Their comparison shows that 4-chloro-2-methoxybenzoates of Co(II), and Ni(II) are probably isostructural compounds. The structures of the complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have not been determined, because their single crystals have not been obtained.

In order to verify the compositions of the complexes, to determine the temperature ranges of their thermal stability, and decomposition during heating in air, to estimate the intermediate and final products of their decomposition and to evaluate the type of processes that occur during heating, the thermal stability of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was studied in the range of 293–1273 K. Some results are presented in Table 3, and

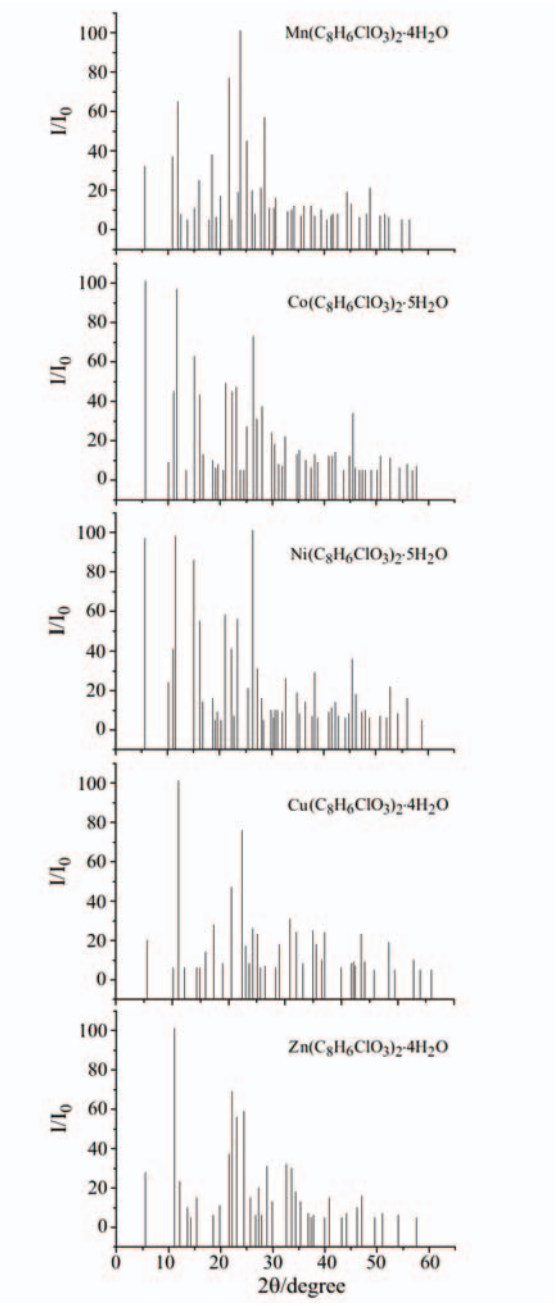

Fig. 1 Relationships between I/I_0 and 2θ for 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)

Table 3 Decomposition data for 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in air atmosphere and their solubility in water at 293 K

Compound	ΔT_1/K	Mass loss/%		n	ΔT_2/K	Mass loss/%		Solubility/mol dm^{-3}
		calcd.	found			calcd.	found	
$Mn(C_8H_6ClO_3)_2{\cdot}4H_2O$	364–400	14.46	14.20	4	433–851	84.69	84.50	$1.80{\cdot}10^{-3}$
$Co(C_8H_6ClO_3)_2{\cdot}5H_2O$	360–408	17.31	17.35	5	503–1212	85.75	86.00	$2.20{\cdot}10^{-3}$
$Ni(C_8H_6ClO_3)_2{\cdot}5H_2O$	359–409	17.31	17.37	5	489–973	85.63	85.80	$2.10{\cdot}10^{-3}$
$Cu(C_8H_6ClO_3)_2{\cdot}4H_2O$	330–395	14.21	14.00	4	473–1016	84.31	86.50	$1.50{\cdot}10^{-3}$
$Zn(C_8H_6ClO_3)_2{\cdot}4H_2O$	323–411	14.16	14.28	4	473–903	83.99	85.90	$1.60{\cdot}10^{-3}$

ΔT_1 – temperature range of dehydration process; n – number of crystallization water molecules being lost in one endothermic step; ΔT_2 – temperature range of complex decomposition

Fig. 2. The results reveal that the complexes of Mn(II), Cu(II) and Zn(II) are tetrahydrates whereas those of Co(II) and Ni(II) are pentahydrates. These results were also confirmed by the elemental analysis (Table 1), and the IR spectra data. The complexes are stable up to 323–364 K. Next they dehydrate in one step losing 4 or 5 molecules of crystallization water and form anhydrous compounds. The losses of mass calculated from TG curves (14.00–17.37%) correspond to the losses of 4 and 5 molecules of water (the theoretical values are equal to 14.16–17.31%). The tetrahydrate of 4-chloro-2-methoxybenzoate of Mn(II) is the most thermally stable complex since its initial temperature of dehydration is equal to 364 K, while tetrahydrate of Zn(II) has less thermal stability (323 K). The dehydration process is accompanied by endothermic effect seen in the DTA curves. The anhydrous complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in air are stable up to 411–503 K and heated further they decompose to the respective oxides: Mn_3O_4, CoO, NiO, ZnO and to mixture of CuO and Cu. 4-Chloro-2-methoxybenzoate of Co(II) (Fig. 2) decomposes to CoO with intermediate formation of Co_3O_4. The process of Co_3O_4 reduction to CoO is connected with endo-effect to be seen in DTA curve [22–24]. The combustion of the organic ligand is accompanied by strong exo-effect seen on DTA curves. The final products of decomposition of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were calculated from TG curves and experimentally verified by the X-ray diffraction pattern and IR spectra registration. The mass losses calculated from TG curves are equal to 84.50–86.50% (the theoretical values are 83.99–85.75%). In the case of Cu(II) and Zn(II) complexes the found values of the losses of mass are greater than the theoretical value. This is probably connected with properties of ZnO at higher temperature and with chemical transformation of Cu(II) complex with increasing temperature.

The obtained results indicate that the thermal decomposition of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in air proceeds in the following steps:

$$Mn(C_8H_6ClO_3)_2{\cdot}4H_2O \xrightarrow{364-400\ K} Mn(C_8H_6ClO_3)_2 \xrightarrow{433-851\ K} Mn_3O_4$$

$$Co(C_8H_6ClO_3)_2{\cdot}5H_2O \xrightarrow{360-408\ K} Co(C_8H_6ClO_3)_2 \xrightarrow{503-838\ K} Co_3O_4 \xrightarrow{1181-1212\ K} CoO$$

$$Ni(C_8H_6ClO_3)_2{\cdot}5H_2O \xrightarrow{359-409\ K} Ni(C_8H_6ClO_3)_2 \xrightarrow{489-973\ K} NiO$$

$$Cu(C_8H_6ClO_3)_2{\cdot}4H_2O \xrightarrow{330-395\ K} Cu(C_8H_6ClO_3)_2 \xrightarrow{473-1016\ K} CuO, Cu$$

$$Zn(C_8H_6ClO_3)_2{\cdot}4H_2O \xrightarrow{323-411\ K} Zn(C_8H_6ClO_3)_2 \xrightarrow{473-903\ K} ZnO$$

The solubility of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in water at 293 K was measured (Table 3). Its values amount to: $1.8{\cdot}10^{-3}$ mol dm^{-3} (for Mn(II) complex), $2.2{\cdot}10^{-3}$ mol dm^{-3} (for Co(II) complex), $2.1{\cdot}10^{-3}$ mol dm^{-3} (for Ni(II) complex), $1.5{\cdot}10^{-3}$ mol dm^{-3} (for Cu(II) complex) and $1.6{\cdot}10^{-3}$ mol dm^{-3} (for Zn(II) complex). The complex of Co(II) is the most soluble salt while that of Cu(II) is the least soluble one.

The magnetic susceptibility of 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) was measured in the temperature range of 76–303 K (Table 4). All the complexes show paramagnetic properties and essentially obey the Curie–Weiss law, since

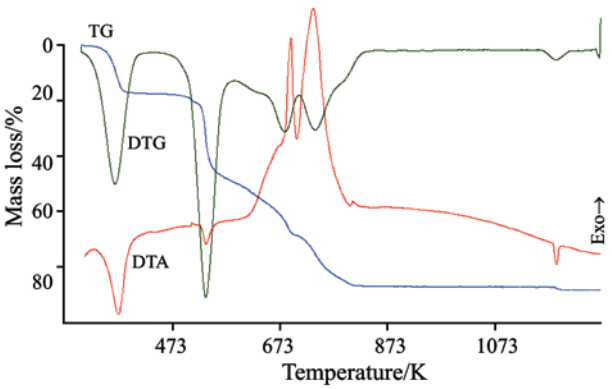

Fig. 2 TG, DTG and DTA curves of 4-chloro-2-methoxybenzoate of Co(II)

Table 4 Values of μ_{eff} and χ_M^{corr} for 4-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II)

$Mn(C_8H_6ClO_3)_2{\cdot}4H_2O$			$Co(C_8H_6ClO_3)_2{\cdot}5H_2O$			$Ni(C_8H_6ClO_3)_2{\cdot}5H_2O$			$Cu(C_8H_6ClO_3)_2{\cdot}4H_2O$		
T/K	$\chi_M^{corr}{\cdot}10^6$	μ_{eff}/μ_B	*T*/K	$\chi_M^{corr}{\cdot}10^6$	μ_{eff}/μ_B	*T*/K	$\chi_M^{corr}{\cdot}10^6$	μ_{eff}/μ_B	*T*/K	$\chi_M^{corr}{\cdot}10^6$	μ_{eff}/μ_B
76	58579	5.97	76	25701	3.96	76	8828	2.32	76	5402	1.81
123	36712	6.01	123	18628	4.28	123	6745	2.58	123	3245	1.79
133	33217	5.95	133	17412	4.31	133	6366	2.60	133	2967	1.78
143	30360	5.90	143	16447	4.34	143	6061	2.63	143	2750	1.77
153	28254	5.88	153	15659	4.38	153	5806	2.67	153	2631	1.80
163	26551	5.89	163	14930	4.41	163	5585	2.70	163	2453	1.79
173	24949	5.88	173	14193	4.43	173	5389	2.73	173	2324	1.79
183	23661	5.89	183	13544	4.46	183	5184	2.76	183	2196	1.79
193	22507	5.90	193	13029	4.49	193	5030	2.79	193	2097	1.80
203	21532	5.92	203	12543	4.52	203	4867	2.81	203	2057	1.83
213	20031	5.85	213	12093	4.54	213	4717	2.84	213	1928	1.81
223	19673	5.93	223	11622	4.56	223	4554	2.85	223	1849	1.82
233	18788	5.92	233	11172	4.57	233	4408	2.87	233	1810	1.84
243	18082	5.93	243	10804	4.59	243	4283	2.89	243	1721	1.83
253	17421	5.94	253	10487	4.61	253	4183	2.91	253	1681	1.85
263	16951	5.98	263	10185	4.63	263	4112	2.94	263	1661	1.87
273	16379	5.98	273	9942	4.66	273	3999	2.96	273	1602	1.87
283	15965	6.02	283	9750	4.70	283	3907	2.98	283	1532	1.86
293	15483	6.03	293	9522	4.73	293	3824	3.00	293	1612	1.94
303	15013	6.04	303	9301	4.75	303	3749	3.02	303	1473	1.89

the values of their 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 4 and those only for Co(II) complex in Fig. 3. The experimental data suggest that the 4-chloro-2-methoxybenzoates of Co(II), Ni(II) and Mn(II) are high-spin complexes of octahedral coordination with a weak ligand field (Tables 4 and 5). From the data presented in Tables 4 and 5 it follows that there is no significant orbital contribution to the magnetic moments of the complexes (spin only for complexes of Mn(II) and Ni(II)), or its contribution is essential (complex of Co(II)). In the case where no orbital contribution to the magnetic moments is to be expected its experimentally measured values differ from the spin-only moment. The values of μ_{eff}=5.88–6.04 μ_B obtained for Mn(II) 4-chloro-2-methoxybenzoate suggest that it is high-spin compound with LK=6. In the coordination sphere of Mn(II) ion there are probably four molecules of water and two monodentate groups of acid anions. This was confirmed by the IR spectral analysis and it appears that the carboxylate groups are monodentate. The magnetic moment values of Ni(II) 4-chloro-2-methoxybenzoate change from 2.32–3.02 μ_B. This indicate that in the solid state the Ni^{2+} ion exists in an octahedral triplet ground state with the five molecules of water and probably with one monodentate carboxylate group coordinated to the cation. The IR spectrum reveals that the carboxylate groups in this compound are in fact monodentates. The effective magnetic moments calculated for the complex of Co(II) are equal to 3.96–4.75 μ_B. The values indicate that it is also a high-spin complex with octahedral structure. In the co-

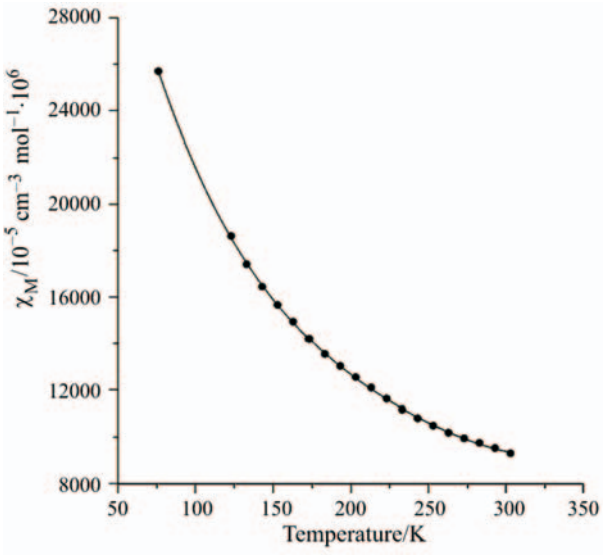

Fig. 3 Dependence of magnetic susceptibility values *vs*. temperature for 4-chloro-2-methoxybenzoate of Co(II)

Table 5 Magnetic moments of complexes with the central ions of Mn(II), Co(II), Ni(II) and Cu(II) with octahedral coordination

	Central atom			
	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
Number of *d* electrons	5	7	8	9
High-spin complexes				
Number of unpaired electrons	5	3	2	1
Spin-only moment (μ_B)	5.92	3.88	2.83	1.73
Magnetic moment (μ_B)	5.32–6.10	4.30–5.20	2.80–3.50	1.70–2.20
Low-spin complexes				
Number of unpaired electrons	1	1	0	–
Magnetic moment (μ_B)	1.80–2.10	1.80	–	–

ordination sphere of Co(II) ion there are probably five molecules of water and one monodentate carboxylate group. Such character of carboxylate groups was also confirmed by the IR spectral analysis. The magnetic and X-ray powder diffraction measurements indicate that complexes of Co(II) and Ni(II) have probably the same structure. The results of thermal analysis of complexes of Mn(II), Co(II) and Ni(II) show that molecules of water are lost in one step which suggests that they may be bound in the same way. The changing magnetic moment values of Cu(II) complex from 1.77 to 1.94 μ_B, the decreasing of magnetic susceptibility data with rising temperature, and the interpretation of IR spectra may suggest it to be monomeric compound [14, 25–32].

Conclusions

4-Chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were characterized by elemental analysis, thermal stability in air atmosphere, IR spectral data, X-ray powder investigations, solubility in water at room temperature and magnetic properties. The obtained results indicate that complexes crystallize as tetra- or pentahydrates. When heated they dehydrate to form anhydrous salts which next are decomposed to the oxides of the respective metals. The solubility of the analysed compounds of *d* block elements in water is of the order of 10^{-3} mol dm^{-3}. The complexes of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} with 4-chloro-2-methoxybenzoic acid anion obey the Curie–Weiss law, since the values of their magnetic susceptibility decrease with rising temperature. The obtained μ_{eff} values for Mn(II), Co(II) and Ni(II) complexes may suggest that they are high-spin complexes with octahedral coordination and with the weak electrostatic field of ligands in the coordination sphere of central ion.

References

1 V. Aldea and E. R. Oltenau, Patent – Rom. 62,894 (Cl. C07C103/29), 25 Aug. 1977, Appl. 77,645, 12 Feb. 1974, p. 3.
2 M. Ogata and H. Matsumoto, Patent – Ger. Offen. 2,803,651 (Cl. C07D207/08), 03 Aug. 1978, Japan, Appl. 77/8,443, 27 Jan, 1977, p. 34.
3 M. Thominet, J. Acher and J. C. Monier, Patent – Ger. Offen. 2,901,170 (Cl. C07D207/08), 26 Jul. 1979, Fr., Appl. 78/1,633, 20 jan. 1978, p. 86.
4 J. Skoršepa, E. Godoćiková and J. Černák, J. Therm. Anal. Cal., 75 (2004) 773.
5 F. C. D. Lemos, M. Muraro, J. Zukerman-Schpector, É. T. G. Cavalheiro and R. R. Dockal, J. Therm. Anal. Cal., 75 (2004) 599.
6 I. Labadi, I. Lakos, G. Kenessey and G. Liptay, J. Therm. Anal. Cal., 76 (2004) 829.
7 K. Györyová, J. Chomič and J. Kováčová, J. Therm. Anal. Cal., 80 (2005) 375.
8 W. Ferenc, B. Bocian and B. Czajka, ACH-Models Chem., 136 (1999) 571.
9 W. Ferenc and B. Bocian, J. Therm. Anal. Cal., 62 (2000) 831.
10 W. Ferenc, B. Bocian and B. Czajka, ACH-Models Chem., 137 (2000) 659.
11 B. Bocian, B. Czajka and W. Ferenc, J. Therm. Anal. Cal., 66 (2001) 729.
12 B. Czajka, B. Bocian and W. Ferenc, J. Therm. Anal. Cal., 67 (2002) 631.
13 B. Bocian and W. Ferenc, J. Serb. Chem. Soc., 67 (2002) 605.
14 W. Ferenc and B. Bocian, J. Therm. Anal. Cal., 74 (2003) 521.
15 W. Ferenc and B. Bocian, Annals of the Pol. Chem. Soc., 2 (2003) 541.
16 W. Ferenc, A. Walków-Dziewulska and B. Bocian, J. Therm. Anal. Cal., 79 (2005) 145.
17 W. Ferenc, B. Bocian and A. Walków-Dziewulska, J. Therm. Anal. Cal., 76 (2004) 179.
18 E. König, Magnetic Properties of Coordination and Organometallic Transition Metal Compounds, Springer Verlag, Berlin 1966.
19 E. Pretsch, T. Clerc, J. Seibl and W. Simon, Tables of Spectral Data for Structure Determination of Organic Compounds, Springer Verlag, Berlin 1989.
20 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, Toronto 1997.

21 S. Manhas and A. K. Trikha, J. Indian Chem. Soc., 59 (1982) 315.
22 J. Garcia-Oricain and A. Fuster Camps, J. Thermal Anal., 29 (1984) 793.
23 D. Dollimore and D. L. Griffiths, J. Thermal Anal., 2 (1970) 229.
24 D. Czakis-Sulikowska, A. Malinowska and J. Radwańska-Doczekalska, Pol. J. Chem., 74 (2000) 607.
25 S. F. A. Keetle, Inorganic Physical Chemistry, PWN, Warszawa 1999 (in Polish).
26 C. I. O. O'Connor, Progress in Inorganic Chemistry, Wiley, New York 1982.
27 J. Mroziński, Mater. Sci., 14 (1988) 23.
28 J. Mroziński and L. Natkaniec, Mater. Sci., 14 (1988) 69.
29 M. Hvastijova, J. Kohout, J. Mroziński and L. Jäger, Pol. J. Chem., 69 (1995) 852.
30 M. Melnik and J. Mroziński, Mater. Sci., 14 (1988) 3.
31 M. Melnik, D. Mrozińska and J. Mroziński, Mater. Sci., 4 (1989) 65.
32 M. Melnik, Z. Sabova, J. Mroziński and A. Szymaszek, J. Mol. Struct., 240 (1990) 285.

Received: September 30, 2005
Accepted: November 8, 2005
OnlineFirst: May 23, 2006

DOI: 10.1007/s10973-005-7379-z