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Magnetic, thermal and spectroscopic properties of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)

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Abstract: The 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were synthesized as solids and their magnetic, spectral and thermal properties studied. The complexes possess colours typical of the M(II) ions. The thermal stabilities were examined in air and nitrogen atmospheres and the products of decompositions were also identified. The magnetic susceptibilities of the complexes were measured over the temperature range 4.4–300 K and the magnetic moments were calculated. The results show that the 5-chloro-2-methoxybenzoates of Mn(II), Co(II) and Ni(II) are octahedral, high-spin complexes.

Keywords: 5-chloro-2-methoxybenzoates, Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes, magnetic moments, thermal stability, FTIR spectra.

INTRODUCTION

The complexes of 5-chloro-2-methoxybenzoic acid with various cations are little known.[1–3] Only the compounds of this acid with rare earth elements are known in the literature.[4,5] The thermal and magnetic properties of the 5-chloro-2-methohoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have not been investigated so far. Therefore, the aim of this work was the preparation and characterization of these compounds including an investigation of their thermal stability in air and nitrogen during heating to 1673 K (in air) and 1173 K (in nitrogen). IR spectral characterization, and X-ray powder investigations were carried out in order to determine whether the compounds appear in crystalline or amorphous phases. Finally, the magnetic features of the compounds were investigated to reveal the nature of the metal – ligand bonding, and to examine their magnetic properties in various temperature ranges. The thermal stability investigations enabled the role and location of crystallization water molecules to be revealed, *i.e.*, to indicate in which sphere of coordination (outer or inner) these molecules occur, the pathways of complex decomposition to be determined, as well as to assign the endothermic or exothermic effects accompanying

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such processes as: dehydration, melting, crystallization, oxidation, reduction and to estimate the strength of the bonding between groups of atoms and ions.

EXPERIMENTAL

The complexes of 5-chloro-2-methoxybenzoic acid with 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 these metal ions 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.

Elemental analysis for C, H was performed using a CHN 2400 Perkin Elmer analyzer and for Cl the Schöniger method. The contents of M^{2+} metals were established by the ASA method.

The FTIR and FIR spectra of complexes were recorded over the ranges 4000–400 cm^{-1} and 650–100 cm^{-1}, respectively using an FTIR 1725X Perkin Elmer and a DIGILAB FTS-14 spectrometer. The samples for FTIR spectroscopy were prepared as KBr discs while those for FIR spectroscopy were used in Apieson suspensions. Some of the results are presented in Table I.

TABLE I. Frequencies of the COO^- absorption bands for the 5-chloro-2-methoxybenzoate of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and sodium and that of CO for 5-chloro-2-methoxybenzoic acid (cm^{-1})

Complex $L=C_8H_6ClO_3$	ν(C=O)	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu(COO^-)$	ν(C–Cl)	ν(M–O)
$MnL_2{\cdot}4H_2O$	–	1603	1419	184	695	435, 282
$CoL_2{\cdot}5H_2O$	–	1603	1412	191	705	432, 259
$NiL_2{\cdot}5H_2O$	–	1602	1409	193	708, 692	431, 271
$CuL_2{\cdot}H_2O$	–	1609	1417	192	693	477, 278
		1606	1409	197		
$ZnL_2{\cdot}2H_2O$	–	1547	1440	107	720, 695	444, 287
NaL	–	1560	1402	158	700	–
HL	1729	–	–	–	722–682	–

The thermal stability and decomposition of the complexes were studied in air using a Q-1500D derivatograph with a Derill converter, which simultaneously records TG, DTG and DTA curves. The measurements were made at a heating rate of 10 K min^{-1}. The 100 mg samples were heated in platinum crucibles in static air to 1273 K with a TG sensitivity of 100 mg (*i.e.*, the whole scale of the balance was equal to 100 mg). The DTG and DTA sensitivities were regulated by the Derill computer programme. The paper speed was 2.5 mm min^{-1} and Al_2O_3 was used as the standard. The decomposition products were calculated from the TG curves and verified by powder diffraction analysis (Table II). The measurements in nitrogen were made on an OD-102 derivatograph at a heating rate of 10 K min^{-1}. The samples were heated with a TG sensitivity of 100 mg (*i.e.*, the whole scale of the balance was 100 mg) and with sensitivities of DTA-1/10 and DTG-1/5. The nitrogen flowed through gas washers filled with pyrogallol and silica gel at a rate of 115 cm^3 min^{-1}. Some of the results are presented in Table II.

The DSC/TG analysis was also performed at temperatures 303–1150 K using a differential thermoanalyser Netzsch STA 409C 3F. The experiments were carried out under a dynamic argon atmosphere. The values of the enthalpy of the dehydration process were calculated (Table II). The gaseous decomposition products were analysed over the range 4000–400 cm^{-1} using the Bruker IFS 66 spectrometer (Fig. 1, Table III).

In order to study the magnetic behaviour of the 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) at low temperatures, the magnetizations of the samples at 4.5 K were also measured at a magnetic field strength of 0–56 kθe (Figs. 2–4). On the basisi of the obtained results, the magnetic susceptibility was determined according to Eq. (1):

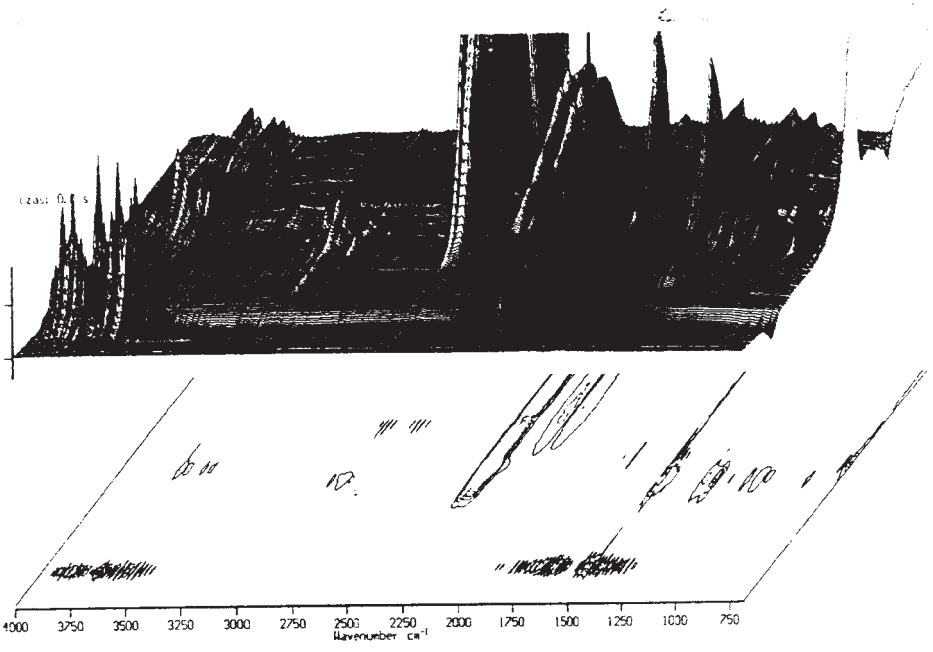

Fig. 1. The FTIR spectra of the gaseous products evolved during the decomposition of the 5-chloro-2-methoxybenzoate of Ni(II).

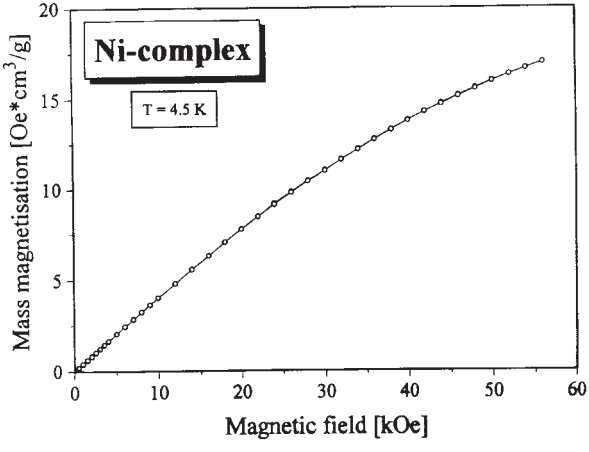

Fig. 2. The dependence between magnetisation and magnetic field for the 5-chloro-2-methoxybenzoate of Ni(II).

$$\chi = \frac{M}{H} \tag{1}$$

where M is the magnetisation, H is the value of the applied magnetic field. The dependence of the magnetisation on the field intensity is presented in Fig. 2. The magnetic susceptibilities of the samples were only studied at a magnetic field strength of 0.5 kOe (where there is a maximum of the susceptibility) between the temperatures of 4.4–200 K. The parameters of the fitting of the experimental data to the Curie-Weiss law are presented in Fig. 3. The alternating current susceptibilities in the narrow temperature range were measured using an AC susceptometer.

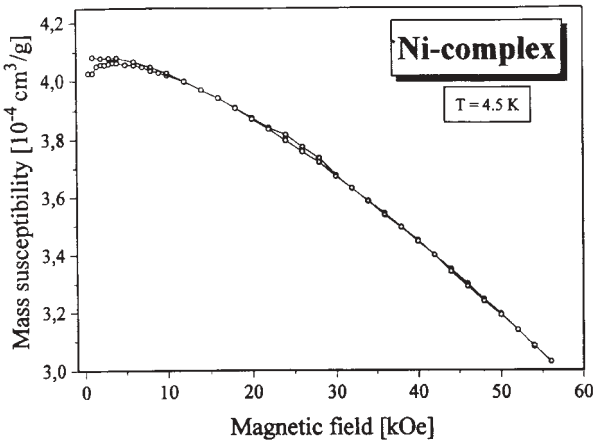

Fig. 3. Relationship between mass susceptibility and magnetic field for the 5-chloro-2-methoxybenzoate of Ni(II).

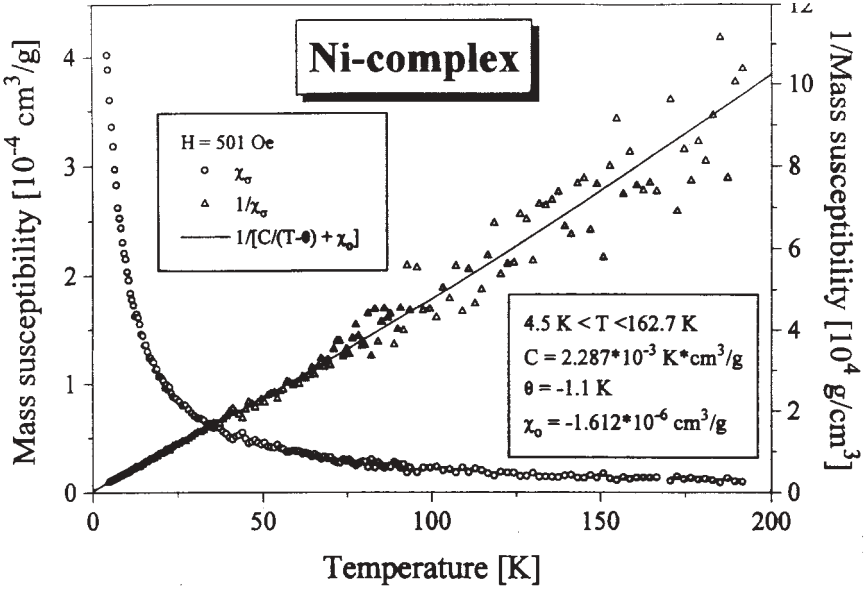

Fig. 4. Mass susceptibility for the 5-chloro-2-methoxybenzoate of Ni(II) as a function of temperature.

The magnetic susceptibilities of the samples of the 5-chloro-2-methoxybenzoates of Zn(II), Co(II), Ni(II) and Cu(II) were measured by the Gouy method using a sensitive Cahn RM-2 balance. The measurements were made at a magnetic field strength of 9.9 kOe. The calibrant employed was $Co[Hg(SCN)_4]_2$, for which a magnetic susceptibility of 1.644×10^{-5} cm^{-3} g^{-1} was taken.[6] The corresction for diamagnetism of the constituent atoms was calculated by use of the Pascal constants.[7] The magnetism of the samples was found to be field independent. The magnetic moments were calculated according to Eqs. (2) and (3):

$$\mu_{eff} = 2.83\ (\chi_M T)^{1/2} \quad (2)$$

$$\mu_{eff} = 2.83\ [\chi_M (T-\theta)]^{1/2} \quad (3)$$

where θ is the Weiss constant.

The calculated magnetic moment values for the 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) are presented in Table IV.

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 polycrystalline solids 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). Their colours are typical for the appropriate divalent ions (Mn(II) – slightly pink, Co(II) – pink, Ni(II) – green, Cu(II) – blue and Zn(II) – white).

Some of the results of the FTIR analysis are presented in Table I. There are two bands arising from asymmetric and symmetric vibrations of the COO^- group occurring at 1609–1602 cm^{-1} and 1419–1409 cm^{-1}, respectively. The bands with maxima at 3495–3400 cm^{-1}, characteristic for ν (OH) vibrations,[8,9] and the narrow band of $\delta(H_2O)$ at 1609–1605 cm^{-1} confirm the presence of crystallization water molecules in the compounds. The bands of ν (C⋯C) ring vibrations appear at 1590 cm^{-1}, 1390–1385 cm^{-1}, 1195–1130 cm^{-1}, 1040–1025 cm^{-1} and at 231–225 cm^{-1}. The valency ν (C–Cl) vibration bands occur at 710–700 cm^{-1} and the bands at 648–644 cm^{-1} confirm the ν (C–OCH_3) and ring vibrations.[10–21] The bands at 473–434 cm^{-1} result from ν (M–O), ν (C–OCH_3) and ρ (COO^-) vibrations. The oscillation ring vibrations result in the bands at 387–378 cm^{-1}. The bands at 287–259 cm^{-1} correspond to the ν (M–O) vibrations.[11] The bands at 129–119 cm^{-1} are due to the O–H···O stretching vibrations[22,23] and they change their shapes according to the atomic number of the central ions and the degree of hydration in the 5-chloro-2-methoxybenzoates. The bands at 137–135 cm^{-1} confirm the internal C–C torsion.[22,23] Table I presents the maxima of the frequencies of the absorption bands of the asummetric and symmetric vibrations of the COO^- group for the 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and sodium(I). The magnitude of the separation. $\Delta\nu_{COO^-}$, between the frequencies of ν_{asCOO^-} and $\nu_{s\,COO^-}$ in these complexes are much greater ($\Delta\nu_{COO^-}$ = 197–184 cm^{-1}) or lower (in the case of Zn complex) than the ionic value ($\Delta\nu_{COO^-}$ = 158 cm^{-1}). Accordingly, the carboxylate ion in these complexes appears to be monodentate (Mn(II), Co(II), Ni(II), Cu(II) compleexs) and also bridging (Zn(II) complex).[11,24–28] The 5-chloro-2-methoxybenzoate of Zn(II) contains probably one monodentate and one bidentate bridging carboxylate group in one molecule.[24–28]

The thermal stability of the 5-chloro-2-methoxybenzoate of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was studied in air and nitrogen atmospheres. Some results are presented in Table II. The 5-chloro-2-methoxybenzoate of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) are stable in air up to 338–403 K. They lose water molecules in one step and form the anhydrous compounds. The dehydration process is associated with an endothermic effect on the DTA curve. The values of the enthalpy of this process, determined using the DSC technique, lay in range 74.67–262.92 kJ mol^{-1} and are proportional to the energy of the bonding of a definite number of water molecules in the corresponding 5-chloro-2-methoxybenzoates complexes. The monohydrate of the 5-chloro-2-methoxybenzoate of Cu(II) is

TABLE II. Temperature range of thermal stability of the 5-chloro-2-methoxybenzoates Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in air and nitrogen atmospheris

Complex $L=C_8H_6ClO_3$	ΔT_1[a] K	Weight loss/%		n[b]	A (Air) N (N_2)	ΔH[c] kJ mol^{-1}	ΔT_2[d] K	Oxide/%		Residue/%	Gaseus products of decomposition
		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		CO_2, CO, HCl, H_2O, hydrocarbons
	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		
	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		
	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		
	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		
	353–383		7.82		N		493–883			52.63	

[a]ΔT_1 = The temperature range of the dehydration process; [b]n = the number of crystallization water molecules being lost in one endothermic step; [c]ΔH = enthalpy of the dehydration process; [d]ΔT_2 = the temperature range of the decomposition of the anhydrous complex

the most thermally stable, while that of Co(II) is the least thermally stable one. The anhydrous 5-chloro-2-methoxybenzoate of Mn(II) decomposes to Mn_3O_4 with the intermediate formation of Mn_2OCl_2. The anhydrous 5-chloro-2-methoxybenzoates of Co(II), Ni(II) and Zn(II) heated further to 1273 K decompose to the respective oxides: Co_3O_4, NiO and ZnO. The anhydrous 5-chloro-2-methoxybenzoate of Cu(II) decomposes to Cu_2O, Cu and CuO with the intermediate formation of Cu_2OCl. The found value of the ZnO mass is smaller than that calculated theoretically. This is probably connected with the properties of ZnO at higher temperatures.[29,30] In the case of the Cu(II) complex, the found value of the mass of the final product of its decomposition is also smaller relative to the theoretical value. It is probably connected with the chemical transformation of the 5-chloro-2-methoxybenzoate of Cu(II) with increasing of temperature.[29–31]

TABLE III. Frequencies of the absorption bands of some gaseous products evolved during the decomposition of the 5-chloro-2-methoxybenzoates of Co(II), Ni(II), Mn(II), Zn(II) and Cu(II) (cm^{-1})

Range of frequency	Identified gaseous products
4000–3500 2000–1350 1820–1330	H_2O
3800–3500 2400–2280 670	CO_2
3059–2650	HCl
2220–2060	CO
3100–1420 1000 915	Hydrocarbons

The thermal stability of the 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was also studied under a nitrogen atmosphere (Table II). When heated to 1173 K, they decompose in two steps. They are stable up to 333–393 K and then they exist as anhydrous complexes. The dehydration process is accompanied by an endothermic effect observed in the DTA curve. During heating, the anhydrous complexes decompose to a mixture of the oxides of the respective metals and carbon.

The FTIR spectra of the gaseous products evolved during the decomposition of the 5-chloro-2-methoxybenzoates of Mn(II), Cu(II), Co(II), Ni(II) and Zn(II) are presented in Tables II and III and in Fig. 1. Their interpretation reveals them to be molecules of H_2O, HCl, CO_2, CO and hydrocarbons.[11,12,19–21]

The magnetic susceptibility of the 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was determined in the range 4.4–300 K in order to study a paramag-

TABLE IV. Values of μ_{eff} for the 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) (L=$C_8H_6ClO_3$) at the chosen temperatures

$MnL_2 \cdot 4H_2O$ C=1.05×10^{-2} Θ=–20.6 K			$CoL_2 \cdot 5H_2O$ C=9.600×10^{-3} Θ=–60.7 K			$NiL_2 \cdot 5H_2O$ C=6.742×10^{-3} Θ=–107.5 K			$CuL_2 \cdot H_2O$ C=1.203×10^{-3} Θ=–12 K		
T/K	$\chi_g\times10^6$	μ_{eff}/BM	*T*/K	$\chi_g\times10^6$	μ_{eff}/BM	*T*/K	$\chi_g\times10^6$	μ_{eff}/BM	*T*/K	$\chi_g\times10^6$	μ_{eff}/BM
80	82.5	5.78	80	29.8	4.22	80	24.6	2.90	80	7.0	1.58
111	63.7	5.80	91	27.9	4.24	93	21.5	2.92	100	5.8	1.60
132	56.8	5.90	113	24.8	4.28	125	15.5	2.90	122	4.9	1.62
141	53.8	5.92	121	23.3	4.24	151	13.7	3.00	134	4.7	1.66
152	57.7	5.92	131	22.7	4.30	160	13.4	3.02	146	4.5	1.70
168	45.8	5.95	137	21.9	4.30	172	12.4	3.04	156	4.5	1.75
173	45.7	5.98	161	19.8	4.32	181	11.5	3.02	167	4.4	1.80
182	44.3	6.01	176	18.7	4.34	190	11.2	3.05	175	4.2	1.80
191	43.4	6.01	188	17.8	4.36	203	11.0	3.14	186	4.1	1.83
206	42.5	6.04	199	17.3	4.40	211	9.3	2.94	198	4.0	1.85
215	42.0	6.06	211	16.9	4.44	221	8.6	2.91	214	3.8	1.88
222	41.4	6.07	224	16.4	4.48	232	8.3	2.92	224	3.7	1.90
231	36.2	6.07	236	15.7	4.48	239	8.0	2.92	239	3.6	1.91
241	35.0	6.09	245	15.5	4.52	246	7.8	2.93	247	3.5	1.94
253	33.3	6.08	257	15.1	4.56	255	7.6	2.95	257	3.2	1.92
262	32.7	6.12	267	14.8	4.58	266	7.3	2.95	265	3.1	1.94
271	31.9	6.14	278	14.6	4.62	280	7.2	3.01	275	3.1	1.95
280	30.7	6.13	283	14.5	4.64	293	7.0	3.04	283	3.0	1.96
291	29.8	6.14	294	14.0	4.64				291	2.9	1.94
300	28.0	6.09							293	2.8	1.93
									297	2.8	1.94
									299	2.7	1.93

L=$C_8H_6ClO_3$

netic saturation or magnetic dipole arrangements. All the complexes (with the exception of that of Zn(II)) show paramagnetic properties and essencially obey the Curie-Weiss law. However, clear magnetic orientation regions were not observed for them in the whole temperature range. For example, the parameters of the fitting to the Curie-Weiss law for the Ni(II) complex are presented in Figs. 2–4. In the case of the Mn(II) complex: magnetic saturation is almost attainable. The values of the Weiss constant, Θ, for all the complexes were found to be negative, which probably arises from an antiferromagnetic spin interaction, or from a crystal field splitting of the paramagnetic spin state.[32–35] The magnetic susceptibility values of the complexes of Co(II), Ni(II), Mn(II) and Cu(II) obey the Curie-Weiss law (Table IV). The experimental data suggest that the 5-chloro-2-methoxybenzoates of Co(II), Ni(II) and Mn(II) are high-spin complexes of octahedral coordination with a weak ligand field (Tables IV, V). The ion of Zn(II) is diamagnetic in nature. The results obtained for the μ_{eff} for the Cu(II) complex may suggest it to be monomeric, since the values of the magnetic susceptibil-

TABLE V. Magnetic moment values of the complexes with the central ions of Mn(II), Co(II), Ni(II) and Cu(II) in 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/BM	5.92	3.88	2.83	1.73
Magnetic moment/BM	5.62–6.10	4.30–5.20	2.80–3.50	1.70–2.20

ity decrease with increasing temperature.[36,37] The magnetic moment values also furnish valuable information on the electronic configuration of the central ion in the complexes.[38,39] From the data presented in Tables IV and V it follows that there is no significant orbital contribution to the magnetic moments of the complexes (spin only complexes of Mn(II) and Ni(II), or its contribution is essential (complex of Co(II)). In the cases where no orbital contribution to the magnetic moment is to be expected its experimentally measured values differ from the spin-only moment. The small discrepancy is due to the fact that spin-orbital coupling in the ion can mix the ground state representing no orbital momentum with higher levels of identical multiplicity. The magnetic moment values of Ni(II) 5-chloro-2-methoxybenzoate change from 2.88–3.04 BM in the range 77–300 K. This indicates that in the solid state the nickel(II) cation exists in an octahedral triplet ground state with the five molecules of water and probably with one monodentate carboxylate group coordinated to the nickel(II) ion. This was confirmed by the IR spectral analysis and it follows that the carboxylate group is a monodentate ligand (Table I). The ground state configuration of the nickel(II) ion in a regular octahedral field is $^3A_{2g}$ ($t_{2g}^6 e_g^2$) and it will be paramagnetic with two unpaired electrons. The contribution to the magnetic susceptibility is given by a spin-only term, second order spin-orbital coupling, and the temperature independent paramagnetism.

The effective magnetic moments for the 5-chloro-2-methoxybenzoate of Co(II) determined in the range 77–300 K are equal to 4.20–4.64 BM. The values indicate that it is a high-spin complex with octahedral structure.[37] In this complex spin-orbit coupling in the state of $^4T_{1g}$ (P) occurs causing a pseudooctahedral coordination with the five molecules of water and with probably one monodentate carboxylate group coordinated to the cobaltous ion. The FTIR spectrum reveals that the carboxylate group is in fact a monodentate ligand (Table I).

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ИЗВОД

МАГНЕТНЕ, ТОПЛОТНЕ И СПЕКТРОСКОПСКЕ ОСОБИНЕ 5-ХЛОРО-2-МЕТОКСИБЕНЗОАТА Mn(II), Co(II), Ni(II), Cu(II) и Zn(II)

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Синтетизовани су 5-хлоро-2-метоксибензоати Mn(II), Co(II), Ni(II), Cu(II) и Zn(II) у чврстом облику и проучене њихове магнетне, спектроскопске и топлотне особине. Комплекси имају боју типичну за M(II) јоне. Испитивана је њихова термичка стабилност на ваздуху и атмосфери азота, а идентификовани су и продукти њиховог разлагања. Магнетна сусцептибилност је одређивана у температурној области 4,4 – 300 K и израчунати су одговарајући магнетни моменти. Резултати показују да су 5-хлоро-2-метоксибензоати Mn(II), Co(II) и Ni(II) октаедарски, високо-спински комплекси.

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