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Physicochemical properties of 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Zn(II)

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Abstract: The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 3,4,5-trimethoxybenzoic acid anion of the formula: $M(C_{10}H_{11}O_5)_2 \cdot nH_2O$, where $n = 6$ for Ni(II), $n = 1$ for Mn(II), Co(II), Cu(II), and $n = 0$ for Zn, have been synthesized and characterized by elemental analysis, IR spectroscopy, X–ray diffraction measurements, thermogravimetry and magnetic studies. They are crystalline compounds characterized by various symmetry. They decompose in various ways when heated in air to 1273 K. At first, they dehydrate in one step and form anhydrous salts. The final products of decomposition are oxides of the respective metals (Mn_2O_3, Co_3O_4, NiO, CuO, ZnO). The solubilities of the analysed complexes in water at 293 K are in the orders of 10^{-2} – 10^{-4} mol dm^{-3}. The magnetic susceptibilities of the Mn(II), Co(II), Ni(II) and Cu(II) complexes were measured over the range of 76–303 K and the magnetic moments were calculated. The results show that the 3,4,5-trimethoxybenzoates of Mn(II), Co(II) and Ni(II) are high-spin complexes but that of Cu(II) forms a dimer $[Cu_2(C_{10}H_{11}O_5)_4(H_2O)_2]$. The carboxylate groups bind as monodentate or bidentate chelating or bridging ligands.

Keywords: 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), thermal stability, IR spectroscopy, magnetic moments, X-ray diffraction.

INTRODUCTION

The complexes of various isomers of mono-, di- and trimethoxybenzoic acid anions with some metal ions have been described.[1–22] 3,4,5-Trimethoxybenzoic acid of formula $C_{10}H_{12}O_5$ is a white, crystalline solid, sparingly soluble in water but readily soluble in alcohol, ether and chloroform.[1] The compounds of 3,4,5-trimethoxybenzoic acid anion with only some metal ions: K(I), Cu(II), Ag(I), Ca(II), Ba(II), La(III)–Lu(III)[1–3] have been studied. They were obtained and studied as solids or were investigated only in solution. There is no information concerning investigations of the solid-state properties of the 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Zn(II). Therefore, it was decided to synthesize those

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complexes, as well as the Cu(II) complex, and to examine some of their properties, such as: thermal stability in air, solubility in water, magnetic features, the nature of the metal ion–ligand coordination and to record their IR spectra and X-ray powder diffractograms.

The aim of thermal stability investigations was to estimate the positions of the molecules of cryastallization water in coordination sphere of the complexes, to resolve the manner of their decompositions, to determine the relative character of the bonding strength between the central ions and the surrounding atoms, groups of atoms and ions.

The X-ray powder diffractograms were recorded in order to obtain information as to whether the compounds form crystalline or amorphous phases.

The determination of the solubility in water at 293 K provides valuable data concerning the practical use of the employed acid for the separation of elements (*i.e.*, Co(II) and Ni(II)) by extraction or ion-exchange chromatographic methods.

The magnetic susceptibilities of the 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) were measured in order to estimate the nature of the metal ion–ligand bonds, to obtain information about the possible structures of the complexes or the coordination symmetry of the central ions and to determine the nature of metal ion–ligand coordination by defining the character of the ligand dentates.[23–38]

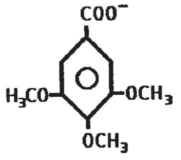
EXPERIMENTAL

The complexes of 3,4,5-trimethoxybenzoates 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 3,4,5-trimethoxybenzoate (pH ≈ 5) to a 0.1 M hot aqueous 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 to constant mass. The contents of carbon and hydrogen in the complexes were determined by elemental analysis using a CHN 2400 Perkin–Elmer analyser. The contents of M^{2+} metals were established by the ASA method (Table I).

TABLE I. Elemental analysis data of the 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and their solubilities in water at 293 K

Complex L = $C_{10}H_{11}O_5$	C / %		H / %		M / %		Solubility mol dm^{-3}
	Calcd.	Found	Calcd.	Found	Calcd.	Found	
$MnL_2 \cdot H_2O$	48.49	48.4	4.85	4.7	11.09	11.5	3.42×10^{-2}
$CoL_2 \cdot H_2O$	48.10	48.3	4.81	4.7	11.80	12.2	6.19×10^{-2}
$NiL_2 \cdot 6H_2O$	40.76	40.6	5.77	5.1	9.97	10.3	6.15×10^{-3}
$[Cu_2L_4(H_2O)_2]$	47.66	47.8	4.77	4.7	12.61	12.9	6.58×10^{-4}
ZnL_2	49.24	49.4	4.51	4.4	13.41	13.2	4.01×10^{-2}

L =



The IR spectra of complexes were recorded over the range 4000 – 400 cm^{-1} using a Perkin–Elmer FTIR 1725X spectrometer. The samples for the FTIR spectra measurements were prepared as KBr discs (Table II and Fig. 1).

TABLE II. Spectroscopic data of the 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Na(I) and 3,4,5-trimethoxybenzoic acid (cm^{-1})

Complex L = $C_{10}H_{11}O_5$	ν(C=O)	$\nu_{as}(OCO^-)$	$\nu_s(OCO^-)$	$\Delta\nu(OCO^-)$	ν(M–O)
$MnL_2{\cdot}H_2O$	–	1552	1400	152	408
$CoL_2{\cdot}H_2O$	–	1560	1400	160	420
$NiL_2{\cdot}6H_2O$	–	1576	1388	188	410
$[Cu_2L_4(H_2O)_2]$	–	1572	1396	176	440
ZnL_2	–	1576	1396	180	416
NaL	–	1580	1410	170	–
HL	1684	–	–	–	–

The X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss-Jena) diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range $2q$ = 4 – 80° by means of the Debye–Scherrer–Hull method. The relationships between I/I_0 for these complexes are presented in Fig. 2.

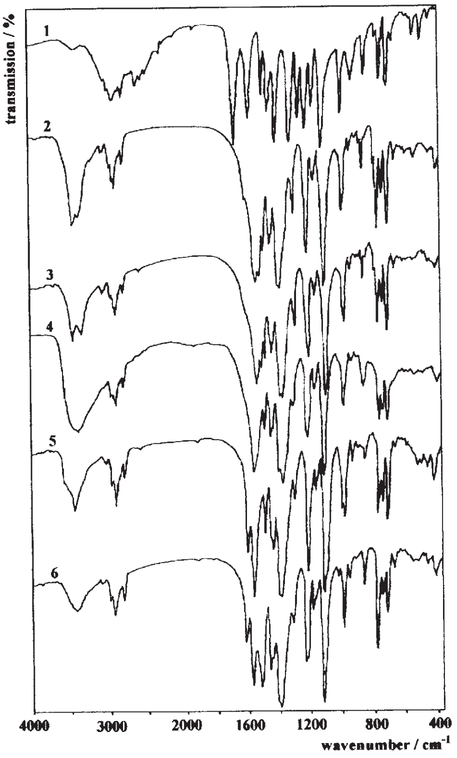


Fig. 1. FTIR Spectra of 3,4,5-trimethoxybenzoic acid (1), 3,4,5-trimethoxybenzoates of Mn(II) (2), Co(II) (3), Ni(II) (4), Cu(II) (5) and Zn(II) (6).

The thermal stabilities and decompositions of the prepared complexes were determined by a Paulik–Paulik–Erday Q-1500 D derivatograph with a Derill converter. TG, DTG and DTA curves were recorded (Fig. 3). The measurements were performed at a heating rate of 10 K/min with full scale deffection. The samples (100 mg) were heated in platinum crucibles in static air to 1273 K with a sensi-

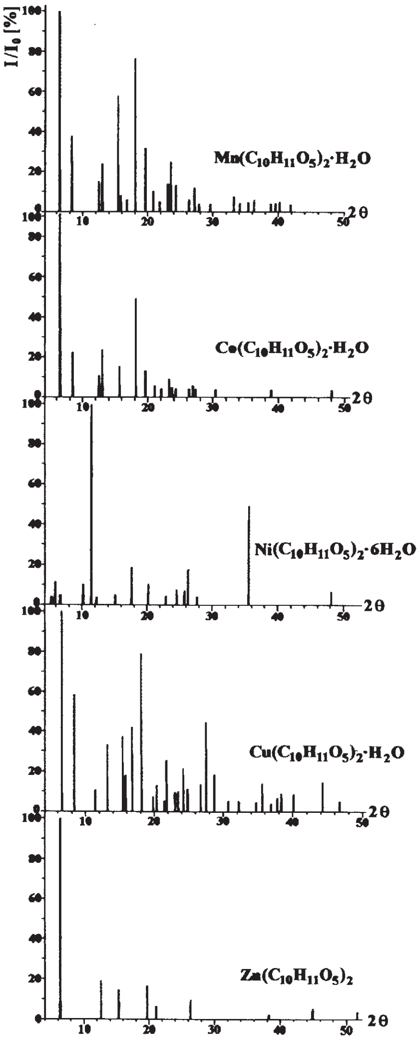


Fig. 2. Relationships between I/I_0 and 2θ for 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Zn(II).

tivity of TG–100 mg. The DTG and DTA sensitivities were regulated by a Derill computer programme. The products of the decompositions were calculated from the TG curves and verified by the registration of the diffraction pattern. The results are presented in Table III. The nature of the solid decomposition products was established on the basis of the TG curves and confirmed by IR and X-ray spectroscopy.

The magnetic susceptibilities of the polycrystalline samples of the 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) were measured by the Gouy method using a sensitive Cahn RM-2 balance. The measurements were carried out at a magnetic field strength of 9.9 k0e. $HgCo(SCN)_4$, with a magnetic susceptibility of 1.644×10^{-5} cm^3/g, was employed as the calibrant. The correction for diamagnetism of the constituent atoms was calculated using Pascal's constants.[39,40] The magnetism of the samples was found to be field independent. The magnetic moments were calculated according to Eq. (1)

$$\mu_{\mathrm{eff}} = 2.83\ (\chi_{\mathrm{M}} \times T)^{1/2} \tag{1}$$

and are presented in Table IV.

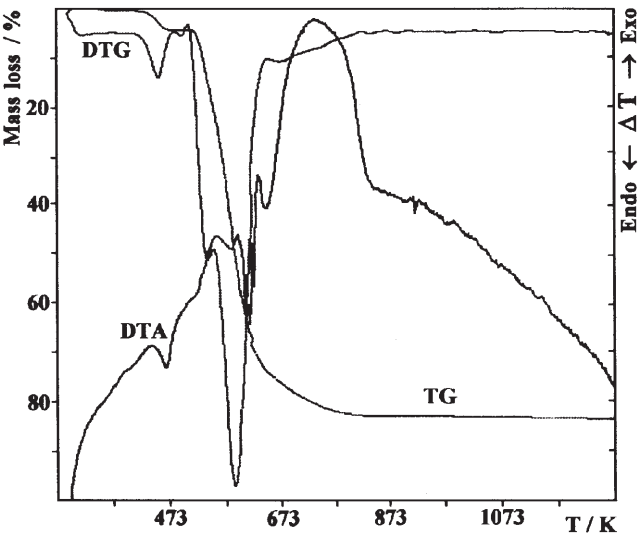


Fig. 3. TG, DTG and DTA curves of monohydrate of 3,4,5-trimethoxybenzoate of Cu(II).

RESULTS AND DISCUSSION

3,4,5-Trimethoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were obtained as crystalline hydrated or anhydrous products with a metal to ligand ratio of 1:2 and general formula: $M(C_{10}M_{11}O_5)_2 \cdot nH_2O$, $[Cu_2(C_{10}H_{11}O_5)_4(H_2O)_2]$, where M = Mn(II), Co(II), Ni(II), and Zn(II). For Ni(II) $n = 6$, for Mn(II) and Co(II) $n = 1$ and for Zn(II) $n = 0$. The colours of the complexes are typical for the respective M^{2+} ions (*i.e.*, Mn slightly pink, Co–pink, Ni–green, Cu–blue, Zn–white), which is connected with the electron density in the system.[41,42]

The complexes were characterized by elemental analysis (Table I) and IR spectroscopy (Table II, Fig. 1). The 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) show similar solid state IR spectra. However, the characteristic frequencies related to the carbonyl group are altered markedly when the acid is compared with the salts. The band at 1684 cm^{-1} originating from the –COOH group vibration, present in the spectrum of the acid, disappears in the spectra of the complexes and two bands arising from the asymmetric and symmetric vibrations of the COO^- group occur at 1552–1576 cm^{-1} and 1388–1400 cm^{-1}, respectively.[43–46] Bands attributed to asymmetric and symmetric C–H stretching modes of the $–CH_3$ groups are observed at 2944–2960 cm^{-1} and 2840 cm^{-1}, respectively. The bands of the ν(C–C) ring vibrations appear at 1616–1624, 1464–1520, 1268–1320 cm^{-1}. The bands of C–H stretching vibrations are observed at 936–1000 cm^{-1} and their out-of-plane deformation modes appear at 1184–1236 cm^{-1}. The bands with the values of their maxima at 3424–3504 cm^{-1}, characteristic of ν(O–H) vibrations, confirm the presence of water of crystallization molecules in the complexes. The bands due to metal–oxygen bond vibrations occur at 408–416 cm^{-1}. Their values increase in the following order: Mn(II) < Ni(II) < Zn(II) < Co(II) < Cu(II).[42,43,46] The values of the frequencies of the absorption bands of the

TABLE III. Temperature range of the thermal decomposition of the 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in air

Complex	ΔT_1/K	Mass loss / %		n	ΔT_2/K	Mass loss / %		Product of decomp.	ΔT_3/K	Mass loss / %		T_K / K	Final product of decomp.
		Calcd.	Found			Calcd.	Found			Calcd.	Found		
$MnL_2 \cdot H_2O$	421–468	3.64	3.8	1	545–1010	84.06	83.4	Mn_2O_3	–	–	–	1046	Mn_2O_3
$CoL_2 \cdot H_2O$	375–437	3.60	4.1	1	541–891	84.98	84.8	CoO	919–965	83.91	83.3	1023	Co_3O_4
$NiL_2 \cdot 6H_2O$	317–434	1834	17.6	6	497–860	89.99	88.7	Ni	877–924	87.31	86.8	1003	NiO
$[Cu_2L_4(H_2O)_2]$	424–468	3.57	3.5	1	518–811	84.21	83.8	CuO	–	–	–	841	CuO
ZnL_2	–	–	–	–	566–904	83.30	83.5	ZnO	–	–	–	933	ZnO

L = $C_{10}H_{11}O_5^-$, ΔT_1 = temperature range of the dehydration process, n = number of molecules of crystallization water lost in the endothermic dehydration step, ΔT_2, ΔT_3 = temperature ranges of anhydrous complex decomposition, T_K = temperature of oxide formation valency vibrations of the COO$^-$ group, ν_{as}(OCO) and ν_s(OCO) (Table II) indicate the various ways of the coordination of the carboxylate group[43–46] in the 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The separations $\Delta\nu$(OCO) in the complexes ($\Delta\nu$(OCO) = ν_{as}(OCO) – ν_s(OCO)) are smaller 152 cm^{-1}, 160 cm^{-1}), practically the same (176 cm^{-1}) and also greater (180 cm^{-1}, 188 cm^{-1}) than that in the sodium salt of 3,4,5-trimethoxybenzoic acid ($\Delta\nu$(OCO) = 170 cm^{-1}). This indicates the various degrees of ionic bonds in the analysed complexes and the different dentates of the carboxylate groups. The degree of ionic bond is smaller in the complexes of Mn(II) and Co(II) and greater in the 3,4,5-trimethoxybenzoates of Ni(II), Cu(II) and Zn(II) than that in the sodium salt. For all the complexes, the shifts of the frequencies of the ν_{as}(OCO) and ν_a(OCO) bands are smaller and lower, respectively, compared to those for sodium 3,4,5-trimethoxybenzoate. Accordingly, taking into account the spectroscopic criteria[43,44] and with regard to the Nakamoto criterion, the carboxylate groups appear to be monodentate (in the complexes of Zn(II) and Ni(II)), bidentate chelating (in the complexes of Mn(II) and Co(II)) and bidentate bridging (in the Cu(II) complex).

TABLE IV. Magnetic data of the 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II)

T / K	$MnL_2 \cdot H_2O$		$NiL_2 \cdot 6H_2O$		
	$\chi_M \times 10^6$	μ_{eff} / BM	T / K	$\chi_M \times 10^6$	μ_{eff} / BM
76	51172.67	5.58	76.15	17423.79	3.26
123	33081.43	5.71	123.15	9766.79	3.10
133	30731.04	5.72	133.15	8777.40	3.06
143	28850.73	5.75	143.15	8132.15	3.05
153	27171.89	5.77	153.15	7658.96	3.06
163	26030.27	5.83	163.15	7142.76	3.06
173	25022.96	5.89	173.15	6798.62	3.07
183	23881.35	5.92	183.15	6411.47	3.07
193	22806.89	5.94	193.15	6153.37	3.09
203	22001.04	5.98	203.15	5895.27	3.10
213	20926.58	5.97	213.15	5594.15	3.09
223	20657.96	6.07	223.15	5336.05	3.09
233	19919.27	6.10	233.15	5120.97	3.09
243	19449.19	6.15	243.15	4905.88	3.09
253	18844.81	6.18	253.15	4690.80	3.08
263	18374.73	6.22	263.15	4561.75	3.10
273	17770.35	6.23	273.15	4389.68	3.10

TABLE IV. Continued

T / K	$MnL_2 \cdot H_2O$		$NiL_2 \cdot 6H_2O$		
	$\chi_M \times 10^6$	μ_{eff} / BM	T / K	$\chi_M \times 10^6$	μ_{eff} / BM
283	17367.43	6.27	283.15	4303.64	3.12
293	17031.66	6.32	293.15	4131.58	3.11
303	16427.27	6.31	303.15	4045.54	3.13

where L = $C_{10}H_{11}O_5^-$

The X-ray diffractograms of all complexes were recorded. Their analysis suggests that they are polycrystalline compounds of various symmetries and different structures (Fig. 2)[47,48] The hydrated complexes of Mn(II), Co(II), Ni(II) and Cu(II) are characterized by low symmetry, wereas the anhydrous 3,4,5-trimethoxybenzoate of Zn(II) by a higher symmetry. The structures of the complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have not been determined because single crystals have not been obtained.

The thermal stability of the 3,4,5-trimethoxybenoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was studied in air in the range of 293–1273 K (Table III, Fig. 3). Their thermal decompositions reveal them to be hexahydrate (complex of Ni(II)), monohydrates (complexes of Mn(II), Co(II) and Cu(II)) and anhydorus (complex of Zn(II)), which is consistent with the elemental and IR spectral analyses (Table I). The complexes were stable in air at room temperature. They decompose in various ways when heated in air. The monohydrate of the 3,4,5-trimethoxybenzoate of Co(II) is stable up to 375 K, on heating it loses water in one step in the temperature range of 375–437 K. The weight loss calculated from the TG curve is equal to 4.1 % (the theoretical value is 3.6 %) which corresponds to the loss of one water molecule. Considering the temperature at which the dehydration process of the Co(II) complex occurs and the way in which it proceeds, it is assumed that the water molecule is in the outer sphere of the complex coordination.[46,49,50] The anhydrous 3,4,5-trimethoxybenozate of Co(II) forms CoO in the range of 541–891 K which is oxidized to Co_3O_4 (919–965 K), the final product of the complex decomposition. The hexahydrate of Ni(II) 3,4,5-trimethoxybenzoate is stable up to 317 K when heated in air. During subsequent heating, it dehydrates in one step and forms the anhydrous complex. The mass loss calculated from the TG curve being equal to 17.6 % corresponds to the loss of six water molecules (theoretical value is 18.34 %). The anhydrous compound decomposes in the temperature range of 497–860 K forming Ni, which is oxidized (877–924 K) to the final product of decomposition, NiO. The reduction process is connected with an endothermic effect seen in the DTA curve, while the oxidation of Ni to NiO with an exothermic one. The anhydrous Zn(II) 3,4,5-trimethoxybenzoate decomposes to ZnO in one step in the temperature range of 566–904 K. The mass loss calculated from the TG curve is equal to 83.5 % (theoretical value is 83.30 %). The monohydrates of Mn(II) and Cu(II) 3,4,5-trimethoxybenzoates are stable up to 421–424 K and subsequently they first lose one water molecule in one step forming the anhydrous complexes, before decomposing directly to the oxides of the corresponding metals (Mn_2O_3, CuO). The dehydration processes are connected with an endothermic effect seen on the DTA curves (Fig. 3).

The results indicate the following routes thermal decompositions of the complexes:

$MnL_2{\cdot}H_2O \rightarrow MnL_2 \rightarrow Mn_2O_3$
$CoL_2{\cdot}H_2O \rightarrow CoL_2 \rightarrow CoO \rightarrow Co_3O_4$
$NiL_2{\cdot}6H_2O \rightarrow NiL_2 \rightarrow Ni \rightarrow NiO$
$[Cu_2L_4(H_2O)_2] \rightarrow Cu_2L_4 \rightarrow CuO$
$ZnL_2 \rightarrow ZnO$; where $L = C_{10}H_{11}O_5^-$

In the series of hydrated Mn(II), Co(II), Ni(II) and Cu(II) 3,4,5-trimethoxybenzoates, the most stable are the complexes of Mn(II) and Cu(II), while the least thermally stable is Ni(II) hexahydrate (Table III, Fig. 4). The temperatures of the

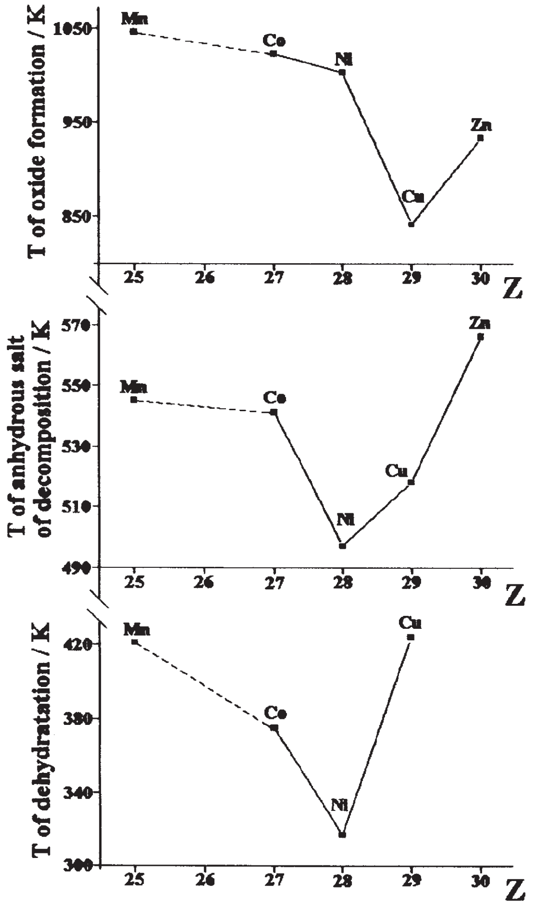


Fig. 4. Dependences of the temperatures of the initial dehydration process, of anhydrous complex decompositions and of oxide formation of 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II).

thermal stabilities of the anhydrous 3,4,5-trimethoxybenazoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) do not change regularly with increasing atomic number of the element (Fig. 4). The anhydrous complex of Zn(II) is the most thermally stable, while the least thermally stable is the anhydrous 3,4,5-trimethoxybenzoate of Ni(II). The temperature of oxide formation is the highest for Mn_2O_3 and the lowest for CuO (Table III, Fig. 4).

The solubility values of the 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in water (293 K) are given in Table I. They are in the order of $10^{-2} - 10^{-4}$ mol dm^{-3}. The complex of Co(II) is the most soluble salt while that of Cu(II) is the least. From the solubility data, it appears that 3,4,5-trimethoxybenzoic acid may be used for the separation of Co(II) and Cu(II) by ion-exchange chromatography or by extraction methods because of the great difference in their solubility values.

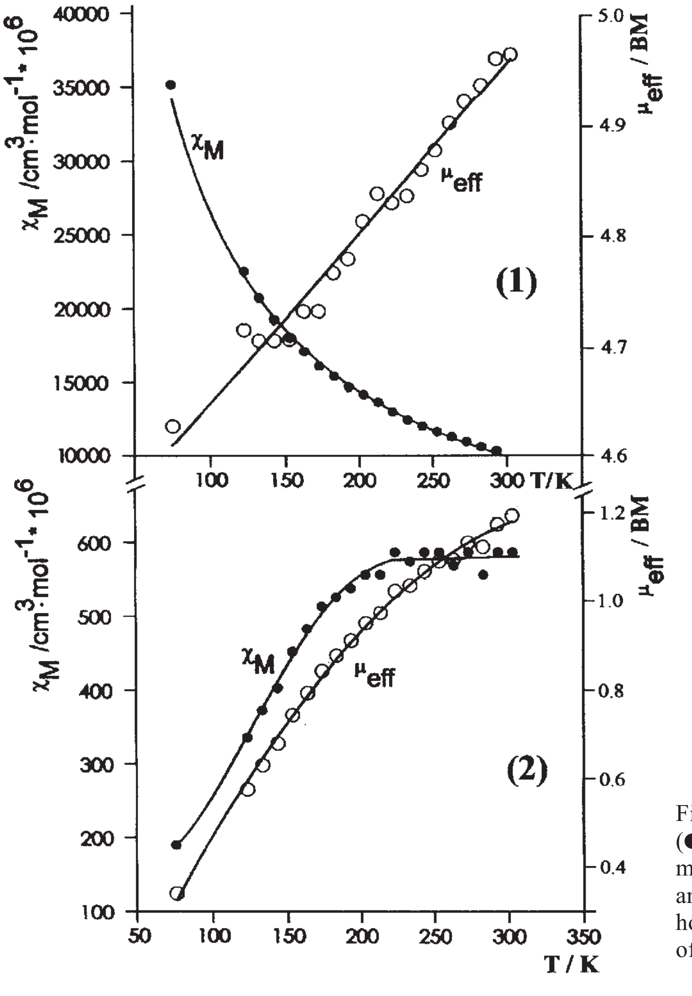
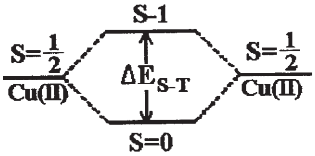


Fig. 5. Molar susceptibilities (●) and effective magnetic moments (o) of the Co(II) (1) and Cu(II) (2) 3,4,5-trimethoxybenzoates as a function of temperature.

The magnetic susceptibilities of Mn(II), Co(II), Ni(II) and Cu(II) 3,4,5-trimethoxybenzoates were measured in the temperature range of 76 – 303 K (Table IV, Fig. 5). The 3,4,5-trimethoxybenzoate of Zn(II) is, as expected, diamagnetic. The values of the magnetic susceptibilities of the Mn(II), Co(II) and Ni(II) complexes obey the Curie–Weiss law, since they decrease gradually with increasing temperature. The paramagnetic dependences of magnetic susceptibility values as a function of temperatures are presented in Table IV and Fig. 5. The χ_M values for Mn(II), Co(II) and Ni(II) 3,4,5-trimethoxybenzoates show a gradual decrease with increasing temperature, which may indicate a ferromagnetic interaction between the metal ions. The experimentally determined magnetic moment values for the 3,4,5-trimethoxybenzoates of Mn(II), Co(II) and Ni(II) were found to be in the ranges: 5.58–6.31 BM, 4.63–4.96 BM and 3.05–3.26 BM, respectively, The experimental data reveal that the magnetic moments of the 3,4,5-trimethoxybenzoates of Mn(II) and Ni(II) are connected with spin-only moments. Their theoretical values at room temperatures are equal to 5.92 BM for Mn(II) and 2.83 BM for Ni(II). In the case of Co(II) 3,4,5-trimethoxybenzoate, the μ_{eff} values are equal to 4.63–4.96 BM (Table IV). The measured magnetic moment for the Co(II) complex at room temperature is 4.96 BM. This value differs from the $\mu_{\text{s.o}}$ value (3.88 BM). This relatively a large difference results from a spin-orbital coupling.[23] The experimental data suggest that the Mn(II), Co(II) and Ni(II) complexes are high-spin complexes with octaedral coordination with weak ligand fields. They probably crystallized as monomers. The μ_{eff} values of Cu(II) 3,4,5-trimethoxybenzoate determined in the temperature range of 76–303 K change from 0.34 BM (at 76 K) to 1.19 BM (at 303 K). Such a dependence is behaviour typical of copper dimers. The μ_{eff} values display a minimum at 76 K and a maximum at room temperature. The room temperature magnetic moment per Cu ($\mu_{\text{eff}} = 1.19$ BM) is similar to those observed for other dinuclear Cu(II) compounds[24,25] and is lower than the $\mu_{\text{s.o}} = 1.73$ BM. This behaviour indicates an antiferromagnetic coupling between the two Cu(II) centres. The temperature dependence of the magnetic results are plotted in Fig. 5. The magnetic moment values of the Cu(II) complex decrease from 1.19 BM at 303 K to 0.34 BM at 76 K, as a consequence of depopulation of the excited triplet (S = 1) state. It is well-known that the interaction between two S = 1/2 metal atoms in a dimer leads to two molecular states: a spin singlet (S = 0) and a triplet (S = 1) separated by 2 J. The interaction will be antiferromagnetic ($J < 0$) if S = 0 is the ground state; on the contrary, if S = 1 is the ground state, the interaction will be ferromagnetic ($J > 0$).[26,27] Whereas ferromagnetic contributions are usually small, antiferromagnetic ones may be considered as being proportional to the square of the gap between the molecular orbitals constructed from the magnetic orbitals.[28] For Cu(II) dinuclear complexes, the magnetic coupling constant J is directly related to the energy separation of the singlet and triplet-states (Eq. (2)).

$$2J = E_S - E_T \tag{2}$$

In the lower temperature range, only the lowest levels are occupied in the dimer. They may be followed by the course of $\chi_{Cu} = f(T)$ for copper(II) dimers with states S = 1 and S = 0.



ST = singlet-triplet energy gap

The electron population in both levels is combined with the Boltzman contribution law and is temperature dependent. At higher temperatures and for relatively high exchange parameters |J| ($J > 0$), both states are occupied (the triplet state dominates) and the magnetic moment has values close to the pure spin one (1.73 BM), but is usually lower. With decreasing temperature, the population of the triplet state decreases and within the lowest temperature ranges only the singlet state is occupied (S = 0) and $\mu = 0$ BM.

The type and the magnitudes of magnetic exchange interaction in dinuclear complexes depend on the bridged identity, on the distance between the metal ions, on the bond angles at the bridging atom, on the dihedral angle between the planes containing the Cu(II) ions and also on the metal-bridging ligand bond length. The magnetic behaviour of Cu(II) 3,4,5-trimethoxybenzoate indicates the mode of metal–ligand coordination and the geometry around the metal ions. The geometry exerts a marked influence on the magnetic exchange interaction. Therefore, the weak antiferromagnetic interaction may be brought about mainly by the geometric structures of this complex and the properties of the bridged ligand.[29–38] The magnetic properties reveal that the complex of Cu(II) is a dimer with a bidentate bridging carboxylate group. Such a dentate of the COO^- group was confirmed by IR spectral data (Table II).

ИЗВОД

ФИЗИЧКОХЕМИЈСКЕ ОСОБИНЕ 3,4,5-ТРИМЕТОКСИБЕНЗОАТА Mn(II), Co(II), Ni(II), Cu(II) И Zn(II)

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Синтетизована су једињења Mn(II), Co(II), Ni(II), Cu(II) и Zn(II) са анјоном 3,4,5-триметоксибензоеве киселине опште формуле $M(C_{10}H_{11}O_5)_2 \cdot nH_2O$, где је $n = 6$ за Ni(II), $n = 1$ за Mn(II), Co(II), Cu(II) и $n = 0$ за Zn. Ова једињења су карактерисана елементалном анализом, IR спектроскопијом, рендгенском дифракцијом, термогравиметријом и магнетним проучавањима. То су кристална једињења које карактеришу различите симетрије. При грејању на ваздуху до 1273 K ова једињења се распадају на различите начине. Прво, у једном ступњу она се дехидришу до анхидроване соли. Крајњи производ разлагања су оксиди одговарајућих метала (Mn_2O_3, Co_3O_4, NiO, CuO, ZnO). Растворљивости анализираних комплекса у води на 293 K су реда величине 10^{-2} – 10^{-4} mol dm^{-3}. Магнетни сусцептибилитети комплекса Mn(II), Co(II), Ni(II) и Cu(II) мерени су у опсегу 76 – 303 K и изражунати магнетни моменти. Резултати показују да су Mn(II), Co(II) и Ni(II) 3,4,5-триметоксибензоати високоспински комплекси, док Cu(II) ствара димер $[Cu_2(C_{10}H_{11}O_5)_4(H_2O)_2]$. Карбоксилатне групе се везују као монодентантни или бидентатни хелатни или премошћујући лиганди.

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