

Magnetic, Spectral, and Thermal Characterization of 2,3,4- and 3,4,5-Trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II)

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The physicochemical properties and thermal stability in air of 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) were compared and the influence of the position of —OCH₃ substituent on their thermal stability and magnetic properties was investigated. The complexes of these series are crystalline, hydrated or anhydrous salts with colours typical of M²⁺ ions. The carboxylate ion is a monodentate and bidentate chelating or bridging group. The thermal stability of complexes was studied in the temperature range of 293—1273 K. The solubility in water at 293 K for these analyzed complexes is in the order of 10⁻³—10⁻⁴ mol dm⁻³ for 2,3,4-trimethoxybenzoates and 10⁻²—10⁻⁴ mol dm⁻³ for 3,4,5-trimethoxybenzoates. The magnetic susceptibilities for trimethoxybenzoates were measured over the range of 76—303 K and their magnetic moments were calculated. The results show that compounds of Mn(II), Co(II), and Ni(II) are high-spin complexes but those of Cu(II) form dimers.

2,3,4- and 3,4,5-Trimethoxybenzoic acids having formula C₁₀H₁₁O₅ are white, crystalline solids, sparingly soluble in cold water. Their solubility in water increases with the rise of temperature [1, 2]. The literature survey shows that there is some information about the complexes of 2,3,4-trimethoxybenzoic acid anion with rare-earth element ions(III) [3—5]. The salts of 3,4,5-trimethoxybenzoic acid anion only with the following cations: K⁺, Cu²⁺, Ag⁺, Ca²⁺, Ba²⁺, and rare-earth elements(III) have been also obtained as solids [4, 6—8].

In the literature there is no information about these acid complexes with Mn(II), Co(II), Ni(II), and Cu(II). Therefore we decided to obtain them as solids, to examine some of their physicochemical properties and to compare them in order to investigate the influence of the positions of methoxy groups in the benzene ring on such properties of these compounds as: thermal stability, solubility in water at room temperature, dentates of carboxylate groups, colours of the complexes, and their magnetic characterizations.

EXPERIMENTAL

For the preparation of the complexes the following nitrates(V) of *d*-block elements were used: Mn(NO₃)₂ · 6H₂O, Co(NO₃)₂ · 6H₂O, Ni(NO₃)₂ · 6H₂O, and Cu(NO₃)₂ · 3H₂O (REAGENTS – Chemical Enter-

prise in Lublin, Poland). The 2,3,4- and 3,4,5-trimethoxybenzoic acids used for the preparation of complexes were produced by Aldrich Chemical Company. In the experiments the solution of NH₃aq (25 %) produced by Polish Chemical Reagents in Gliwice was also used.

The complexes of 2,3,4- and 3,4,5-trimethoxybenzoic acid anions with cations of Mn(II), Co(II), Ni(II), and Cu(II) were obtained by the addition of equivalent quantities of 0.1 M-ammonium 2,3,4- or 3,4,5-trimethoxybenzoate (pH ≈ 5) to hot solutions containing the nitrates(V) of these 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 analyzer.

The IR spectra of complexes were recorded over the $\tilde{\nu}$ range of 400—4000 cm⁻¹ using M-80 spectrophotometer (Zeiss, Jena). Samples for IR spectra measurements were prepared as KBr discs.

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

The thermal stability and decomposition of complexes were determined by Paulik—Paulik—Erday Q-

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Table 1. Elemental Analysis Data of Complexes and their Solubilities in Water (at 293 K)

Complex	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			Solubility mol dm ⁻³
	H	C	M	
MnL ₂	4.61	50.28	11.50	2.77×10^{-3}
	4.62	50.32	14.34	
CoL ₂	4.57	49.86	12.24	7.15×10^{-4}
	4.56	49.69	13.47	
NiL ₂	4.57	49.89	12.20	7.51×10^{-4}
	4.57	49.50	12.28	
CuL ₂ · H ₂ O	4.76	47.63	12.62	2.19×10^{-4}
	4.78	47.77	12.78	
MnL ₂ [*] · H ₂ O	4.85	48.49	11.09	3.42×10^{-2}
	4.70	48.40	11.50	
CoL ₂ [*] · H ₂ O	4.81	48.10	11.80	6.19×10^{-2}
	4.70	48.30	12.20	
NiL ₂ [*] · 6H ₂ O	5.77	40.76	9.97	6.15×10^{-3}
	5.10	40.60	10.30	
CuL ₂ [*] · H ₂ O	4.77	47.66	12.61	6.58×10^{-4}
	4.70	47.80	12.90	

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 a Derill computer program. The products of decompositions were calculated from TG curves and verified by the diffraction pattern registration. The nature of the solid products of decomposition was established on the basis of the data of TG curves and it was confirmed by IR and X-ray spectra as well.

Magnetic susceptibilities of polycrystalline samples of complexes were investigated in the temperature range of 76–303 K. The measurements were carried out using the Gouy method. The calibrant employed was Co[Hg(SCN)₄] for which the magnetic susceptibility was assumed to be 1.644×10^{-5} cm⁻³ g⁻¹. All the measured susceptibility values were corrected for diamagnetism of the constituent atoms using the Pascal's constants [9, 10]. Magnetic moments were calculated according to the equation

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

RESULTS AND DISCUSSION

2,3,4-(L) and 3,4,5-Trimethoxybenzoates (L^{*}) of the studied metals were obtained as crystalline products with a metal ion to ligand mole ratio of 1 : 2 and a general formula M(C₁₀H₁₁O₅)₂ · nH₂O where M = Mn, Co, Ni, Cu and n = 6 for

3,4,5-trimethoxybenzoate of Ni(II), n = 1 for 2,3,4-trimethoxybenzoate of Cu(II) and 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Cu(II), and n = 0 for 2,3,4-trimethoxybenzoates of Mn(II), Co(II), and Ni(II) (Table 1). In these two series of trimethoxybenzoates the number of crystallization water molecules changes with the change of —OCH₃ group positions in benzene ring. The colours of the complexes are typical of the appropriate divalent ions, which is connected with the structure of molecules and electron density in benzene ring. In these molecules the d → d electronic transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wavelengths, which depends on the nature of metal ion [11, 12]. The compositions of the complexes were established on the basis of elemental analysis and IR spectral data. Their external crystalline forms were also estimated and X-ray spectra analysis of 2,3,4- and 3,4,5-trimethoxybenzoates suggests them to be polycrystalline compounds with low symmetry and different structures [13]. From the IR spectra analysis it appears that the carboxylate groups have various positions. They may be: monodentate (MnL₂, CoL₂, NiL₂, and NiL₂^{*} · 6H₂O), bidentate chelating (MnL₂^{*} · H₂O and CoL₂^{*} · H₂O) and bidentate bridging groups (CuL₂ · H₂O and CuL₂^{*} · H₂O) [14–16] (Table 2). The magnitudes of separation Δν_{OCO} (Δν_{OCO} = ν_{asOCO} – ν_{sOCO}) characterizing the type of metal–oxygen bond change in the ranges from 152–188 cm⁻¹ for 3,4,5-trimethoxybenzoates to 160–258 cm⁻¹ for 2,3,4-trimethoxybenzoates. In these complexes being compared the participation of M–O ionic bond is presumably larger in the case of 2,3,4-trimethoxybenzoates of Mn(II), Co(II), and Ni(II) than that in 3,4,5-trimethoxybenzoates of these elements. The bands of metal–oxygen bond change depending on the position of —OCH₃ substituents in aromatic ring. In the case of 3,4,5-trimethoxybenzoates of Mn(II), Co(II), and Ni(II) they appear in the range of 408–420 cm⁻¹ while for 2,3,4-trimethoxybenzoates they are only at 420 cm⁻¹. For 2,3,4-trimethoxybenzoate of Cu(II) the M–O bond vibration band occurs at 420 cm⁻¹, whereas for 3,4,5-trimethoxybenzoate it is at 440 cm⁻¹. The frequencies of the bands due to ν_{asOCO} vibration change depending on the position of —OCH₃ groups in aromatic ring and they are at 1560–1628 cm⁻¹ for 2,3,4-trimethoxybenzoates and at 1552–1576 cm⁻¹ for 3,4,5-trimethoxybenzoates. Similarly, the frequencies of the bands of ν_{sOCO} vibrations have various values: 1370–1400 cm⁻¹ for 2,3,4-trimethoxybenzoates and 1388–1400 cm⁻¹ for 3,4,5-trimethoxybenzoates. In the case of 2,3,4-trimethoxybenzoates of Mn(II), Co(II), and Ni(II) the bands of ν_{asOCO} and ν_{sOCO} vibrations are changed to higher and lower frequencies, respectively, compared to those for 3,4,5-trimethoxybenzoates of these elements but for 2,3,4-trimethoxybenzoate of Cu(II) these bands are moved, conversely, to lower and higher

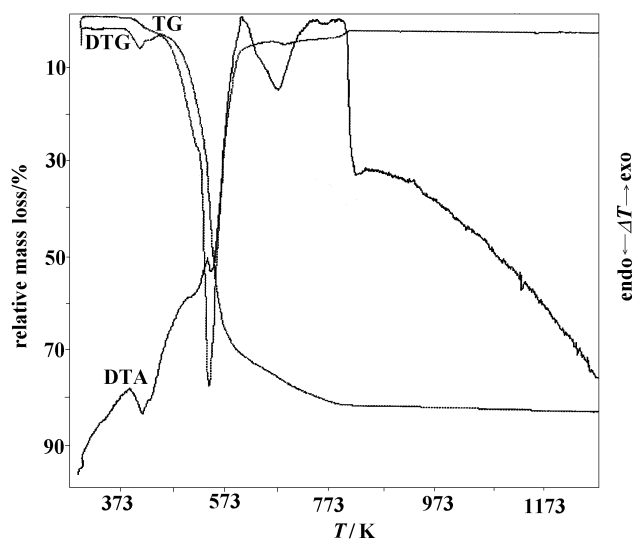
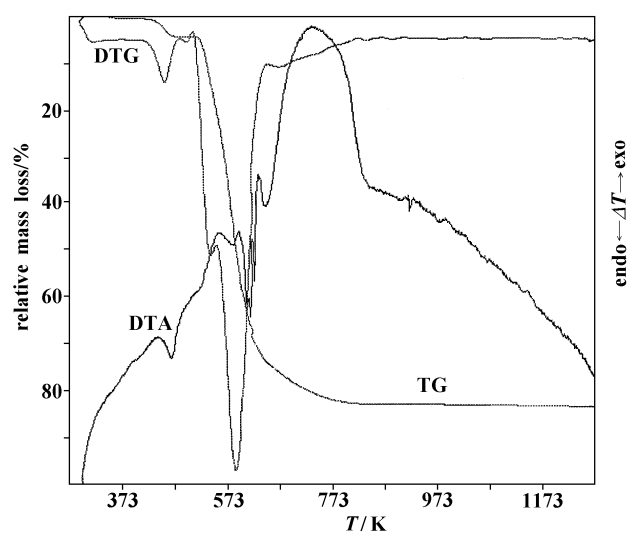
Table 2. Frequencies of the Maxima of the Absorption Bands of COO⁻ for the Studied Complexes and Na

Complex	$\tilde{\nu}/\text{cm}^{-1}$				Complex	$\tilde{\nu}/\text{cm}^{-1}$			
	ν_{asOCO}^-	ν_{sOCO}^-	$\Delta\nu_{\text{OCO}}^-$	$\nu_{\text{M-O}}$		ν_{asOCO}^-	ν_{sOCO}^-	$\Delta\nu_{\text{OCO}}^-$	$\nu_{\text{M-O}}$
MnL ₂	1620	1380	240	420	MnL ₂ * · H ₂ O	1552	1400	152	408
CoL ₂	1628	1370	258	420	CoL ₂ * · H ₂ O	1560	1400	160	420
	1620		250						
NiL ₂	1628	1370	258	420	NiL ₂ * · 6H ₂ O	1576	1388	188	420
CuL ₂ · H ₂ O	1560	1400	160	420	CuL ₂ * · H ₂ O	1572	1396	176	440
NaL	1610	1390	220		NaL*	1580	1410	170	

Table 3. Decomposition Data for the Studied Complexes

Complex	$\Delta T_1/\text{K}$	Relative mass loss/%		<i>n</i>	$\Delta T_2/\text{K}$	Relative mass loss/%		Final product of decomposition
		calc.	found			calc.	found	
MnL ₂	—	—	—	—	505—989	84.03	80.90	Mn ₃ O ₄
CoL ₂	—	—	—	—	517—1205	84.44	80.43	CoO
NiL ₂	—	—	—	—	507—906	83.37	83.61	NiO
CuL ₂ · H ₂ O	390—443	3.57	3.49	1	443—813	84.22	84.00	CuO
MnL ₂ * · H ₂ O	421—468	3.64	3.80	1	545—1010	84.06	83.40	Mn ₂ O ₃
CoL ₂ * · H ₂ O	375—437	3.60	4.10	1	541—965	83.91	83.30	Co ₃ O ₄
NiL ₂ * · 6H ₂ O	317—434	18.34	17.60	6	497—924	87.31	86.80	NiO
CuL ₂ * · H ₂ O	424—468	3.57	3.50	1	518—811	84.21	84.00	CuO

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

**Fig. 1.** TG, DTG, and DTA curves of 2,3,4-trimethoxybenzoate of Cu(II) in air.**Fig. 2.** TG, DTG, and DTA curves of 3,4,5-trimethoxybenzoate of Cu(II) in air.

frequencies, respectively, in comparison with those for 3,4,5-trimethoxybenzoate of Cu(II) (Table 2). The changes in the values of these band frequencies result from the different position of —OCH₃ groups in benzene ring and from various influences of inductive and mesomeric effects on electron densities in the molecules of these complexes [17, 18].

The thermal stability of these complexes was stud-

ied in air in the range of 293—1273 K. The obtained results are presented in Table 3 and Figs. 1 and 2. When heated at 293—1273 K the complexes decompose in various steps. The anhydrous 2,3,4-trimethoxybenzoates of Mn(II), Co(II), and Ni(II) are stable up to 505—517 K. The most thermally stable is 2,3,4-trimethoxybenzoate of Co(II), while that of Mn(II) has the least thermal stability. In the range

of 505—1205 K 2,3,4-trimethoxybenzoates of Mn(II), Co(II), and Ni(II) are directly decomposed to the oxides of appropriate elements. The relative mass losses calculated from TG curves change from 80.90 % to 83.61 %, which corresponds to the formations of the oxides of respective metals: Mn_3O_4 , CoO, and NiO to be the final products of complex decompositions. The monohydrate of 2,3,4-trimethoxybenzoate of Cu(II) is stable up to 390 K. When heated in the temperature range of 390—443 K, it dehydrates and forms an anhydrous complex. The relative mass loss calculated from TG curve being equal to 3.49 % corresponds to the loss of one molecule of crystallization water (theoretical value is 3.57 %). The dehydration process is connected with an endothermic effect seen on DTA curve. In the temperature range of 443—813 K the anhydrous 2,3,4-trimethoxybenzoate of Cu(II) is finally decomposed to CuO.

Monohydrates of 3,4,5-trimethoxybenzoates of Mn(II), Co(II), and Cu(II) are stable up to 375—424 K. The most thermally stable is the complex of Cu(II), whereas that of Co(II) is of the least thermal stability. During heating the complexes dehydrate (375—468 K) in one step losing water molecule and form the anhydrous compounds. The relative mass losses calculated from TG curve are in the range of 3.49—4.10 % (the theoretical values are 3.57—3.64 %), which corresponds to the loss of only one water molecule. The dehydration process is connected with an endothermic effect. Next, when heated in the range of 518—1010 K the anhydrous 3,4,5-trimethoxybenzoates of Mn(II), Co(II), and Cu(II) are finally decomposed to the oxides of the appropriate elements. The relative mass losses calculated from TG curves are changed from 83.30 % to 84.00 %, which is indicative of the formations of the oxides of respective metals: Mn_2O_3 , Co_3O_4 , and CuO are the final products of complex decompositions. The hexahydrate of 3,4,5-trimethoxybenzoate of Ni(II) heated in air is stable up to 317 K. Next, during the rise of temperature it dehydrates in one step and forms the anhydrous complex. The relative mass loss calculated from TG curve being equal to 17.6 % corresponds to the loss of six water molecules (theoretical value is 18.34 %). The anhydrous 3,4,5-trimethoxybenzoate of Ni(II) in the temperature range of 497—924 K is decomposed to NiO, which is the final product of decomposition. The temperatures of the thermal stabilities of anhydrous 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) do not change regularly with the increase of atomic number of elements. The least thermally stable is anhydrous 3,4,5-trimethoxybenzoate of Ni(II) while the most thermally stable is the complex of Mn(II). Considering the temperatures at which the dehydration process of 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) takes place and the way by which it proceeds, it is possible to assume that the molecules of water are differently bound

in the outer sphere of complex coordination. According to Nikolaev *et al.* [20] and Singh *et al.* [21] water eliminated below 424 K can be considered as water of crystallization and water eliminated above 424 K may be that coordinated to the central ion [22]. In our hydrated complexes water is generally eliminated below 424 K. Therefore, it is assumed to be crystallization water. From the comparison of the ways of decompositions of 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) it appears that 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II) and Co(II) form different metal oxides being the final products of complex decompositions. The final products of complex decompositions were identified roentgenographically and on the basis of IR spectra analysis. From the comparison of the decomposition way results for the two series of trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) it follows that the different position of $-OCH_3$ substituents in benzene ring influences the decomposition process being connected with the various participations of the inductive and mesomeric effects of methoxy groups in the electron density of the system. The thermal stability of anhydrous trimethoxybenzoates of Mn(II), Co(II), and Cu(II) increases in the order: 2,3,4-, 3,4,5-. In the case of Ni(II) complexes thermal stability decreases: 3,4,5-, 2,3,4-. The various positions of methoxy groups in benzene ring influence the number of crystallization water molecules in the complexes and the positions of the bands of M—O, and asymmetrical and symmetrical vibrations of carboxylate groups in their IR spectra. In principle, 2,3,4-trimethoxybenzoate ion forms with Mn(II), Co(II), Ni(II) the anhydrous complexes, while the 3,4,5- isomer the hydrated ones. The number of crystallization water molecules, the positions of the bands of asymmetrical vibration bonds of carboxylate group and M—O for complexes of Cu(II) and those for symmetrical vibration bonds of COO^- group for trimethoxybenzoates of Mn(II), Co(II), Ni(II) increase in the order: 2,3,4-, 3,4,5-. The positions of the bands of asymmetrical vibration bonds of COO^- group and M—O for complexes of Mn(II), Co(II), Ni(II), and of the bands of symmetrical vibration bonds of COO^- group for trimethoxybenzoates of Cu(II) decrease in the sequence: 2,3,4-, 3,4,5-.

The solubilities of the 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) in water at 293 K were measured and they are in the orders of 10^{-4} — 10^{-3} mol dm^{-3} for 2,3,4-trimethoxybenzoates and 10^{-4} — 10^{-2} mol dm^{-3} for 3,4,5-trimethoxybenzoates. The complexes of 3,4,5-trimethoxybenzoates are better soluble than those of 2,3,4-trimethoxybenzoates (Fig. 3). The 3,4,5-trimethoxybenzoate of Co(II) is the most soluble salt, while the 2,3,4-trimethoxybenzoate of Cu(II) is the least soluble. In the case of 3,4,5-trimethoxybenzoates the complex of Co(II) is also the most soluble, whereas that of Cu(II) is the least soluble. In the series of 2,3,4-

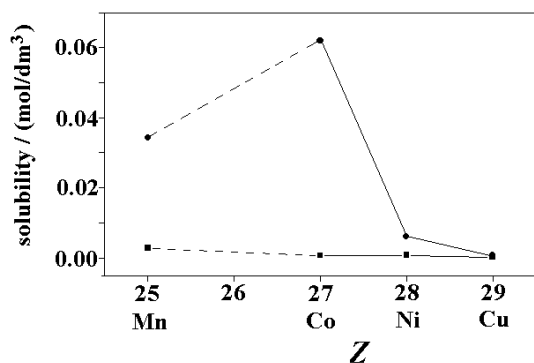


Fig. 3. Relationship between the values of solubilities of complexes and Z of the elements. ■ 2,3,4-Trimethoxybenzoates; ● 3,4,5-trimethoxybenzoates.

trimethoxybenzoates the complex of Mn(II) is the best soluble, while that of Cu(II) is the least soluble. The changes in the values presented above are connected with the various influences of inductive, mesomeric, and steric effects of methoxy groups on the electron density of the system depending on their position in benzene ring. The inductive effects of each methoxy group cause the delocalization of the electrons in the molecule and the change of its energy state brought about the conjugation of electrons. It leads to the stabilization of the system [17–19]. The appearance of the mesomeric effect causes the characteristic changes in the molecule of the organic compound. Therefore, the lengths of some of σ bonds may be changed. This can be observed in the positions of the bands of the characteristic group vibrations in the IR spectra of complexes and in their various thermal stabilities in air during heating from 293 K to 1273 K.

2,3,4-Trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) differ from the 3,4,5-trimethoxybenzoates of those elements in the positions of $-\text{OCH}_3$ groups in benzene ring, which causes the various steric effects in these complexes. The steric effect entirely depends on the spatial arrangements of atoms in the molecule. It is caused by the intensive repulsive forces, when approaching nonbonded atoms are so close that they may be repellent. From the obtained results it appears that 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) contain more water molecules than 2,3,4-trimethoxybenzoates of those elements. They are more thermally stable (except Ni(II) complex) in air and are better soluble in water (at 293 K) than the complexes of 2,3,4-isomer. 2,3,4-Trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) are anhydrous compounds because the $-\text{OCH}_3$ groups are close to COO^- group and the water molecules cannot be easily bonded in the complexes because of the steric effects. In the 3,4,5-trimethoxybenzoates of d -block elements the lack of steric effects round COO^- group causes the formation of hydrated com-

plexes and their greater thermal stability and better solubility in water than in the case of 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II).

In order to define the nature of metal ion—oxygen atom of carboxylate group bonding in complexes and to estimate the ways of metal ion—ligand coordinations, the magnetic susceptibilities of compounds were determined over the range of 76–303 K (Table 4).

The values of magnetic susceptibilities for 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II), Co(II), and Ni(II) obey the Curie—Weiss law because they decrease gradually with rising temperature. The paramagnetic dependences of magnetic susceptibility values as functions of temperatures are presented in Table 4. They give information about the magnetic interaction between paramagnetic centres. When the χ_M values increase with rising temperature, it indicates the antiferromagnetic interaction but if the χ_M values decrease with an increase in temperature, the magnetic interaction is ferromagnetic. The χ_M values for 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II), Co(II), and Ni(II) show a gradual decrease with rising temperature. It indicates the tendency to a ferromagnetic interaction between metal ions. The magnetic moment values experimentally determined for 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II), Co(II), and Ni(II) were found to be in the ranges of: 5.64–6.57 μ_B and 5.58–6.32 μ_B for Mn(II) complexes, respectively, 4.73–5.17 μ_B and 4.63–4.96 μ_B for complexes of Co(II), and 3.26–3.35 μ_B and 3.13–3.26 μ_B for complexes of Ni(II), respectively. The experimental data show that the magnetic moments of 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II), and Ni(II) are connected with spin-only moments. In the case of 2,3,4- and 3,4,5-trimethoxybenzoates of Co(II) the effective magnetic moments are equal to 4.73–5.17 μ_B and 4.63–4.96 μ_B , respectively (Table 4). The magnetic moments measured for Co(II) complexes are 5.09 μ_B and 5.06 μ_B at room temperature. These values differ from that of the spin-only moment which amounts to 3.88 μ_B . This relatively a large difference between measured and calculated values results from a spin-orbit coupling [23]. The experimental data suggest that 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II), Co(II), and Ni(II) are the high-spin complexes with octahedral coordination and the weak ligand fields. Probably they crystallize as monomers.

The effective magnetic moment values of 2,3,4- and 3,4,5-trimethoxybenzoates of Cu(II) determined in the temperature range of 76–303 K change from 0.27 μ_B (at 77 K) to 1.42 μ_B (at 296 K) for 2,3,4-trimethoxybenzoate, and from 0.34 μ_B (at 77 K) to 1.19 μ_B (at 298 K) for 3,4,5-trimethoxybenzoate. This type of dependence is typical behaviour of copper dimers exhibiting characteristic antiferromagnetic interactions between Cu(II) centres which obey the

Table 4. Values of μ_{eff} for the Complexes of Metals

Mn			Co			Ni			Cu		
T	$\chi_M \cdot 10^6$	μ_{eff}	T	$\chi_M \cdot 10^6$	μ_{eff}	T	$\chi_M \cdot 10^6$	μ_{eff}	T	$\chi_M \cdot 10^6$	μ_{eff}
K	$\text{dm}^3 \text{mol}^{-1}$	μ_B	K	$\text{dm}^3 \text{mol}^{-1}$	μ_B	K	$\text{dm}^3 \text{mol}^{-1}$	μ_B	K	$\text{dm}^3 \text{mol}^{-1}$	μ_B
2,3,4-Trimethoxybenzoates											
76	520923	5.64	76	36560	4.73	77	17280	3.26	76	58	0.27
123	36109	5.98	123	23919	4.87	122	11360	3.25	123	226	0.63
133	33909	6.02	133	22103	4.87	132	10527	3.38	133	318	0.73
143	31062	5.98	143	20664	4.89	143	9517	3.33	143	348	0.78
153	29703	6.05	153	19302	4.98	153	9036	3.34	153	409	0.85
163	28279	6.09	163	18091	4.88	164	8289	3.32	163	470	0.92
173	27049	6.14	173	17485	4.95	173	7763	3.32	173	501	0.97
183	25367	6.12	183	16577	4.95	183	7324	3.29	183	531	1.02
193	25820	6.34	193	15744	4.96	193	7194	3.32	193	562	1.07
203	23879	6.25	203	15593	5.06	199	6754	3.33	203	592	1.12
213	23231	6.32	213	14912	5.07	208	6359	3.31	213	605	1.15
223	20967	6.14	223	14155	5.06	221	6052	3.33	223	623	1.20
233	20902	6.27	233	13701	5.09	237	5527	3.30	233	635	1.23
243	19802	6.23	243	13057	5.07	247	5263	3.29	243	641	1.26
253	19672	6.34	253	12754	5.12	256	5043	3.28	253	623	1.27
263	19478	6.43	263	12300	5.12	263	5000	3.31	263	635	1.31
273	18896	6.45	273	11922	5.14	273	4956	3.35	273	647	1.34
283	18442	6.49	283	11619	5.17	283	4824	3.36	283	666	1.38
293	17990	6.53	293	11241	5.17	303	4117	3.35	293	641	1.39
303	17602	6.57	303	10862	5.17				303	653	1.42
3,4,5-Trimethoxybenzoates											
76	51173	5.58	76	34977	4.63	76	17424	3.26	76	189	0.34
123	33081	5.71	123	22372	4.71	123	9767	3.10	123	336	0.58
133	30731	5.72	133	20590	4.70	133	8777	3.06	133	372	0.63
143	28851	5.75	143	19138	4.71	143	8132	3.05	143	403	0.68
153	27172	5.77	153	17884	4.71	153	7659	3.06	153	452	0.74
163	26030	5.83	163	16960	4.73	163	7143	3.06	163	482	0.79
173	25023	5.89	173	15971	4.73	173	6799	3.07	173	513	0.84
183	23881	5.92	183	15311	4.77	183	6411	3.07	183	525	0.88
193	22807	5.94	193	14585	4.78	193	6153	3.09	193	537	0.91
203	22001	5.98	203	14057	4.81	203	5895	3.10	203	556	0.95
213	20927	5.97	213	13529	4.84	213	5594	3.09	213	556	0.97
223	20658	6.07	223	12869	4.83	223	5336	3.09	223	586	1.02
233	19919	6.10	233	12341	4.84	233	5121	3.09	233	574	1.04
243	19449	6.15	243	11945	4.86	243	4906	3.09	243	586	1.07
253	18845	6.18	253	11549	4.88	253	4691	3.08	253	586	1.09
263	18375	6.22	263	11219	4.90	263	4562	3.10	263	568	1.09
273	17770	6.23	273	10889	4.92	273	4390	3.10	273	586	1.13
283	17367	6.27	283	10560	4.94	283	4304	3.12	283	556	1.12
293	17032	6.32	293	10295	4.96	293	4132	3.11	293	586	1.17
303	16427	6.31	303	9965	4.96	303	4046	3.13	303	586	1.19

Bleaney—Bowers equation [23—27]

$$\chi = \frac{N g_{\text{av}}^2 \beta^2}{3kT} \left[1 + \frac{1}{3} (e^{-2J/kT}) \right]^{-1} \quad (2)$$

where N , β , k , T , J , g_{av} have their usual meanings [23—29].

The μ_{eff} values display minimum at 76 K and maximum at room temperature. The room temperature magnetic moment per Cu is similar to those observed for other dinuclear Cu(II) compounds [30, 31] and is rather lower than the spin-only magnetic moment. This behaviour indicates an antiferromagnetic coupling between the two Cu(II) centres. The

variable temperature magnetic results for 2,3,4- and 3,4,5-trimethoxybenzoates of Cu(II) are given in Table 4. The magnetic susceptibility reaches the highest values at room temperature and it decreases with lowering temperature. The magnetic moment values of the Cu(II) complex decrease from 1.42 μ_B and 1.19 μ_B at 303 K to 0.27 μ_B and 0.34 μ_B at 77 K, respectively for 2,3,4- and 3,4,5-trimethoxybenzoates, as a consequence of depopulation of the excited triplet ($S = 1$) state. The interaction between two $S = 1/2$ metal atoms in a dimer leads to molecular states: a spin singlet ($S = 0$) and a triplet ($S = 1$) separated by $2J$. The interaction will be antiferromagnetic ($J < 0$) if $S = 0$ is the ground state; on the other hand, if $S = 1$, the in-

teraction will be ferromagnetic [24, 32]. According to *Kahn's* theory, the exchange coupling constant is the sum of ferromagnetic and antiferromagnetic contributions [33]. The ferromagnetic contribution is weak when the metal ions are bridged polyatomic extended ligands [34]. However, the magnitude of antiferromagnetic interactions is primarily governed by an overlap of two magnetic orbitals centred on the nearest neighbour copper(II) ions [35]. Whereas ferromagnetic contributions are usually small, antiferromagnetic ones may be considered as proportional to the square of the gap between the molecular orbitals constructed from the magnetic orbitals [36]. For Cu(II) dinuclear complexes the magnetic coupling constant J is directly related to energy separation between the singlet and triplet states.

$$2J = E_S - E_T \quad (3)$$

At lower temperature range for dimers only the lowest levels are occupied. They may be followed on the example of the course of $\chi_{\text{Cu}} = f(T)$ for the copper(II) dimers with states $S = 1$ and $S = 0$ [37].

Electron population in both levels is combined with the Boltzmann contribution law and is temperature-dependent. At the higher temperatures and for the relatively high exchange parameters $|J|$ ($J < 1$) both states are occupied (triplet state is dominating) and the magnetic moment has the values close to the pure spin ($1.73 \mu_B$), but usually lower. With temperature lowering the population of the triplet state decreases and within the lowest temperature ranges only singlet state is occupied ($S = 0$) and $\mu = 0 \mu_B$.

The magnetic properties of 2,3,4- and 3,4,5-trimethoxybenzoates of Cu(II) indicate the mode of metal-ligand coordination and the geometry around the metal ions. The geometry exerts marked influence on the magnetic exchange interaction. Therefore the weak antiferromagnetic interaction may be brought out mainly by the geometry structures of this complex and the properties of the bridged ligands [27, 38–40]. From the obtained results it appears that the complexes of Cu(II) form dimers with bidentate bridging carboxylate group. This character of dentates of COO^- groups was confirmed by IR spectral data (Table 2).

In comparison with 2,3,4-trimethoxybenzoate of Cu(II) the electron densities of the oxygen atoms increase in 3,4,5-trimethoxybenzoate of that metal ion, which leads to the stronger covalent metal–oxygen bonds and thereby to an increased overlap of the orbitals of the two unpaired electrons in the binuclear units [26]. However, in the case of 2,3,4-trimethoxybenzoate of Cu(II) the decrease of electron density on the oxygen atom causes the weakening of the metal–oxygen bond and the decrease of overlap of the two unpaired electron orbitals in the binuclear units.

Concluding, from the obtained results it appears that the M—O bond in 2,3,4- and 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II), and Cu(II) is mainly electrostatic in nature and the colours of the complexes are the same as those in the free M(II) ions. The electron density in the molecules makes the $d \rightarrow d$ electronic transitions of central ions to be those of the lowest energy and the absorption occurs at relatively high wavelengths.

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