

Physicochemical Properties of 2,3- and 3,5-Dimethoxybenzoates of Co(II), Ni(II), and Cu(II)

W. FERENC*, A. WALKÓW-DZIEWULSKA, and P. SADOWSKI

*Department of Inorganic and General Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University,
PL-20 031, Lublin, Poland
e-mail: wetafer@hermes.umcs.lublin.pl*

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Some physicochemical properties of 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II), and Cu(II) were studied and compared to observe the influence of the position of $-\text{OCH}_3$ substituents in benzene ring on these properties. The compounds of studied series are crystalline hydrated or anhydrous salts. The carboxylate group in analyzed dimethoxybenzoates shows the various coordination modes (a monodentate or a symmetrical, bidentate chelating, or bridging). The thermal stabilities of 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II), and Cu(II) were investigated in air in the range of 293–1273 K. Their solubilities in water at room temperature are in the orders of 10^{-4} – 10^{-3} mol dm^{-3} and 10^{-5} – 10^{-3} mol dm^{-3} . The magnetic susceptibilities for the analyzed dimethoxybenzoates were measured over the range of 77–300 K and the magnetic moments were calculated. The results reveal that the complexes of Ni(II) and Co(II) are the high-spin ones and those of Cu(II) probably form dimers. The electronic spectra of the studied compounds were also recorded and the values of the change of absorption bands were observed for 3,5-dimethoxybenzoates of Co(II), Ni(II), and Cu(II) greater than for 2,3-dimethoxybenzoates of those elements. The various positions of $-\text{OCH}_3$ groups in benzene ring in the studied dimethoxybenzoates cause the different steric effects in the compounds. From the obtained results it appears that complexes of *d*-electron elements with 3,5-dimethoxybenzoic acid anion contain the greater number of water molecules and have greater thermal stability than 2,3-dimethoxybenzoates of those elements.

2,3- and 3,5-Dimethoxybenzoic acids are crystalline solids sparingly soluble in cold water [1–5]. According to literature survey the compounds of various metal ions with different carboxylic acid ligands have been scarcely studied. However, there are papers on the complexes of rare-earth element ions with, for example, 2,4- and 3,4-dimethoxy-, 4-chloro-2-nitro- and 4-chloro-3-nitrobenzoic acid anions [6–10]. These complexes containing different substituents in benzene ring have various properties the details of which are presented in the above cited literature. For instance, 2,4-dimethoxybenzoates of rare-earth elements are dihydrates, while those element 3,4-dimethoxybenzoates contain three or four molecules of crystallization water. 2,4-Dimethoxybenzoates are better soluble than 3,4-dimethoxybenzoates. Such differences result from differentiated influence of mesomeric and steric effects on the electron densities. From the obtained results it appears that various positions of the $-\text{Cl}$ and $-\text{NO}_2$ substituents on the benzene ring affect the values of the frequencies of the bands of $\text{M}-\text{O}$ and asymmetric and symmetric vibrations of $-\text{COO}^-$ group. They are higher for 4-chloro-3-nitrobenzoates of rare-earth

elements than for 4-chloro-2-nitrobenzoates. Depending on the $-\text{Cl}$ and $-\text{NO}_2$ substituent positions on benzene ring the thermal stability of the complexes is also changed. 4-Chloro-3-nitrobenzoates of rare-earth elements are not explosive compounds in the range of 293–1173 K, while the 4-chloro-2-nitrobenzoates of those elements are stable only up to 523 K, which is connected with the *ortho*-position of $-\text{NO}_2$ group. The temperatures of the initial dehydration of the 4-chloro-3-nitrobenzoates of rare-earth elements are higher compared to the 4-chloro-2-nitrobenzoates. It results from the various positions of the $-\text{Cl}$ and $-\text{NO}_2$ substituents on the benzene ring and various mesomeric and inductive effects of these substituents on the electron density in benzene ring.

Papers exist also on the complexes of 2,3- and 3,5-dimethoxybenzoic acid anions with the following cations only: Cu(II), Ag(I), Zn(II), Pb(II), and rare-earth elements(III) [11–19]. They were obtained as solids or were investigated in solution. Some of their physicochemical properties were studied. There is no information about the comparison of properties of solid complexes of 2,3- and 3,5-dimethoxybenzoic acid

*The author to whom the correspondence should be addressed.

anions with Co(II), Ni(II), and Cu(II). Therefore, we decided to prepare them in the solid state and to examine such their properties as the thermal stability in air, solubility in water at room temperature, to present their IR, UV, VIS spectral characterizations, crystalline forms, and magnetic features. The influence of the positions of methoxy groups in the benzene ring on the properties of these compounds was also investigated and the details of their comparison are presented in this paper.

EXPERIMENTAL

For the preparation of the complexes the following chlorides were used: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Polish Chemical Reagents, Gliwice). The 2,3- and 3,5-dimethoxybenzoic acids employed were produced by Aldrich Chemical Company. The solutions of NH_3aq (25 %) and HCl (36 %) used in the experiments were produced by "Standard" Chemical Company and Polish Chemical Reagents in Gliwice, respectively.

2,3- and 3,5-Dimethoxybenzoates of Co(II), Ni(II), and Cu(II) were prepared by the addition of equivalent quantities of 0.1 M-ammonium 2,3- or 3,5-dimethoxybenzoates ($\text{pH} \approx 5$) to a hot aqueous solution containing the chlorides of the given ion metals and crystallizing at 293 K. The solids were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to a constant mass. The carbon and hydrogen contents were determined by elemental analysis using a CHN 2400 Perkin—Elmer analyzer. The contents of metal(II) ions were determined by the ASA method using ASA 880 spectrophotometer.

The IR and FIR spectra of the complexes were recorded over the ranges $\tilde{\nu} = 400\text{—}4000\text{ cm}^{-1}$ and $100\text{—}600\text{ cm}^{-1}$, respectively, using an FTIR 1725X Perkin—Elmer and a Nicolet MAGNA FIR 760 spectrometer, respectively. The samples for the FTIR spectra measurements were prepared as KBr discs and those for the FIR spectra with polyethylene of masses from 0.8 to 1.0 mg.

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 of $2\theta = 4\text{—}80^\circ$ by means of the Debye—Scherrer—Hull method.

The thermal stabilities and decomposition of the prepared complexes were determined by Paulik—Paulik—Erday Q-1500 D 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 being equal to 100 mg. DTG and DTA sensitivities were regulated by a Derill computer program. The products of decomposition were calculated from TG curves and verified by the diffrac-

tion pattern registration. The nature of the solid products of decomposition was established from the TG curves and confirmed by IR and X-ray spectra.

The gaseous products of thermal decompositions of 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II), and Cu(II) were identified by the registration of TG-FTIR spectra in the range of $500\text{—}4500\text{ cm}^{-1}$ in the TG-FTIR system using Netzsch TG-209. The measurements were carried out in argon atmosphere at a heating rate of 20 K min^{-1} . The samples of masses ranging from 7.75 to 13.96 mg were heated to 1273 K. The argon flowed at a rate of $50\text{ cm}^3\text{ min}^{-1}$.

Magnetic susceptibilities of polycrystalline samples of analyzed compounds were measured by the Gouy method using a sensitive Cahn RM-2 balance. Measurements were carried out at a magnetic field strength of $9.9 \times 79.58\text{ A m}^{-1}$. $\text{Hg}[\text{Co}(\text{SCN})_4]$ with the magnetic susceptibility of $16.44 \times 10^{-6}\text{ cm}^3/\text{g}$ [20] was employed as calibrant. The correction of diamagnetism of the constituent atoms was calculated by using Pascal's constants [21]. The magnetism of the samples was found to be field-independent. The magnetic moments were calculated according to the equation

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

The electronic spectra of studied complexes of Co(II), Ni(II) and Cu(II), and their chlorates(VII) applied as standards were recorded using UV VIS Specord spectrometer.

The solubilities of the title compounds in water (at 293 K) were determined by measuring the concentrations of M(II) ions by the ASA method.

RESULTS AND DISCUSSION

The 2,3- (L) and 3,5-dimethoxybenzoates (L*) of Co(II), Ni(II), and Cu(II) were obtained as crystalline compounds with metal ion to ligand mole ratio of 1 : 2 (Table 1). Their general formula is $\text{M}(\text{C}_9\text{H}_9\text{O}_4)_2 \cdot n\text{H}_2\text{O}$, where M = Co(II), Ni(II), Cu(II), and $n = 2$ for Cu(II)L, and Cu(II)L*₂ and for Co(II)L*₂, $n = 3$ for Ni(II)L*, $n = 1$ for Ni(II)L, and $n = 0$ for Co(II)L. The colours of the compounds are following: blue for Cu^{2+} , green for Ni^{2+} , and pink for Co^{2+} .

The compositions of the complexes were also established by IR spectral analysis (Table 2). All dimethoxybenzoates show similar solid-state IR spectra. However, the characteristic frequencies related to the carbonyl group are altered markedly in going from the acid to the salts. The bands due to the —COOH group at 1686 cm^{-1} for the 2,3-dimethoxybenzoic acid, and at 1684 cm^{-1} for the 3,5-dimethoxybenzoic acid are replaced in the complexes by two bands: asymmetric ($1578\text{—}1629\text{ cm}^{-1}$ for L and $1581\text{—}1598\text{ cm}^{-1}$ for L*) and symmetric vibrations of —COO[−] group ($1401\text{—}1448\text{ cm}^{-1}$ for L and $1392\text{—}1428\text{ cm}^{-1}$ for L*), respectively [22—26]. The bands correspond-

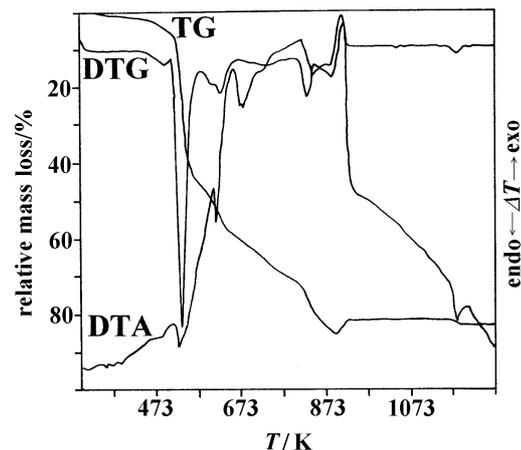
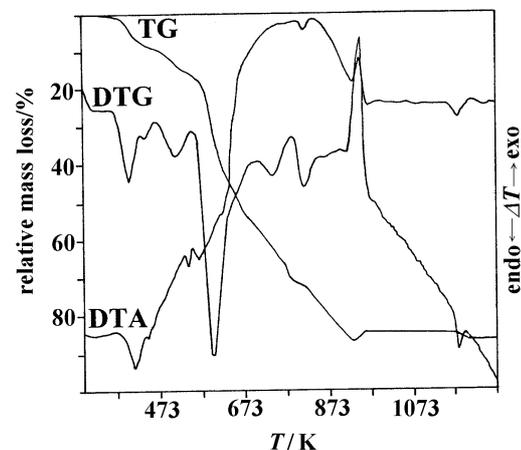
Table 1. Elemental Analysis Data of Compounds and their Solubilities in Water (at 293 K)

Complex	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			Solubility mol dm ⁻³
	H	C	M	
CoL ₂	4.27	51.31	13.99	2.8×10^{-3}
	4.21	51.46	14.25	
NiL ₂ · H ₂ O	4.55	49.23	13.37	2.1×10^{-4}
	4.24	50.16	13.87	
CuL ₂ · 2H ₂ O	4.95	46.75	13.85	7.9×10^{-4}
	4.69	47.20	14.42	
CoL* ₂ · 2H ₂ O	4.81	47.27	12.89	1.5×10^{-3}
	4.60	46.73	12.59	
NiL* ₂ · 3H ₂ O	5.05	45.50	12.36	5.4×10^{-4}
	4.66	44.86	12.18	
CuL* ₂ · 2H ₂ O	4.95	46.75	14.85	6.5×10^{-5}
	4.43	47.45	14.63	

ing to metal ion—oxygen stretching appear in the ranges 208—278 cm⁻¹ and 409—497 cm⁻¹. The magnitudes of the separation, $\Delta\tilde{\nu}(\text{OCO}^-)$ ($\Delta\tilde{\nu}(\text{OCO}^-) = \tilde{\nu}_{\text{as}}(\text{OCO}^-) - \tilde{\nu}_{\text{s}}(\text{OCO}^-)$), which characterize the type of metal ion—oxygen bond, change from 131—220 cm⁻¹ for L to 153—197 cm⁻¹ for L*. According to the spectroscopic criteria and with regard to *Nakamoto* [23] and [25] the carboxylate group shows in the complexes the different modes of coordination. In L it may function as a monodentate, bidentate chelating or bidentate bridging group and in L* only as bidentate chelating or bridging one.

The X-ray diffraction patterns spectra of L and L* of Co(II), Ni(II), and Cu(II) were recorded. The analysis of the diffractograms suggests that the complexes are polycrystalline compounds with various degrees of crystallinity and different structures [27]. Their structures have not been examined since attempts to obtain single crystal have failed.

The thermal stability of complexes under study in air in the range of 293—1273 K was examined by the

**Fig. 1.** TG, DTG, and DTA curves for 2,3-dimethoxybenzoate of Co(II) in air.**Fig. 2.** TG, DTG, and DTA curves for 3,5-dimethoxybenzoate of Co(II) in air.

TG, DTG, and DTA techniques. The obtained results are presented in Figs. 1 and 2 and in Table 3. When heated to 1273 K the Co(II)L is gradually decomposed to CoO with the intermediate formations of Co at first, and then of Co₃O₄. The found mass loss is equal to

Table 2. Frequencies of the Maxima of the Absorption Bands of COO⁻ for the Studied Complexes of Co(II), Ni(II), Cu(II), and Na

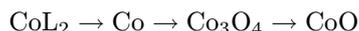
Complex	$\tilde{\nu}/\text{cm}^{-1}$			Complex	$\tilde{\nu}/\text{cm}^{-1}$		
	$\nu_{\text{as}}(\text{OCO}^-)$	$\nu_{\text{s}}(\text{OCO}^-)$	$\Delta\nu(\text{OCO}^-)$		$\nu_{\text{as}}(\text{OCO}^-)$	$\nu_{\text{s}}(\text{OCO}^-)$	$\Delta\nu(\text{OCO}^-)$
CoL ₂	1629	1409	220	CoL* ₂ · 2H ₂ O	1598	1401	197
	1579	1444	135			1428	170
NiL ₂ · H ₂ O	1628	1436	192	NiL* ₂ · 3H ₂ O	1582	1392	190
	1579	1448	131			1426	156
CuL ₂ · 2H ₂ O	1607	1401	206	CuL* ₂ · 2H ₂ O	1581	1392	189
	1578	1442	136			1428	153
NaL	1604	1396	208	NaL*	1580	1385	195

Table 3. Decomposition Data for Dimethoxybenzoates in Air

Substance	$\Delta T/K$	Mass loss/%		n	Final product of decomposition in solid state
		calc.	found		
CoL ₂	369—809	86.00	85.60	—	Co
Co	907—974	80.93	80.70	—	Co ₃ O ₄
Co ₃ O ₄	1158—1206	82.19	81.90	—	CoO
NiL ₂ · H ₂ O	331—398	4.10	3.70	1	NiL ₂
NiL ₂	463—871	86.62	86.40	—	Ni
Ni	880—911	82.97	84.60	—	NiO
CuL ₂ · 2H ₂ O	385—407	3.89	4.10	1	CuL ₂ · H ₂ O
CuL ₂ · H ₂ O	416—433	7.79	7.20	1	CuL ₂
CuL ₂	453—800	74.90	74.00	—	CuO
CoL* ₂ · 2H ₂ O	376—468	7.88	8.00	2	CoL* ₂
CoL* ₂	546—924	87.10	87.00	—	Co
Co	942—973	82.43	82.60	—	Co ₃ O ₄
Co ₃ O ₄	1161—1221	83.60	84.10	—	CoO
NiL* ₂ · 3H ₂ O	334—440	11.37	11.00	3	NiL* ₂
NiL* ₂	578—835	87.78	85.10	—	Ni
Ni	859—921	84.40	83.60	—	NiO
CuL* ₂ · 2H ₂ O	325—442	7.79	7.00	2	CuL* ₂
CuL* ₂	521—848	74.90	74.20	—	CuO

ΔT – temperature range of decomposition processes, n – number of water molecules lost in the dehydration process.

80.7 % and calculated value is 80.93 %. In the range of 1158—1206 K Co₃O₄ is reduced to CoO, which is the final product of decomposition. The process of reduction is connected with the *endo*-effect, while that of oxidation with exothermic one. The decomposition of Co(II)L may be presented by the following way (Fig. 1)



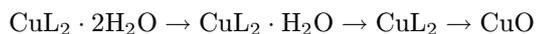
The products of the thermal decomposition were roentgenographically identified.

The monohydrate of Ni(II)L dehydrates in one step and forms the anhydrous complex. The mass loss calculated from TG curve being equal to 3.7 % corresponds to the loss of one water molecule. The anhydrous compound is decomposed to Ni that is next oxidized (880—911 K) to NiO to be the final product of decomposition. The mass losses calculated from TG curve are equal to 86.4 %, which corresponds to the Ni formation and to 84.60 % in the case of NiO. The decomposition process of analyzed complex may proceed as follows



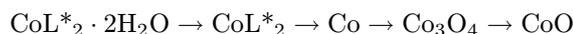
Considering the temperature at which the dehydration process of the compound takes place and the way by which it proceeds, it is possible to assume that the water molecules may be in the outer sphere of complex coordination [28].

During heating to 1273 K the dihydrate of Cu(II)L dehydrates in two steps. At first, it loses (385—407 K) one water molecule and next the second molecule of crystallization water is lost to form anhydrous complex. The found loss of mass is equal to 7.2 % (theoretical value is 7.79 %). Next the anhydrous compound is decomposed (453—800 K) to CuO. The thermal decomposition of Cu(II)L may be presented by the scheme



From the obtained results it is possible to suppose that one water molecule may be in the inner sphere of complex coordination, while the second one is in its outer sphere.

When heated to 1273 K the Co(II)L* is gradually decomposed to CoO with the intermediate formations, at first of CoL*₂, next Co, and finally Co₃O₄. In the range of 1161—1221 K the Co₃O₄ is reduced to CoO, which is the final product of decomposition. The decomposition process of Co(II)L*₂ may proceed as follows (Fig. 2)



The trihydrate of Ni(II)L* dehydrates in one step and forms the anhydrous complex. The mass loss calculated from TG curve being equal to 11 % corresponds to the loss of three water molecules (theoretical value is 11.37 %). The anhydrous Ni(II)L* in the

Table 4. Magnetic Data of the Studied Compounds

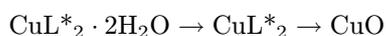
CoL ₂			NiL ₂ · H ₂ O			CuL ₂ · 2H ₂ O			CoL* ₂ · 2H ₂ O			NiL* ₂ · 3H ₂ O			CuL* ₂ · 2H ₂ O			
<i>T</i>	$\chi_M \cdot 10^6$	μ_{eff}	<i>T</i>	$\chi_M \cdot 10^6$	μ_{eff}	<i>T</i>	$\chi_M \cdot 10^6$	μ_{eff}	<i>T</i>	$\chi_M \cdot 10^6$	μ_{eff}	<i>T</i>	$\chi_M \cdot 10^6$	μ_{eff}	<i>T</i>	$\chi_M \cdot 10^6$	μ_{eff}	
K	dm ³ mol ⁻¹	μ_B	K	dm ³ mol ⁻¹	μ_B	K	dm ³ mol ⁻¹	μ_B	K	dm ³ mol ⁻¹	μ_B	K	dm ³ mol ⁻¹	μ_B	K	dm ³ mol ⁻¹	μ_B	
77	34389	4.61	77	17280	3.28	77.0	94.7	0.47	77	30294	4.33	103	15000	3.54	77	462	0.67	
103	28033	4.82	103	14210	3.44	96.4	138.6	0.56	101	26273	4.63	114	13196	3.50	91	508	0.75	
114	26097	4.90	112	12807	3.41	109.5	231	0.66	104	25405	4.62	121	11772	3.41	101	554	0.81	
119	24498	4.85	117	11973	3.37	120.0	277.2	0.72	109	24308	4.60	131	11060	3.44	109	600	0.87	
124	23572	4.85	122	11359	3.26	132.0	369.6	0.82	113	23349	4.61	143	10063	3.43	117	646	0.92	
129	22940	4.88	127	11052	3.38	140.0	415.8	0.87	119	22480	4.65	157	9398	3.48	125	693	0.98	
134	21762	4.85	132	10526	3.37	149.0	508.0	0.96	123	21932	4.67	168	8591	3.44	136	831	1.09	
139	21551	4.92	137	10043	3.35	159.0	554.0	1.02	128	21430	4.71	178	7879	3.40	143	924	1.16	
149	20246	4.93	143	9517	3.33	169.5	600.0	1.08	133	20881	4.74	188	7357	3.38	147	970	1.20	
159	18899	4.93	148	9254	3.35	180.0	600.0	1.11	138	20104	4.74	198	6693	3.37	152	1016	1.25	
169	17805	4.93	153	9035	3.36	195.0	646.0	1.19	143	19647	4.77	207	6313	3.29	155	1062	1.28	
179	17384	5.02	157	8772	3.36	207.0	693.0	1.26	148	19328	4.81	217	6076	3.31	161	1108	1.33	
190	16247	5.00	164	8289	3.34	217.0	693.0	1.29	153	19053	4.86	228	5981	3.37	170	1155	1.39	
200	15363	4.99	173	7763	3.32	227.0	739.0	1.35	158	18505	4.86	238	5648	3.35	176	1201	1.43	
211	14943	5.06	180	7324	3.29	239.0	693.0	1.36	163	18003	4.87	248	5506	3.37	182	1247	1.48	
220	13806	4.96	190	7193	3.35	250.5	693.0	1.38	173	17089	4.89	258	5316	3.38	189	1247	1.51	
230	13469	5.01	197	6754	3.33	259.5	693.0	1.41	183	15992	4.87	269	5126	3.40	198	1293	1.57	
240	12880	5.01	208	6359	3.31	269.5	693	1.44	193	15306	4.90	277	1841	3.35	208	1293	1.61	
250	12417	5.02	221	6052	3.33	284.5	648	1.48	203	14666	4.92	287	4746	3.38	217	1293	1.64	
254	12206	5.02	229	5833	3.33	296.4	646	1.47	214	13936	4.92	298	4462	3.35	228	1339	1.68	
269	11786	5.08	237	5526	3.30				221	13159	4.86				237	1293	1.72	
280	11365	5.09	247	5263	3.29				227	12794	4.86				245	1247	1.75	
288	10986	5.08	256	5043	3.28				236	12565	4.91				255	1247	1.76	
299	10649	5.09	263	5000	3.31				245	12337	4.96				262	1247	1.78	
			271	4956	3.35				251	11925	4.94				272	1201	1.79	
			281	4824	3.36				260	11651	4.97				280	1108	1.76	
			297	4517	3.36				271	11194	4.97				287	1108	1.76	
									281	10966	5.01				298	1016	1.75	
									297	10555	5.06							

range of 578–835 K is decomposed to Ni that is next oxidized to NiO. The dehydration and reduction processes are connected with endothermic effects, while the combustion of the organic ligand and the oxidation of Ni to NiO with the exothermic ones. The decomposition process of analyzed complex may be presented by the following way



Probably the water molecules are also in the outer sphere of complex coordination [22, 28–31].

During heating to 1273 K the dihydrate of Cu(II)L* dehydrates in one step. In the range of 325–442 K it loses two water molecules and forms anhydrous complex. The loss of mass experimentally found is equal to 7.0 % (the theoretical value is 7.79 %). The anhydrous compound is next decomposed (521–848 K) to CuO. The scheme of thermal decomposition of the studied complex may be presented as follows



The decomposition process with the gas product analysis was recorded for complexes. FTIR spectra

of the gas-phase products indicate that the decomposition of 2,3- and 3,5-dimethoxybenzoates is connected with the release of CO₂, CO, H₂O (H₂O in the case of hydrated complexes), hydrocarbons, and monohydroxy alcohols. The characteristic stretching and deformation vibration bands of water molecules in FTIR spectra appear in the wavenumber ranges of 3700–3750 and 1300–1600 cm⁻¹, respectively. The bands characteristic of CO₂ molecule vibrations occur in the following regions: 2800–3000 cm⁻¹, 2350 cm⁻¹, 1750 cm⁻¹, 1050–1600 cm⁻¹, and 625–800 cm⁻¹. The bands at 2700–3100 cm⁻¹, 1640–1700 cm⁻¹, 1300–1500 cm⁻¹ confirm the vibrations of hydrocarbons present in the gaseous product of thermal decomposition of the studied complexes [24, 32]. The bands resulting from the monohydroxy alcohols appear in the ranges of 2800–2900 cm⁻¹ and 1050–1250 cm⁻¹ [32]. With increasing temperature the molecules of CO are released and their characteristic absorption bands occur in the region of 2060–2220 cm⁻¹ [24, 32].

The analysis of FTIR spectra of hydrated and anhydrous complexes shows that with the rise of temperature the hydrated compounds release the water molecules the presence of which in the gaseous mixture is confirmed by the bands in the range of 3700–

3750 cm^{-1} . During further heating the organic ligand decomposes and the molecules of CO_2 , CO, hydrocarbons, and monohydroxy alcohols are liberated.

The solubilities of analyzed dimethoxybenzoates in water at room temperature were determined (Table 1). They are of the order of 10^{-4} – 10^{-3} mol dm^{-3} for L and of 10^{-5} – 10^{-3} mol dm^{-3} for L*. L of Co(II) and Cu(II) are better soluble than L* of those elements.

Magnetic susceptibility of the studied compounds was measured in the range of 77–300 K (Table 4). The values determined for Co(II) and Ni(II) dimethoxybenzoates obey the Curie–Weiss law decreasing gradually with rising temperature. The χ_M values for L and L* of Co(II) and Ni(II) show a ferromagnetic interaction between metal ions. The magnetic moment values experimentally determined for Co(II) and Ni(II) compounds are in the ranges of 4.61–5.09 BM and 4.33–5.06 BM for complexes of Co(II), respectively, and 3.26–3.44 BM, and 3.29–3.54 BM for Ni(II) dimethoxybenzoates, respectively. It suggests that these magnetic moments are probably connected only with spin moments. In the case of L and L* of Co(II) the effective magnetic moments are equal to 4.61–5.09 BM and 4.33–5.06 BM, and at room temperature they are 5.09 BM and 5.06 BM. These values differ from that of the spin-only moment which amounts to 3.88 BM. This relatively large difference between measured and calculated values results from a spin-orbital coupling [33]. The experimental data may suggest that the studied dimethoxybenzoates of Co(II) and Ni(II) are the high-spin complexes with probably octahedral coordination and weak ligand fields. The effective magnetic moment values of L and L* of Cu(II) in the range of 77–300 K change from 0.47 BM (at 77 K) to 1.47 BM (at 296 K) and from 0.67 BM (at 77 K) to 1.75 BM (at 298 K), respectively. Such dependence is typical behaviour of copper dimers. The μ_{eff} values display minimum at 77 K and maximum at 284 K and 272 K. The room temperature magnetic moment per Cu is similar to those observed for its other dinuclear compounds [34, 35] and is rather lower than the spin-only magnetic moment in the case of 2,3-dimethoxybenzoates. This behaviour indicates an antiferromagnetic coupling between the two Cu(II) centres. The variable-temperature magnetic results for complexes of Cu(II) are given in Table 4. The magnetic moment values of the Cu(II) complexes decrease from 1.47 BM and 1.75 BM at 300 K to 0.47 BM and 0.67 BM at 77 K, as a consequence of depopulation of the excited triplet ($S = 1$) state [36, 37]. 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 [38–42]. The magnetic behaviour of L and L* of Cu(II) may indicate the mode of metal–ligand coordination and the geometry around the metal ions. The geometry exerts marked influence on the magnetic exchange

interaction [39–42]. The magnetic properties reveal that the complexes of Cu(II) are dimers with bidentate bridging carboxylate groups. Such dentates of COO^- group were confirmed by IR spectral data (Table 2). In the case of L of Cu(II) the electron densities of the oxygen atoms increase, 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 ($\mu_{\text{eff}} = 1.47$ BM at room temperature). However, in the case of Cu(II) L* the electron density of the oxygen atom decreases causing the weakening of the metal–oxygen bond and the decrease of the overlap of two unpaired electron orbitals in the binuclear units. Therefore its μ_{eff} at room temperature is equal to 1.75 BM.

Concluding, from the obtained results it appears that the M–O bond in analyzed compounds of Co(II), Ni(II), and Cu(II) is mainly electrostatic in nature. 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.

The electronic spectra of the studied compounds of Co(II), Ni(II), and Cu(II) and their chlorates(VII) as standards were recorded in the UV and VIS ranges from 200 nm to 900 nm. The data obtained for the absorption bands in the spectra recorded for these complexes and the standards in the ranges of 15000–25000 cm^{-1} for Co(II), 11500–14500 cm^{-1} for Cu(II), and 22000–28000 cm^{-1} and 12300–15300 cm^{-1} for Ni(II) are presented in Table 5. The absorption bands characteristic of Co^{2+} , Ni^{2+} , and Cu^{2+} ions in the aqueous solutions of 2,3- and 3,5-dimethoxybenzoates change to the shorter wavelengths yielding the hypsochromic shift, which depends on the character and stability of metal ion–ligand bond, hydration degree of central ions, and the kind of solvents. It also depends on the character of interaction between central ion and the group of atoms in its surroundings. The oxygen atoms of COO^- groups, of water molecules, and of the OCH_3 substituents may variously influence the orbitals of central ions because the COO^- ions and OCH_3 groups have different values of inductive and mesomeric effects. Therefore the values of excitation energy are changed causing the movements of absorption bands. With the rise of the complex stabilities the maxima of absorption bands characteristic of the vibrations caused by metal ions are shifted to the shorter wavelengths. The greater the stability of the complex, the stronger the central ion–ligand bonding. The observed hypsochromic replacements of absorption bands in the electronic spectra, in comparison with their positions in the corresponding spectra of standards, are indicative of the greater stability of central ion–ligand bonding. On the basis of this displacement it is not possible to determine the covalency of bonding because this replacement depends on the coordination number of central ion, its ion radius, and

Table 5. Values of the Maxima of Absorption Bands for Co(II), Ni(II), and Cu(II) Ions in the Solution of Chlorates(VII) and 2,3- and 3,5-Dimethoxybenzoates ($\epsilon_{\max}/(\text{m}^2 \text{mol}^{-1})$)

Complex		The range of measurements $\Delta(1/\lambda) \cdot 10^3/\text{cm}^{-1}$	Maxima of absorption bands of M^{2+} ions in the solutions of		$\Delta(1/\lambda) \cdot 10^3/\text{cm}^{-1}$
			sample	chlorate(VII)	
L	Co(II)	15—25	19.53	19.32	0.21
	Ni(II)	12.3—15.3	13.90	13.75	0.15
		22—28	25.38	25.03	0.35
	Cu(II)	11.5—14.5	12.55	12.14	0.41
L*	Co(II)	15—25	19.57	19.32	0.25
	Ni(II)	12.3—15.3	13.92	13.75	0.17
		22—28	25.54	25.03	0.51
	Cu(II)	11.5—14.5	13.93	12.14	1.79

oxidation degree. From the obtained results it follows that the values of movements of absorption bands for Co(II), Ni(II), and Cu(II) are changed with the increase of element atomic number, similarly as their stability constants in the Irving—Williams sequence [23]. The smallest value of change of absorption band was observed for L and L* of Ni(II) in the range of 12300—15300 cm^{-1} . It is indicative of the small stability of metal ion—ligand bonding in the solution and its strong hydration degree. The composition of coordination sphere for central ion is similar to that typical for high-spin aquaion of those elements with octahedral coordination, the coordination number of which is equal to 6. The greatest value of the change of absorption band was observed for 3,5-dimethoxybenzoate of Cu(II), which indicates the greatest stability of metal ion—ligand bonding in this complex compared to the rest of analyzed compounds. From the obtained results it appears that L* of Co(II), Ni(II), and Cu(II) show the greater stabilities of metal ion—ligand bonds compared to L of those elements, which is connected with the different positions of $-\text{OCH}_3$ groups in benzene ring and various mesomeric and inductive effects of the substituents on the electron density in the system of molecule. The compounds exhibit the following colours: blue for Cu^{2+} , green for Ni^{2+} , and pink for Co^{2+} .

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