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Magnetic, thermal and spectroscopic features of 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II)

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Abstract: The 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) were synthesized as solids and their magnetic, spectral and thermal properties studied. The complexes are hydrated or anhydrous compounds which possess colours typical of the M(II) ions. Their thermal stabilities were examined in air and nitrogen and the gaseous and solid state decomposition products 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 2,3- and 3,5-dimethoxybenzoates of Co(II) and Ni(II) are high-spin complexes with weak ligand fields, and that the complexes of Cu(II) form dimers.

Keywords: 2,3- and 3,5-dimethoxybenzoates, complexes of Co(II), Ni(II) and Cu(II), magnetic moments, thermal stability, FTIR and FIR spectra.

INTRODUCTION

According to a literature survey, the compounds of various metal ions with different carboxylic acid anions have been rarely studied. However, there are papers on the complexes of rare earth elements with for instance 2,4-, 3,4-dimethoxy-, 4-chloro-2-nitro- and 4-chloro-3-nitrobenzoic acid anions.[1–5] Papers also exist on the complexes of 2,3- and 3,5-dimethoxybenzoic acid anions with the following cations only: Cu(II), Ag(I), Pb(II), Zn(II), Ni(II), Co(II) and rare earth elements(III).[6–17] They were obtained and studied as solids or were investigated in solution. Some of their physicochemical properties were studied. There is no information about the comparison of the properties of the solid complexes of 2,3- and 3,5-dimethoxybenzoic acid anions with Co(II), Ni(II) and Cu(II). Therefore, it was decided to prepare these complexes in the solid state in order to examine some of their properties, such as their thermal stability in air and nitrogen atmospheres, to present their FTIR and FIR spectra, crystalline forms, magnetic features at 4.4–300 K and to estimate the gaseous thermal decomposition products. The influence of

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the positions of the methoxy- groups in the benzene ring on the properties of the compounds was also investigated.

EXPERIMENTAL

The complexes of 2,3- and 3,5-dimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) were prepared by the addition of equivalent quantities of 0.1 M ammonium 2,3- and 3,5-dimethoxybenzoates (pH ≈ 5) to hot 0.1 M aqueous solutions containing the nitrates(V) of these metal ions and crystallizing at 293 K. The solids wee filtered off, washed several times with hot water and methanol to remove the ammonium ions and dried at 303 K.

Elemental analysis for C, H was performed using a Perkin–Elmer CHN 2400 analyser. The contents of the M^{2+} metals were established by the ASA method using an ASA 880 spectrophotometer.

The FTIR and FIR spectra of the complexes were recorded in the ranges 4000–400 cm^{-1} and 650–100 cm^{-1}, respectively, using a FTIR 1725 X Perkin–Elmer and a MAGNA FTIR 760 (Nicolet Firm) spectrometers. The samples for FTIR spectroscopy were prepared as KBr discs while those for FIR spectroscopy were used in polyethylene of mass ranging from 0.8 to 1.0 mg. Some of the results are presented in Table I.

The thermal stability and decomposition of the complexes were studied in air using a Q-1500 D 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 (Tables II, III). 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 Tables II and III.

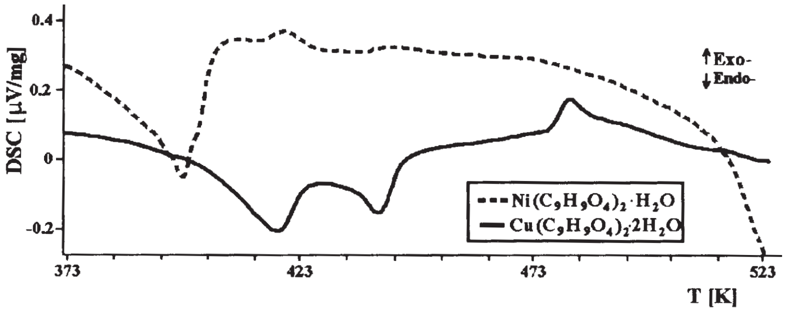


Fig. 1. DSC Curves for the dehydration process of Ni(II) and Cu(II) 2,3-dimethoxybenzoates.

The DSC/TG analysis was also performed in the temperature range 303–1150 K using a Mettler–Toledo differential thermoanalyser (Fig. 1). The experiments were carried out under a dynamic nitrogen atmosphere in the temperature range 293–773 K at a heating rate of 4 K min^{-1}. Alumina crucibles were used. The values of the enthalpy of the dehydration process were calculated (Tables II, III). The gaseous decomposition products were analysed over the range 4000–400 cm^{-1} using a Bruker IFS 66 spectrometer (Tables II and III, Figs. 2, 3).

In order to study the magnetic behaviour of the 2,3- and 3,5-dimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) at low temperatures, the magnetizations of the samples at 4.5 K were also measured at a magnetic field strength of 0–56 k0e (Figs. 4, 5). On the basis of the obrained results, the magnetic susceptibility was determined according to Eq. (1):

$$\chi = M \times H^{-1} \quad (1)$$

TABLE I. Frequencies of the COO^- absorption bands for Co(II), Ni(II), Cu(II) and Na(I) 2,3- and 3,5-dimethoxybenzoates and those of CO for non-coordinated 2,3- and 3,5-dimethoxybenzoic acids (cm^{-1})

Complex L = $C_9H_9O_4^-$	2,3-dimethoxybenzoates					Complex L = $C_9H_9O_4^-$	3,5-dimethoxybenzoates				
	ν_{as}OCO	ν_sOCO	$\Delta\nu$OCO	νM–O	νC=O		ν_{as}OCO	ν_sOCO	$\Delta\nu$OCO	νM–O	νC=O
CoL_2	1629	1409	220	425	–	$CoL_2 \cdot 2H_2O$	1598	1401	197	208	–
	1579	1444	135	227				1428	170		
$NiL_2 \cdot H_2O$	1628	1436	192	440	–	$NiL_2 \cdot 3H_2O$	1582	1392	190	409	–
	1579	1448	131	247				1426	156	228	
$CuL_2 \cdot 2H_2O$	1607	1401	206	481	–	$CuL_2 \cdot 2H_2O$	1581	1392	189	497	–
	1578	1442	136	245				1428	153	278	
NaL	1604	1396	208		–	NaL	1580	1385	195		
HL	–	–	–	–	1686	HL	–	–	–	–	1684

TABLE II. Temperature ranges of the thermal stability of Co(II), Ni(II) and Cu(II) 2,3- and 3,5-dimethoxybenzoates in air and nitrogen

Complex L = $C_9H_9O_4^-$	ΔT_1/K	Weight loss / %		n	A (Air) N (N_2)	ΔH / kJ mol^{-1}	ΔT_2 / K	Oxide / %		Residue %	Gaseous products of decomposition
		Calcd.	Found					Calcd.	Found		
2,3-Dimethoxybenzoates											
CoL_2	–	–	–	–	A	–	369–1206	17.81	18.10		CO_2, CO, H_2O, Hydrocarbons, Monohydric alcohols
					N		353–1133			12.00	
$NiL_2 \cdot H_2O$	331–398	4.10	3.70	1	A	52.6	463–911	17.03	15.40		
	323–383	4.12	4.2	1	N		433–853			6.45	
$CuL_2 \cdot 2H_2O$	385–407	3.89	4.10	1	A	157.6				31.67	
	416–433	7.79	7.20	1	A		453–800	25.10	26.00		
	353–383	3.89	3.60	1	N						
	403–413	7.79	7.30	1	N		433–813			10.76	
3,5-Dimethoxybenzoates											
$CoL_2 \cdot 2H_2O$	376–468	7.88	8.00	2	A	98.4	546–1221	16.40	15.90		
	373–393	5.90	5.60	1.5	N						
	433–473	7.88	8.10	0.5	N		538–1073			31.67	
$NiL_2 \cdot 3H_2O$	334–440	11.37	11.00	3	A	153.2	578–921	15.60	16.40		
	293–413	11.37	11.00	3	N		573–1033			17.34	
$CuL_2 \cdot 2H_2O$	325–442	7.79	7.00	2	A	152.4	521–848	15.10	15.80		
	313–358	3.89	4.50	1	N						
	373–403	7.79	7.30	1	N		533–1013			10.91	

ΔT_1 = The temperature range of the dehydration process, n = the number of crystallization water molecules being lost in the endothermic step, ΔH = enthalpy of the dehydration process, ΔT_2 = the temperature range of the decomposition of the anhydrous complex

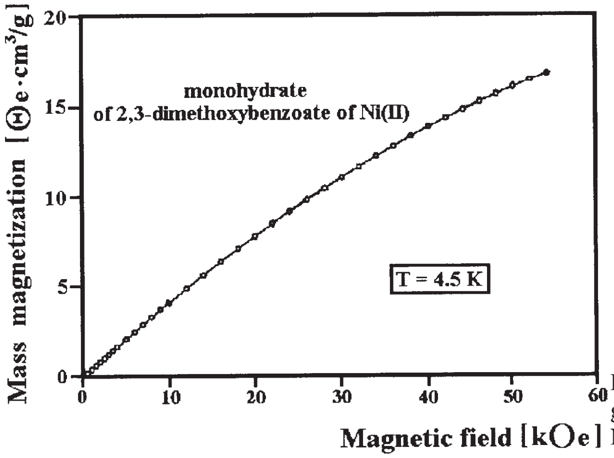


Fig. 2. The dependence between magnetization and magnetic field for Ni(II) 2,3-dimethoxybenzoate.

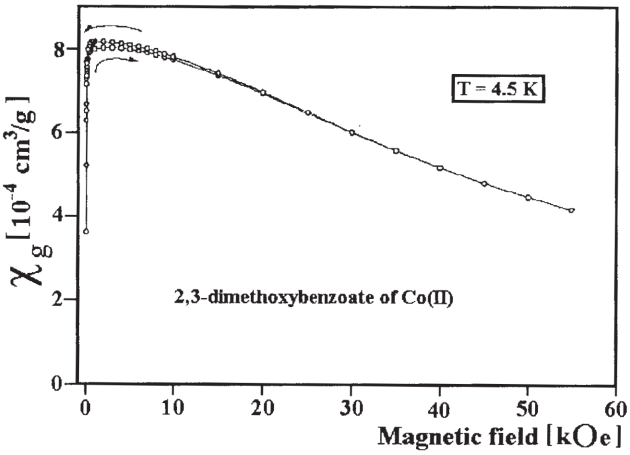


Fig. 3. Relationship between the mass susceptibility and the magnetic field for Co(II) 2,3-dimethoxybenzoate.

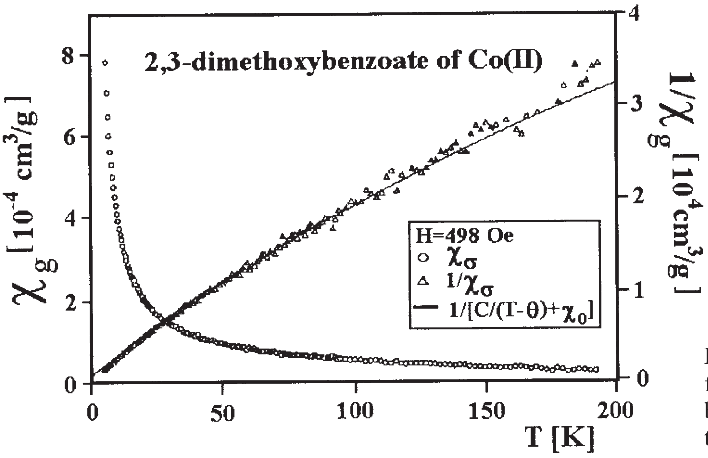


Fig. 4. Mass susceptibility for Co(II) 2,3-dimethoxybenzoate as a function of temperature.

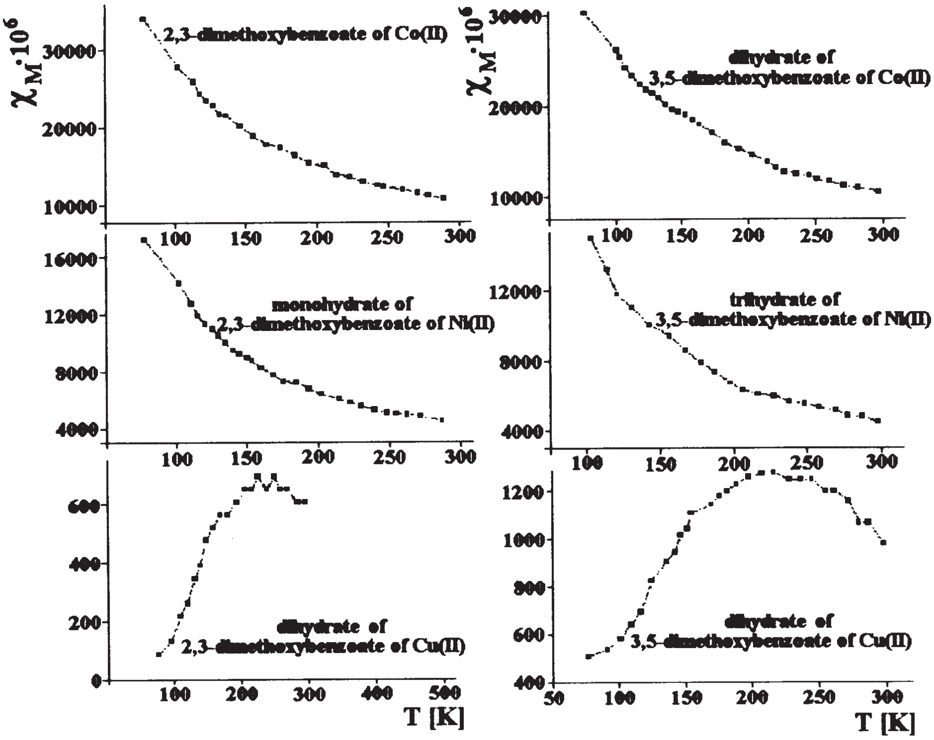


Fig. 5. Relationship between the values of the magnetic susceptibilities of 2,3- and 3,5-dimethoxybenzoates of Co(II) Ni(II) and Cu(II) *versus* temperature.

where M is the magnetization and H is the value of the applied magnetic field. The dependence of the magnetization on the field intensity is presented in Figs. 1,2. The magnetic susceptibilities of the samples were only studied at a magnetic field strength of 0.5 k0e (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. 5. The alternating current susceptibilities in the narrow temperature range were measured using an AC susceptometer.

TABLE III. Frequencies of the absorption bands of some gaseous products evolved during the decomposition of 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) (cm^{-1})

Range of frequency	Identified gaseous product
3750–3700	H_2O
1600–1300	
3000–2800	Hydrocarbons
1750	
1600–1050	
2350	CO_2
625–800	
2200	CO
2900–2800	Monohydric alcohols
1250–1050	

TABLE IV. Values of χ_M and μ_{eff} for 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II)

CoL_2			$NiL_2{\cdot}H_2O$			$CuL_2{\cdot}2H_2O$			$CoL_2{\cdot}2H_2O$			$NiL_2{\cdot}3H_2O$			$CuL_2{\cdot}2H_2O$		
T/K	$\chi_M\times10^6$	μ_{eff}/MB	T/K	$\chi_M\times10^6$	μ_{eff}/MB	T/K	$\chi_M\times10^6$	μ_{eff}/MB	T/K	$\chi_M\times10^6$	μ_{eff}/MB	T/K	$\chi_M\times10^6$	μ_{eff}/MB	T/K	$\chi_M\times10^6$	μ_{eff}/MB
2,3-Dimethoxybenzoates									3,5-Dimethoxybenzoates								
77	34389	4.61	77	17280	3.28	77	94.2	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	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	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	508	0.96	123	21932	4.67	168	8591	3.44	136	831	1.09
139	21551	4.92	137	10043	3.35	159	554	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	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	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	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	1.26	148	19328	4.81	217	6067	3.31	161	1108	1.33
190	16247	5.00	164	8289	3.34	217.0	693	1.29	153	19053	4.86	228	5981	3.37	170	1155	1.39
200	15363	4.99	173	7763	3.32	227.0	7.39	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	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	1.38	173	17089	4.89	258	5316	3.38	189	1247	1.51
230	13469	5.01	199	6754	3.33	259.5	693	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

TABLE IV. Continued

CoL_2			$NiL_2 \cdot H_2O$			$CuL_2 \cdot 2H_2O$			$CoL_2 \cdot 2H_2O$			$NiL_2 \cdot 3H_2O$			$CuL_2 \cdot 2H_2O$		
T/K	$\chi_M \times 10^6$	μ_{eff}/MB	T/K	$\chi_M \times 10^6$	μ_{eff}/MB	T/K	$\chi_M \times 10^6$	μ_{eff}/MB	T/K	$\chi_M \times 10^6$	μ_{eff}/MB	T/K	$\chi_M \times 10^6$	μ_{eff}/MB	T/K	$\chi_M \times 10^6$	μ_{eff}/MB
2,3-Dimethoxybenzoates									3,5-Dimethoxybenzoates								
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	3.35				271	11194	4.97				287	1108	1.76
									281	10966	5.01				298	1016	1.75
									297	10555	5.06						

$L = C_9H_9O_4^-$

The magnetic susceptibilities of the samples of the 2,3- and 3,5-dimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) were also measured by the Gouy method using a sensitive Cahn RM-2 balance. The measurements were made at a magnetic field strength of 9.9 k0e. The employed calibrant was Hg[Co(SCN)$_4$], for which a magnetic susceptibilities of 1.644×10^{-5} cm^{-3} g^{-1} was taken.[18] The correction for diamagnetism of the constituent atoms was calculated using Pascal constants.[19] The magnetism of the samples was found to be field independent. The magnetic moments were calculated according to Eq. (2):

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

The calculated values of the moment for the 2,3- and 3,5-dimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) are presented in Tables IV and V and Fig. 7.

TABLE V. Magnetic moment values of the complexes with the central ions Co(II), Ni(II) and Cu(II) in octahedral coordination

	Central ion		
	Co^{2+}	Ni^{2+}	Cu^{2+}
Number of d electrons	7	8	9
High-spin complexes			
Number of unpaired electrons	3	2	1
Spin-only moment / BM	3.88	2.83	1.73
Magnetic moment / BM		2;3-Dimethoxybenzoates	
	4.61–5.09	3.28–3.44	0.47–1.47
		3;5-Dimethoxyenzoates	
	4.33–5.06	3.29–3.54	0.67–1.75

RESULTS AND DISCUSSION

The complexes of the 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) were obtained as polycrystalline solids with a metal to ligand ratio of 1:2 and the general formula $M(C_9H_9O_4)_2 \cdot nH_2O$, where M = Co(II), Ni(II), Cu(II) and $n = 2$ for the 3,5-dimethoxybenzoates of Cu(II) and Co(II), $n = 3$ of the 3,5-dimethoxybenzoate of Ni(II), $n = 1$ for the 2,3-dimethoxybenzoate of Ni(II) and $n = 0$ for the 2,3-dimethoxybenzoate of Co(II). Their colours are: pink for the Co(II), green for the Ni(II) and blue for the Co(II) complexes.[16,17]

The details connected with the indentification of these complex by spectral analysis were extensively presented in previous papers.[16,17] Therefore, in this paper only some selected results of the FTIR and FIR analysis are presented in Table I. There are two bands arising from asymmetric and symmetric vibrations of the COO$^-$ groups at 1629–1578 cm^{-1} for the 2,3- and at 1598–1581 cm^{-1} for the 3,5-dimethoxybenzoates and symmetric vibrations of the COO$^-$ groups at 1448–1401 cm^{-1} for the 2,3- and 1428–1392 cm^{-1} for the 3,5-dimethoxybenzoates.[20–26] The bands due to ν(M–O) appear in the ranges 481–227 cm^{-1} and 497–208 cm^{-1}, for the 2,3- and 3,5-dimethoxybenzoates, respectively. The magnitudes of the separation, $\Delta\nu$OCO$^-$ (where $\Delta\nu\text{OCO}^- = \nu_{as}\text{OCO}^- - \nu_s\text{OCO}^-$), which characterize the type of metal ion – oxygen bond, change from 220–131 cm^{-1} for the 2,3- to 197–153 cm^{-1} for the 3,5- dimethoxybenzoates. According to spectroscopic criteria and especially with regard to Nakamoto,[22,25,26] the carboxylate groups in the analysed complexes show different modes of coordination. In the 2,3-dimethoxybenzoates, they may function as monodentate, bidentate chelating or bidentate bridging groups and in the 3,5-dimethoxybenzoates, only as bidentate chelating or bridging ones.

The X-ray diffraction patterns of the 2,3- and 3,5-dimethoxybenzoates 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 determined as attempts to obtain single crystals failed.

The thermal stability of Co(II), Ni(II) and Cu(II) 2,3- and 3,5-dimethoxybenzoates was studied in air and nitrogen. All the details concerning the thermal decomposition of these complexes in air were described in previous papers.[16,17] Accordingly, in this paper, only some selected results obtained for their thermal stability in air are presented (Table II). The 2,3-dimethoxybenaozates of Co(II), Ni(II) and Cu(II) are stable in air up to 325–385 K. They lose water molecules in one or two steps 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, lie in the range 52.60–157.6 kJ mol^{-1} and are proportional to the energy of the bonding of a definite number of water molecules in the corresponding 2,3- and 3,5-dimethoxybenzoates (Table II, Fig. 1). The dihydrate of Co(II) 3,5-dimethoxybenzoate is the most thermally stable, while that of Cu(II) has the lowest thermal stability. The anhydrous Co(II), Ni(II) and Cu(II) 2,3- and 3,5-dimethoxybenazoates decompose to the oxides of the corresponding metal: CoO (for the Co(II) dimethoxybenzoates), NiO (for the Ni(II) dimethoxybenzoates) and CuO (for the Cu(II) dimethoxybenzoates) which are the final products of the decomposition of these complexes. During the decompositions of the anhydrous complexes of Co(II) and Ni(II), Co and Co_3O_4 are formed as intermediate products in the case of Co(II) 2,3- and 3,5-dimethoxybenzoates, while Ni is the intermediate product in the case of the Ni(II) complexes.[16,17]

The ways of the thermal decompositions of 2,3-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) are as follows:

$CoL_2 \rightarrow Co \rightarrow Co_3O_4 \rightarrow CoO$

$NiL_2{\cdot}H_2O \rightarrow NiL_2 \rightarrow Ni \rightarrow NiO$

$CuL_2{\cdot}2H_2O \rightarrow CuL_2{\cdot}H_2O \rightarrow CuL_2 \rightarrow CuO$; where $L = C_9H_9O_4^-$

The 3,5-dimethoxybenaozates of Co(II), Ni(II) and Cu(II) decompose in the following ways:

$CoL_2{\cdot}2H_2O \rightarrow CoL_2 \rightarrow Co \rightarrow Co_3O_4 \rightarrow CoO$

$NiL_2{\cdot}3H_2O \rightarrow NiL_2 \rightarrow Ni \rightarrow NiO$

$CuL_2{\cdot}2H_2O \rightarrow CuL_2 \rightarrow CuO$; where $L = C_9H_9O_4^-$

Considering the temperature at which the dehydration processes occur and the ways in which they proceed, it is possible to assume that the water molecules are in the outer or inner coordination spheres of the complexes.[16,17,21,28–31]

The thermal stability of the 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) was also studied under a nitrogen atmosphere (Table II). The hydrated complexes decompose in two steps when heated to 1173 K. They are stable up to 293–373 K and then they dehydrate to form anhydrous complexes. The dehydration process is accompanied by an endothermic effect as observed on the DTA curves. The anhydrous complexes decompose during heating to a mixture of the oxides of the respective metals and carbon.

The FTIR spectra of the gaseous product evolved during the decomposition of the 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) are presented in Table III. Their interpretation reveals them to be molecules of H_2O, CO_2, CO, hydrocarbons and monohydric alcohols.[22,23,32,33]

The magnetic susceptibility of Co(II), Ni(II) and Cu(II) 2,3- and 3,5-dimethoxybenzoates was determined in the range 4.4–300 K in order to study paramagnetic saturation or magnetic dipole arrangements. The complexes show paramagnetic properties and only 2,3- and 3,5-dimethoxybenzoates of Co(II) and Ni(II) obey the Curie–Weiss law (the complexes of Cu(II) do not satisfy it). However, none of the complexes exhibited clear magnetic orientation regions in the whole temperature range. For example, the parameters of the fitting to the Curie–Weiss law for the Ni(II) and Co(II) complexes are presented in Figs. 2–4. 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.[34–37] The paramagnetic dependences of values of the magnetic susceptibility as a function of temperatures are given in Tables IV and V and Fig. 5. They give informations about the magnetic interaction between paramagnetic centers. As a rule, if the χ_M value increase with increasing temperatures, this indicates an antiferromagnetic interaction but when the χ_M values decrease with increasing temperature, the magnetic interaction is ferromagnetic. The χ_M values for the 2,3- and 3,5-dimethoxybenzoates of Co(II) and Ni(II) show a gradual decrease with increaisng temperature. This indicates a tendency of ferromagnetic interaction between the metal ions. The experimentally determined values of the magnetic moment for the 2,3- and 3,5-dimethoxybenzoates of Co(II) and Ni(II) were found to be in the ragnes: 4.61–5.09 BM and 4.33–5.06 BM for complexes of Co(II), respectively, and 3.28–3.44 BM and 3.29–3.54 BM for the Ni(II) complexes, respectively. The experimental data reveal that the magnetic moments of the 2,3- and 3,5-dimethoxybenzoates of Ni(II) are connected with a spin-only moment. This indicates that in the solid state the nickel cation exists in an octahedral triplet ground state with molecules of water and probably with bidentate and monodentate carboxylate groups coordinated to the nickel(II) ion. This was confirmed by the IR spectral analysis (Table I). The ground state configuration of the nickel(II) ion in a regular octahedral field is $^3A_{2g}(t_{2g}{}^6e_g{}^2)$ 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.

In the case of the 2,3- 3,5-dimethoxybenzoates of Co(II), the effective magnetic moments are equal to 4.61–5.09 BM and 4.33–5.06 BM (Table IV, Fig. 5). The magnetic moments measured for the Co(II) complexes are 5.09 BM and 5.06 BM at room temperature. These values differ from that of the spin-only moment, which amounts to 3.88 BM. This relatively large difference between the measured and calculated values results from spin-orbital coupling.[38] The experimental data suggest that the 2,3- and 3,5-dimethoxybenzoates of Co(II) and Ni(II) are high-spin complexes with octahedral coordination and weak ligand fields.

The effective magnetic moment values of the 2,3- and 3,5-dimethoxybenzoates of Cu(II) determined in the temperature range 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 (298 K), respectively. This kind of dependence is typical behaviour of copper dimers exhibiting characteristic antiferromagnetic interactions between the Cu(II) centers, which obey the Bleaney–Bowers equation[34,38–41] (3):

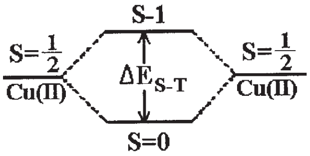
$$\chi = \frac{Ng_{\mathrm{av}}^2\beta^2}{3kT}\left[1+\frac{1}{3}(\mathrm{e}^{-2J/kT})\right]^{-1} \tag{3}$$

where: N – Avogadro constant, B – Bohr magneton, k – Boltzmann constant, T – absolute temperature, J – exchange parameter, g_{av} – average coefficient of the spectroscopic splitting for the dimer experimentally determined from EPR spectra.

The μ_{eff} values display a minimum at 77 K and a maximum at room temperature. The room temperature magnetic moment per Cu is similar to those obeserved for other dinuclear Cu(II) compounds[42,43] and is rather lower than the spin-only magnetic moment. This behaviour indicates an antifferromagnetic coupling between to Cu(II) centers. The variable temperature magnetic results for the 2,3- and 3,5-dimethoxybenzoates of Cu(II) are given in Table IV and Fig. 5. The magnetic susceptibility reaches highest values at room temperature and decreases with decreasing temperature. The magentic 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 the depopulation of the excited triplet (S = 1) state. It is well-know 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, the interaction will be ferromagnetic.[39,44] According to Kahn's theory, the exchange coupling constant is the sum of ferromagnetic and antiferromagnetic contributions.[45] The ferromagnetic contribution is weak when the metal ions are bridged by polyatomic extended ligands.[46] However, the magnitude of the antiferromagnetic interaction is primarily governed by the overlap of two magnetic orbitals centered on nearest-neighbour copper(II) ions.[47] Whereas ferromagnetic contributions are usually small, antiferromagnetic ones may be considered as being proportional to the square of the gap between the molecular constructed from the magnetic orbitals.[48] For dinuclear Cu(II) complexes the magnetic coupling constant J is directly related to energy separation between the singlet and triplet-states (Eq. (4)):

$$2J = E_S - E_T \tag{4}$$

In the lower temperature range only the lowest levels of dimers are occupied. They may be followed by the course of $\chi_{Cu} = f(T)$ for copper(II) dimers with states S = 1 and S = 0.[49]



ST = singlet-triplet energy gap

The electron population in both levels is combined with the Boltzmann 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 dominating) and the magnetic moment has values close to the pure spingrie (1.73 BM), but it is usually lower. With decreasing temperature, the population of the triplet state decreases and within the lowest temperature range, only the singlet state is occupied (S = 0) and μ = 0 BM.

The magnetic features of the 2,3- and 3,5-dimethoxybenzoates of Cu(II) indicate the mode of the metal ion – 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 mainly brought about by the geometrical structures of this complex and the properties of the bridged ligands.[34,50–52]

The magnetic measurements reveal that the 2,3- and 3,5-dimethoxybenzoates of Cu(II) form dimers with bidentate bridging carboxylate groups. This type of dentates COO^- groups was confirmed by IR spectral data (Table I). In the case of the 2,3- dimethoxybenzote of Cu(II), the electron densities on the oxygen atoms increase which leads to stronger covalent metal ion – oxygen bonds and thereby to an increased overlap of the orbitals of the two unpaired electrons in the binuclear units (μ_{eff} = 1.47 BM at room temperature). However, in the case of the 3,5-dimethoxybenazoate of Cu(II), the electron density on the oxygen atoms of the carboxylate group is decreased causing a weakening of the metal – oxygen bond and a decerese of the overlap of the two unpaired electron orbitals in the binuclear units (μ_{eff} = 1.75 BM at room temperature).[41]

In conclusion, from the obtained results it appears that the M–O bond in the 2,3- and 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) is rather electrostatic in nature. The colours of the complexes are the same as those of the free M(II) ions. The electron density in the molecules makes the d→d electronic transitions of the central ions to be those of the lowest energy and the absorption occurs at relatively high wavelengths.

The complexes are crystalline compounds with varying symmetry. The carboxylate groups show different dentates. The 2,3- and 3,5-dimethoxybenzoates of Co(II) and Ni(II) obey the Curie–Weiss law and are high-spin complexes with octahedral coorination and weak ligand fields. The complexes of Cu(II) form dimers with antiferromagnetic interaction between two copper centers. The obtained results also show that, irrespective of the substituent positions in benzene ring, the ratio of the metal:ligand in the complexes and their colours stay the same for both of the two series of Co(II), Ni(II) and Cu(II) dimethoxybenzoates.

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ИЗВОД

МАГНЕТНЕ, ТЕРМИЧКЕ И СПЕКТРОСКОПСКЕ ОСОБИНЕ Co(II), Ni(II) И Cu(II) 2,3- И 3,5-ДИМЕТОКСИБЕНЗОАТА

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Синтетизовани су Co(II), Ni(II) и Cu(II) 2,3- и 3,5-диметоксибензоати као чврсте супстанце и проучавана су њихова магнетна, термичка и спектрална својства. Добивени комплекси су хидратисана или анхидрована једињења боје типичне за одговарајуће M(II) јоне. Термичка стабилност одређивана је у ваздуху и азоту, а идентификовани су чврсти и гасовити продукти разлагања. Магнетна сусцептибилност мерена је у температурном опсегу 4,4 – 300 K и израчунати су одговарајући магнетни моменти. Резултати показују да су 2,3- и 3,5- диметоксибензоати Co(II) и Ni(II) високоспински комплекси са слабим пољем лиганада, док су комплекси Cu(II) у облику димера.

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