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Comparison of some properties of Cu(II) 2,3- , 3,5- and 2,6-dimethoxybenzoates

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Abstract: The physico-chemical properties and thermal stability in air of Cu(II) 2,3- , 3,5- and 2,6-dimethoxybenzoates were compared and the influence of the position of –OCH₃ substituent on their thermal stability was investigated. The complexes are crystalline, hydrated salts with blue colour. The carboxylate ion is a bidentate chelating or bridging group. The thermal stability of analysed Cu(II) dimethoxybenzoates was studied in the temperature range of 293-1173 K. The positions of *methoxy*-groups in benzene ring influence the thermal properties of studied complexes. Their different thermal properties are markedly connected with the various influence of inductive, mesomeric and steric effects of –OCH₃ substituent on the electron density in benzene ring. The magnetic susceptibilities of the complexes were measured over the range of 76-300 K and the magnetic moments were calculated. The results show that they form dimers.

Keywords: dimethoxybenzoates; complexes of Cu(II); magnetic moments; thermal behavior; FTIR spectra.

Introduction

2,3-, 3,5- and 2,6-dimethoxybenzoic acids are crystalline solids sparingly soluble in cold water [1-5]. The literature survey shows that in principle there is no information about the complexes of these acid anions with various cations. Papers exist only on their compounds with rare earth elements in solution and solid state [2, 6, 7]. At present, we decided to obtain the complexes of Cu(II) ions with 2,3- , 3,5- and 2,6-dimethoxybenzoic acid anions as solids, to examine some of their physico-chemical properties and to compare them.

In our previous papers [8-12] we characterized these complexes by elemental

analysis, IR spectral data, thermogravimetric studies and X-ray diffraction measurements but now taking into account the presence and positions of two *methoxy*- groups in benzene ring we decided to compare the properties of Cu(II) compounds in order to investigate the influence of substituent positions on their properties.

Experimental details

2,3- , 3,5- and 2,6-dimethoxybenzoates of Cu(II) were prepared by the addition of equivalent quantities of 0.1 M ammonium 2,3- , 3,5- and 2,6-dimethoxybenzoates (pH 5) to hot 0.1 M aqueous solutions containing the nitrates

(V) of Cu(II) ions and crystallizing at 293 K. The solids were 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 Cu²⁺ metal ions were established gravimetrically, and by ASA method with the use of ASA 880 spectrophotometer (Varian).

The FTIR spectra of the complexes were recorded in the range of 4000 – 400 cm⁻¹ using an FTIR 1725X Perkin – Elmer spectrometer. The samples for the FTIR spectroscopy were prepared as KBr discs. Some of the results are presented in Table 1.

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 of 2Θ=4-80° by means of the Debye-Scherrer-Hull method. The relationships between I/I₀ and 2Θ for these complexes are presented in Fig. 2.

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 Al₂O₃ was used as the standard. The decomposition products were calculated from the TG curve and verified by powder diffraction analysis.

Magnetic susceptibilities of polycrystalline samples of 2,3-, 3,5- and 2,6-dimethoxybenzoates of Cu(II) were investigated at 76-303 K. The measurements were carried out using the Gouy method. Weight changes were obtained from Cahn RM-2 electrobalance. The calibrant employed was Hg[Co(SCN)₄] for which the magnetic susceptibility was assumed to be 1.644·10⁻⁴.

Table 1. Frequencies of the OCO⁻ absorption bands for Cu(II) and Na(I) 2,3-, 3,5- and 2,6-dimethoxybenzoates and those of CO for non-coordinated 2,3-, 3,5- and 2,6-dimethoxybenzoic acids (cm⁻¹)

Complex L=C ₉ H ₉ O ₄ ⁻		ν C=O	ν _{as} OCO	ν _s OCO	ΔνOCO	νM-O	Solubility mol·dm ⁻³
2,3-	CuL ₂ ·2H ₂ O	-	1607	1401	206	481	7.9·10 ⁻⁴
			1578	1442	136		
	NaL	-	1604	1396	208		
	HL	1686	-	-	-		
3,5-	CuL ₂ ·2H ₂ O	-	1581	1392	189	497	6.5·10 ⁻⁵
				1428	153		
	NaL	-	1580	1385	195		
	HL	1684	-	-	-		
2,6-	CuL ₂ ·H ₂ O	-	1596	1412	184	472	1.2·10 ⁻²
	NaL	-	1608	1408	200		
	HL	1712	-	-	-		

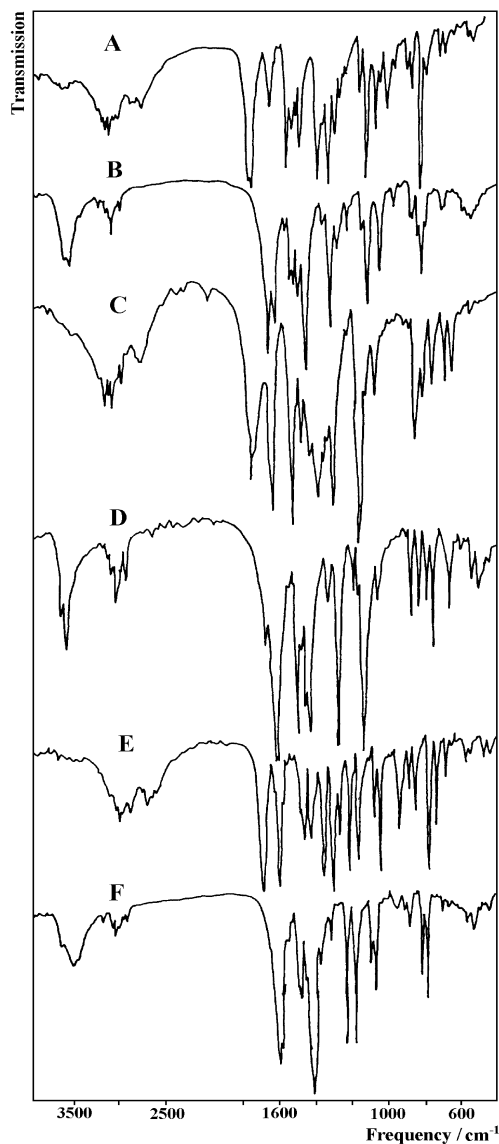


Figure 1. IR spectra of 2,3-dimethoxybenzoic acid (A); 2,3-dimethoxybenzoate of Cu(II) (B); 2,6-dimethoxybenzoic acid (C); 2,6-dimethoxybenzoate of Cu(II) (D); 3,5-dimethoxybenzoic acid (E); 3,5-dimethoxybenzoate of Cu(II) (F).

$^5 \text{ cm}^3 \cdot \text{g}^{-1}$. Correction for diamagnetism of the calibrant atoms was calculated by the use of Pascal's constants [13, 14]. Magnetic moments were calculated from Eq.(1)

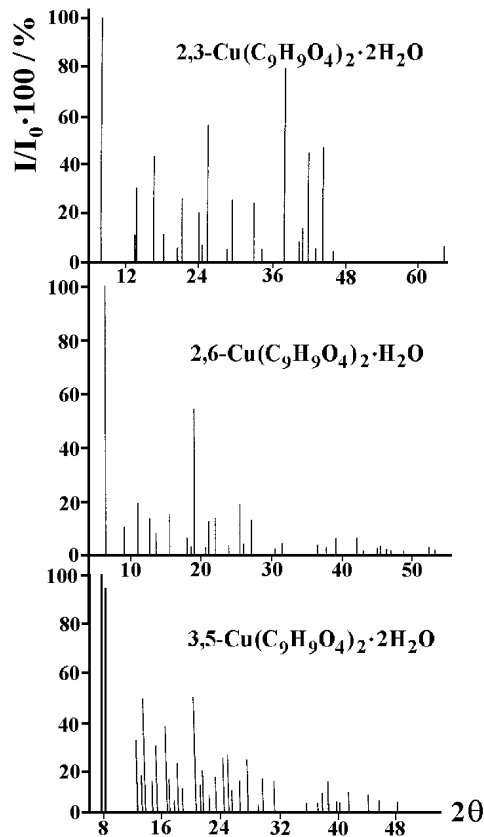


Figure 2. Dependence of I/I_0 vs 2θ for Cu(II) 2,3-, 3,5- and 2,6-dimethoxybenzoates.

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

The solubilities of 2,3-, 3,5- and 2,6-dimethoxybenzoates of Cu(II) in water were measured at 293 K. Saturated solutions of the obtained compounds were prepared under isothermal conditions. The contents of Cu(II) were determined by using ASA 880 spectrophotometer (Varian). The values of solubilities are presented in Table 1.

Results and Discussion

The complexes of the 2,3-, 3,5- and 2,6-dimethoxybenzoates of Cu(II) were obtained as polycrystalline blue solids with a metal to ligand ratio of 1:2 and the general formula

Table 2. Temperature ranges of the thermal stability of Cu(II) 2,3-, 3,5- and 2,6-dimethoxybenzoates in air

Complex		Temperature	Mass loss %		Water	Intermediate
L=C ₉ H ₉ O ₄ ⁻		decomp.range			molecule	and final
		K	Calcd.	Found	n	products of decomp.
2,3-	CuL ₂ ·2H ₂ O	385-407	3.89	4.1	1	CuL ₂ ·H ₂ O
	CuL ₂ ·H ₂ O	416-433	7.79	7.2	1	CuL ₂
	CuL ₂	453-800	74.90	74.0	-	CuO
3,5-	CuL ₂ ·2H ₂ O	325-442	7.79	7.0	2	CuL ₂
	CuL ₂	521-848	74.90	74.2	-	CuO
2,6-	CuL ₂ ·H ₂ O	398-433	4.05	3.4	1	CuL ₂
	CuL ₂	448-742	82.07	82.4	-	CuO

Cu(C₉H₉O₄)₂·nH₂O, where n=2 for 2,3- and 3,5-dimethoxybenzoates and n=1 for 2,6-dimethoxybenzoate [8-12]. The details connected with their identification by elemental and spectral analyses were extensively presented in our pervious papers [8-12]. Therefore, in this article only some selected results of the FTIR investigations were presented in Table 1. There are two bands arising from asymmetric and symmetric vibrations of the COO⁻ groups at 1607-1578 cm⁻¹ and 1442-1392 cm⁻¹, respectively for analysed complexes [15-21]. The bands due to ν(M-O) appear in the range of 497-472 cm⁻¹. The magnitudes of the separation ΔνOCO⁻ (where ΔνOCO⁻ = ν_{as}OCO⁻ - ν_sOCO⁻), which characterize the type of metal ion-oxygen bond change from 206 cm⁻¹ to 184 cm⁻¹. According to spectroscopic criteria and especially with regard to Nakamoto [20, 21] the carboxylate groups in the analysed complexes show different modes of coordination. In the 2,3- and 3,5-dimethoxybenzoates they may function as bidentate chelating or bidentate bridging groups and in the 2,6-dimethoxybenzoate only as bidentate bridging ones.

The X-ray diffraction patterns of the 2,3, 3,5- and 2,6-dimethoxybenzoates of Cu(II) were recorded. The analysis of the diffractograms suggests that the complexes are polycrystalline compounds with various degrees of crystallinity and different structures [22]. Their structures have not been determined as attempts to obtain single crystals failed.

The thermal stability of Cu(II) 2,3-, 3,5- and 2,6-dimethoxybenzoates was studied in air. All the details concerning the thermal decomposition of these complexes in air were described in our previous papers [8-12].

Accordingly, in this paper only some selected results obtained for their thermal stability are presented (Table 2). The 2,3-, 3,5- and 2,6-dimethoxybenzoates of Cu(II) are stable up to 325-398 K. They lose water molecules in one or two steps and form the anhydrous compound. The dehydration processes are associated with an endothermic effect on the DTA curves. The anhydrous Cu(II) dimethoxybenzoates decompose to the CuO which is the final product of the decomposition of these complexes. The thermal stability of anhydrous dimethoxybenzoates

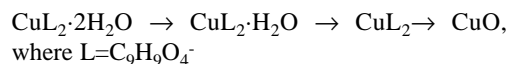
Table 3. Values of χ_M and μ_{eff} for 2,3-, 3,5- and 2,6-dimethoxybenzoates of Cu(II)

CuL ₂ ·2H ₂ O			CuL ₂ ·2H ₂ O			CuL ₂ ·H ₂ O		
2,3-dimethoxybenzoate			3,5-dimethoxybenzoate			2,6-dimethoxybenzoate		
T / K	$\chi_M \cdot 10^6$	$\mu_{\text{eff}} / \text{BM}$	T / K	$\chi_M \cdot 10^6$	$\mu_{\text{eff}} / \text{BM}$	T / K	$\chi_M \cdot 10^6$	$\mu_{\text{eff}} / \text{BM}$
77	94.2	0.47	77	462	0.67	76	364	0.46
96.4	138.6	0.56	91	508	0.75	123	688	0.82
109.5	231	0.66	101	554	0.81	133	770	0.91
120.0	277.2	0.72	109	600	0.87	143	831	0.98
132	369.6	0.82	117	646	0.92	153	880	1.04
140	415.8	0.87	125	693	0.98	163	921	1.10
149	508	0.96	136	831	1.09	173	941	1.14
159	554	1.02	143	924	1.16	183	949	1.18
169.5	600	1.08	147	970	1.20	193	961	1.22
180.0	600	1.11	152	1016	1.25	203	974	1.26
195.0	646	1.19	155	1062	1.28	213	961	1.28
207.0	693	1.26	161	1108	1.33	223	961	1.31
217.0	693	1.29	170	1155	1.39	233	953	1.33
227.0	7.39	1.35	176	1201	1.43	243	941	1.35
239.0	693	1.36	182	1247	1.48	253	945	1.38
250.5	693	1.38	189	1247	1.51	263	929	1.40
259.5	693	1.41	198	1293	1.57	273	921	1.42
269.5	693	1.44	208	1293	1.61	283	913	1.44
284.5	648	1.48	217	1293	1.64	293	904	1.46
296.4	646	1.47	228	1339	1.68	303	892	1.47
			237	1293	1.72			
			245	1247	1.75			
			256	1247	1.76			
			262	1247	1.78			
			272	1201	1.79			
			280	1108	1.76			
			287	1108	1.76			
			298	1016	1.75			

L = C₉H₉O₄⁻

increases in order: 2,6- < 2,3- < 3,5- while that of hydrated ones in the sequence: 3,5- < 2,3- < 2,6-. From the comparison of the decomposition way results it follows that the various position of -OCH₃ substituents in benzene ring influences the decomposition process being strongly connected with the various participations of the inductive and mesomeric effects of *methoxy*- groups in the electron density of the system.

The way of the thermal decomposition of 2,3-dimethoxybenzoate of Cu(II) is as follows:



The 3,5- and 2,6-dimethoxybenzoates of Cu(II) decompose in the following ways:

Table 4. Magnetic moment values of the complexes with the central ion of Cu(II) in octahedral coordination

	Central ion
	Cu ²⁺
Number of d electron	9
Number of unpaired electrons	1
Spin-only moment /BM	1.73
Magnetic moment / BM	<div style="display: flex; align-items: center;"> <div style="font-size: 3em; margin-right: 10px;">{</div> <div> 2,3-dimethoxybenzoate 0.47-1.47 3,5-dimethoxybenzoate 0.67-1.75 2,6-dimethoxybenzoate 0.46-1.47 </div> </div>

$\text{CuL}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{CuL}_2 \rightarrow \text{CuO}$ in the case of 3,5-dimethoxybenzoate and
 $\text{CuL}_2 \cdot \text{H}_2\text{O} \rightarrow \text{CuL}_2 \rightarrow \text{CuO}$, in 2,6-dimethoxybenzoate

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 [23-25].

The solubilities of analysed dimethoxybenzoates in water at room temperature were determined (Table 1). They are of the order of 10^{-5} - 10^{-2} mol·dm⁻³. 2,6-dimethoxybenzoate of Cu(II) is the best soluble salt while that of 3,5-dimethoxybenzoate the least one. The values of solubilities increase in the order: 3,5- < 2,3- < 2,6-. The changes in the values presented above are connected with 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*- groups cause the delocalization of the electrons in the molecule and the change of its energy state brought about the conjugation at electrons. It leads to the stabilization of the system [26-28].

Magnetic susceptibility of the analysed compounds was measured in the range of 76-303 K

(Table 3). Their values increase with rising temperature. The effective magnetic moment values of the 2,3-, 3,5- and 2,6-dimethoxybenzoates of Cu(II) change from 0.47 BM (at 77 K) to 1.47 BM (at 296 K) for 2,3-dimethoxybenzoate, from 0.67 BM (at 77 K) to 1.75 BM (at 298 K) for 3,5-dimethoxybenzoate and from 0.46 BM (at 76 K) to 1.47 BM (at 303 K) for 2,6-dimethoxybenzoate of Cu(II). This kind of dependence is typical behaviour of copper dimers exhibiting characteristic antiferromagnetic interactions between the Cu(II) centres, which obey the Bleaney-Bowers equation [29-33] Eq. (2):

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

where: N-Avogadro constant, β -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 76 K and a maximum at room temperature. 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- and 2,6-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 Tables 3 and 4. The magnetic susceptibility reaches highest values at room temperature and decreases with decreasing temperature. The magnetic moment values of the Cu(II) complexes decrease from 1.46 BM, 1.47 BM and 1.75 BM at about 300 K to 0.46 BM, 0.47 BM and 0.67 BM at 77 K, as a consequence of depopulation of the excited triplet ($S=1$) separated by $2J$ [31, 36]. 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 [31, 36]. According to Kahn's theory, the exchange coupling constant is the sum of ferromagnetic and antiferromagnetic contributions [37]. The ferromagnetic contribution is weak when the metal ions are bridged by polyatomic extended ligands [38]. However, the magnitude of the antiferromagnetic interaction is primarily governed by the overlap of two magnetic orbitals centered on nearest-neighbour copper(II) ions [39]. 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 [40]. For dinuclear Cu(II) complexes the magnetic coupling constant J is directly related to energy separation between the singlet and triplet states. In the lower temperature range only 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 $S=0$ [41]. 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 spin (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 $\mu=0$ BM.

The magnetic features of the 2,3-, 3,5- and 2,6-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 [29, 42-44].

The magnetic measurements reveal that 2,3-, 3,5- and 2,6-dimethoxybenzoates of Cu(II) form dimers with bidentate bridging carboxylate groups. This type of dentate of COO^- groups was confirmed by IR spectral data (Table 1). In the case of the 2,3- and 2,6-dimethoxybenzoates 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 ($\mu_{eff}=1.47$ BM at room temperature). However in the case of the 3,5-dimethoxybenzoate 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 decrease of the overlap of the two unpaired electron orbitals in the binuclear units ($\mu_{eff}=1.75$ BM at room temperature) [33].

Conclusions

From the obtained results it appears that the M-O bond in analyzed compounds of 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 lowest energy and the absorption occurs at relatively high wavelengths. The complexes are crystalline compounds with varying symmetry. The carboxylate groups act as bidentate bridging. 2,3-, 3,5- and 2,6-Dimethoxybenzoates 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 three series of Cu(II) dimethoxybenzoates. From the obtained results it follows that in 2,3-, 3,5- and 2,6-dimethoxybenzoates of Cu(II) the coordination number of Cu(II) ions may be equal to 5. It could be established on the basis of the complete crystal structure determination of monocrystal but it has not been obtained for all analyzed compounds. Therefore according to Cu(II) complexes we can only suppose that each Cu(II) ion may show a five fold coordination in the form of a tetragonal pyramid with four oxygen atoms of bidentate bridging

dimethoxybenzoate anions in the basal plane and one oxygen atom of water molecule at the apex.

The proposed formulae for the analyzed complexes may be following:

$[\text{Cu}_2(2,3\text{-L})_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $[\text{Cu}_2(3,5\text{-L})_4(\text{H}_2\text{O})_4]$, and $[\text{Cu}_2(2,6\text{-L})_4(\text{H}_2\text{O})_2]$, where $\text{L}=\text{C}_9\text{H}_9\text{O}_4^-$.

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