Comparison of some properties of 2,3 – and 3,4 – dimethoxybenzoates of Cu(II), Co(II) and Nd(III)

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Abstract: The physicochemical properties of 2,4-, and 3,4- dimethoxybenzoates of Cu(II), Co(II) and Nd(III) were studied and compared to observe the -OCH$_3$ substituent positions in benzene ring on the character of complexes. The analysed compounds are crystalline hydrated or anhydrous salts with colours depending on the kind of central ions: blue for Cu(II), pink for Co(II) and violet for Nd(III) complexes. The carboxylate groups bind as monodentate, bidentate bridging or chelating and even tridentate ligands. Their thermal stabilities were studied in air at 293-1173K. When heated the hydrated complexes release the water molecules and form anhydrous compounds which are then decomposed to the oxides of respective metals. Their magnetic moment values were determined in the range of 76-303K. The results reveal the compounds of Nd(III) and Co(II) to be the high-spin and that of Cu(II) forms dimer. The various positions of -OCH$_3$ groups in benzene ring influence some of physicochemical properties of analysed compounds.

Keywords: 2,4- and 3,4- dimethoxybenzoates; thermal stability; magnetic properties.

Introduction

2,4- and 3,4- Dimethoxybenzoates of Cu(II), Co(II) and Nd(III) were synthesized, their properties investigated and presented in our previously published papers [1,2]. We undertook the above topic of our paper for studying the influences of the -OCH$_3$ group positions in benzene ring on the complex properties. That presention has been still a continuation of our experiments on the carboxylates with various *d-* and *4f* – metal ions. These type of compounds have the significant positions in inorganic and bioinorganic chemistry and the again many metal cations in a great number of various biological processes especially six-membered ring system are com-

pounds of several vitamins and drugs [3,4]. Moreover, carboxylates of *d* and *4f* ion elements depending on their magnetic properties, as magnets, may be used in the modern branches of techniques and technology as electronic materials, and they have applications as precursors in superconducting ceramic and magnetic material productions. Multifunctional rigid type of carboxylate ligands as tethers for constructions of solid phases were also exploited with diverse and unusual topologies [5].

2,4- and 3,4- Dimethoxybenzoic acids are used in various branches of techniques and technology as electric materials, and for magnetic material productions [6-11]. In medicine and in pharmacy they are applied for the preparation of

antibiotics and various dyes. From the survey of literature it follows that there are papers on the complexes of some of rare earth elements with 2,4- and 3,4-dimethoxybenzoic acid anions and on their properties [12-17].

There is no information about the comparison of properties of solid of 2,4- and 3,4-dimethoxybenzoates of Cu(II), Co(II) and Nd(III). Therefore, we decided to investigate the influence of the positions of methoxy- groups in the benzene ring on such their properties having been presented in our previous papers [1,2] as: thermal stability in air, spectral characterization, X-ray powder investigations and magnetic behaviour in the range of 76 – 303K.

Experimental

The preparation of complexes were given in our previously published papers [1,2].

The carbon and hydrogen analysis was performed using a CHN 2400 Perkin-Elmer analyzer. The contents of M(II) and M(III) metals were calculated from TG curves and for comparison also established gravimetrically [1,2].

The IR spectra of complexes were recorded over the range of 400-4000 cm^{-1} using M-80 spectrophotometer (Carl - Zeiss, Jena). Samples for IR spectra measurements were performed as KBr discs.

The X-ray powder diffraction were taken on a HZG-4 (Carl - Zeiss, Jena) diffractometer using Ni - filtered CuK_{α} radiation. The measurements were made within the range $2\theta = 4 - 80°$ by means of the Debye – Scherrer – Hull method [1,2].

The thermal stability and decomposition of Co(II), Cu(II) and Nd(III) complexes were studied in air using a Q-1500D derivatograph with Derill converter recording TG, DTG and DTA curves. The details of measurements are presented in our papers previously published [1,2].

Magnetic susceptibilities of polycrystalline samples of 2,4- and 3,4- dimethoxybenzoates of Co(II), Cu(II) and Nd(III) were measured by the Gouy method using a sensitive Cahn RM-2 electrobalance [1,2]. The calibrant employed was $Hg[Co(SCN)_4]$ for which the magnetic susceptibility was assumed to be $8.08 \times 10^{-3} cm^3 mol^{-1}$. The correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [18]. Magnetic moments were calculated from the the equations (1) and (1*):

$$\mu_{eff} = 2.83 \, (\chi_M \, (T-\theta))^{1/2} \text{ ; where } \theta - \text{Weiss constant} \tag{1}$$

$$\mu_{eff} = 2.83 \, (\chi_M \, (T-\theta))^{1/2} \cdot 1.257 \times 10^{-6} \, m \cdot kg \cdot s^{-2} A^{-2} \tag{1*}$$

Results and discussion

The complexes of 2,4- and 3,4-dimethoxybenzoates of Cu(II), Co(II) and Nd(III) were obtained as polycrystalline products with a metal to ligand ratio of 1:2 for divalent ions, and 1:3 for Nd(III). The general formula for 2,4-dimethoxybenzoates of Cu(II) and Co(II) is $M(C_9H_9O_4)_2 \cdot nH_2O$, where M(II) = Cu, Co, and n=1 for Cu(II), and n=0 for Co(II). For 3,4-dimethoxybenzoates of Co(II) and Cu(II) the general formula is $M(C_9H_9O_4)_2 \cdot nH_2O$, where M(II)=Cu, Co, and n=2 for Cu(II), and n=0 for Co(II). 2,4- and 3,4- Dimethoxybenzoates of Nd(III) form anhydrous salts $Nd(C_9H_9O_4)_3$. The colours of complexes are following: for Co – pink, Cu – blue, Nd – violet [1,2,19,20].

The compounds exhibit in solid state similar IR spectra. Some of the results taken from our papers [1,2] are presented in Table 1. The bands due to the COOH group at 1670 cm^{-1} for the 2,4- dimethoxybenzoic acid and 1700 cm^{-1} for the 3,4- dimethoxybenzoic acid are replaced in the spectra of the complexes by two bands: asymmetric (1628 – 1608 cm^{-1} for 2,4-dimethoxybenzoates and 1600 – 1590 cm^{-1} for 3,4- dimethoxybenzoates) and symmetric vibrations of COO^- group (1408 – 1372 cm^{-1} for 2,4-dimethoxybenzoates and 1420 – 1380 cm^{-1} for 3,4- dimethoxybenzoates), respectively [1,2,21]. The magnitudes of separation, $\Delta\nu_{COO^-}$ ($\Delta\nu_{COO^-} = \Delta_{asCOO^-} - \Delta_{sCOO^-}$) which characterize the metal – oxygen bond change in the range from 220 – 208 cm^{-1} for 2,4- dimethoxybenzoates to 240 – 180 cm^{-1} for the 3,4- dimethoxybenzoates.

From the comparison of $\Delta\nu_{COO^-}$ values for 2,4- and 3,4- dimethoxybenzoates it appears that they are changed in the following sequence:

Table 1. Frequencies of the absorption of COO- and M-O group vibrations for 2,4- and 3,4–dimethoxybenzoates of Co(II), Cu(II), Nd(III), Na(I), and of the COOH band in 2,4- and 3,4–dimethoxybenzoic acid [1,2].

	Complex L= $C_9H_9O_4^-$	$\nu_{C=O}$	$\nu_{as\,COO}^-$	$\nu_{s\,COO}^-$	$\Delta\nu_{COO}^-$	ν_{M-O}
	CoL_2	-	1628	1408	220	420
	$CuL_2 \cdot H_2O$	-	1608	1400	208	500
I	NdL_3	-	1548	1388	160	500
	NaL	-	1604	1396	208	
	HL	1670	-	-	-	-
	CoL_2	—	1600	1360 1380	240 220	460
	$CuL_2 \cdot 2H_2O$	—	1600	1380	220	420
II	NdL_3	—	1600	1380 1420	220 180	580
	NaL	—	1612	1384	228	—
	HL	1700	—	—	—	—

I – complexes with 2,4-dimethoxybenzoic acid anion; II - complexes with 3,4-dimethoxybenzoic acid anion

Co(II) > Cu(II) > Nd(III),

which indicates that in Nd(III) complexes the M-O bonds are more covalent than those in Cu(II) and Co(II) compounds. These values are greater for 3,4-dimethoxybenzoates than those for 2,4- dimethoxybenzoates which may show the stronger covalent bonds in 2,4- dimethoxybenzoates than in 3,4- dimethoxybenzoates of those elements. The values of frequencies of M-O vibration bands for Co(II) and Nd(III) 2,4- and 3,4-dimethoxybenzoates are changed in sequence: 2,4- < 3,4- , while for Cu(II) complexes they incrase in the order: 3,4- < 2,4-. These relations may indicate that the stronger M-O bonds are in the case of Co(II) and Nd(III) complexes whereas reciprocal relation is observed for Cu(II) compounds.

The IR spectra recorded for complexes show that for 2,4- and 3,4- dimethoxybenzoates of Cu(II), Co(II) and Nd(III) there is only one band of asymmetrical COO- group vibrations but in the case of symmetrical COO- group vibration bands only one is observed for 2,4- and 3,4-dimethoxyben-zoates of Cu(II) and 2,4-dimethoxybenzoates of Co(II) and Nd(III). In the IR spectra of 3,4-dimethoxybenzoates of Co(II) and Nd(III) there are two bands of symmetrical COO- group vibrations, which indicates the various dentates of carboxylate groups in the analysed complexes.

According to the spectroscopic criteria [1,2,21,22] the carboxylate ions appear to be monodentate, bidentate bridging or chelating and tridentate groups. All details connected with the estimations of their dentates are presented in our previously published papers [1,2].

The analysis of the diffractograms of the complexes suggests them to be polycrystalline compounds with different structures [1,2,23].

The thermal stability of analysed dimethoxy-benzoates of Co(II), Cu(II) and Nd(III) was studied in air in the range of 293 – 1173K (Table 2). When heated to 1173K the Cu(II) compounds are dehy-drated in one step and form anhydrous complexes that next are decomposed to CuO [1,2].

Table 2. Temperature ranges of thermal stbility of Nd(III), Co(II), and Cu(II) 2,4- and 3,4-dimethoxybenzoates in air [1,2].

	Complex L⁻= $C_9H_9O_4$	ΔT_1 / K	Mass loss % calcd	found	n	ΔT_2 / K	Mass loss % calcd	found	IDP	ΔT_3 / K	Mass loss % calcd	found	Residue % calcd	found	Final product of decomposition in solid state
I	$CuL_2 \cdot H_2O$	369–413	4.06	4.15	1	495-731	81.31	79.20	Cu,CuO				18.69	20.80	CuO
	CoL_2	-	-	-	-	510-776	80.90	80.00					19.10	20.00	Co_3O_4
	NdL_3					524-685	72.51	73.10	$Nd_2O_2CO_3$	990-1010	75.55	76.00	24.45	24.00	Nd_2O_3
II	$CuL_2 \cdot 2H_2O$	362-450	7.81	6.90	2	501-745	82.70	82.50	—	—	—	—	17.30	17.50	CuO
	CoL_2	—	—	—	—	509-760	80.90	81.00	—	—	—	—	19.10	19.00	
	NdL_3	—	—	—	—	495-645	72.31	72.50	$Nd_2O_2CO_3$	983-1005	75.60	75.20	24.40	24.80	Nd_2O_3

$\Delta T1$= temperature range of dehydration process; n= number of crystallization water molecules lost in one endothermic step; $\Delta T2$= temperature range of decomposition of anhydrous complex; $\Delta T3$= temperature range of decomposition of Nd(III) oxycarbonate; IDP= Intermediate decomposition product

The dehydration process is connected with endo–effect while the combustion of the organic ligands with exothermic one. From the values of temperature at which the dehydration process occurs and from the way in which it proceeds, it is possible to assume that the water molecules are in the outer coordination sphere of these complexes [1,2,24-26].

From the comparison of thermal stability values of 2,4- and 3,4-dimethoxybenzoates of Cu(II) it appears that 2,4- dimethoxybenzoate is more thermally stable complex than that of 3,4-dimethoxybenzoate. It is connected with the various influence of mesomeric, inductive or steric effects on the electron density in the analysed compound molecule. During heating in air to 1173K the anhydrous cobalt(II) 2,4- dimethoxybenzoates decompose directly to Co_3O_4 (Fig.1). The obtained results reveal them to have the similar stability (Table 2). The complexes of Nd(III) with 2,4- and 3,4- dimethoxybenzoic acid anions decompose in two steps. In the range of 495-685K they form the oxycarbonates that next are ultimately decomposed (983-1010K) to Nd_2O_3 [1,2]. The final products of the complex decompositions were identified by X-ray powder diffraction measurements. From the

obtained reasults it appears .that 2,4- dimethoxybenzoate of Nd(III) is more thermally stable than 3,4- dimethoxybenzoate of that element (Table 2). In the case of anhydrous compounds of Cu(II) it
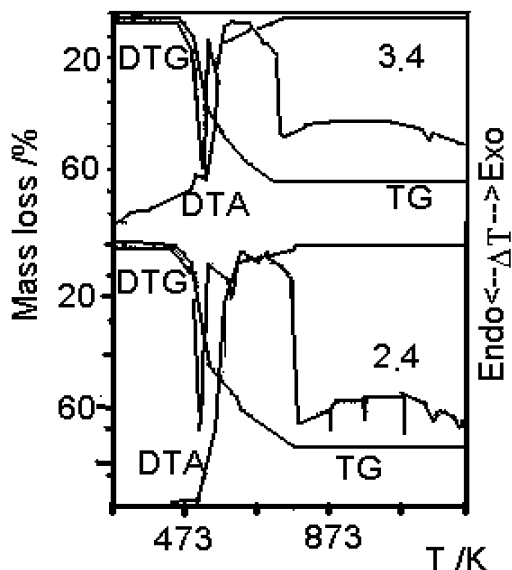

Figura 1. TG, DTG and DTA curves of 2,4- and 3,4-dimethoxybenzoates of Co(II).

follows that 2,4- dimethoxybenzoate of Cu(II) is less thermally stable compared to that of 3,4- dimethoxybenzoate.

In the series of 2,4- and 3,4- dimethoxy-benzoates of Cu(II) and Co(II) it appears that the complexes with Co(II) are more thermally stable than those with Cu(II).

The differences in the presented values show that there is the various influences of inductive, mesomeric and steric effects on the analysed properties of complexes.

The magnetic susceptibility of analysed dimethoxybenzoates was measured over the range of 76–303K [1,2]. The complexes of Co(II) and Nd(III) with both ligands obey the Curie–Weiss law, suggesting a weak ferromagnetic interaction. The magnetic moment values experimentally determined for Co(II) and Nd(III) 2,4- and 3,4- dimethoxybenzoates change from $4,27\mu_B$ to $4,55\mu_B$ for 2,4- dimthoxybenzoate of Co(II), from $4,22\mu_B$ to $4,61\mu_B$ for 3,4- dimethoxybenzoate of Co(II) (Fig. 2), from $2,89\mu_B$ to $3,21\mu_B$ for 2,4- dimthoxybenzoate of Nd(III) and from $2,69\mu_B$ to $3,15\mu_B$ for 3,4- dimethoxybenzoate of Nd(III) (Fig. 3). These values are very close to the spin only ones for the 2,4- and 3,4- dimethoxybenzoates of Co(II) calculated from the equation $\mu_{eff} = [4s (s + 1)]^{1/2}$ in the absence of the magnetic interactions for the present spin system. The theoretical magnetic moment value at 293K for Co(II) ion is equal to $3.88 \mu_B$. The experimental data suggest that the compound of Co(II) seems to be high – spin complexes with probably weak ligand field [1,2]. The values of μ_{eff} determined for Nd^{3+} in the range of 76 – 303K are close to those calculated for Nd(III) ion by Hund ($3.62\mu_B$), and van Vleck ($3.68\ \mu_B$) [27]. This may probably also result from the presence of superexchange magnetic interactions between paramagnetic centers of different molecules of the complexes in the crystal lattice. The 4f electrons causing its paramagnetism are well protected from outside influences and do not participate in the formation of the Nd – O bond.

The magnetic susceptibility values of 2,4- and 3,4- dimethoxybenzoates of Cu(II) incrase with rising temperature suggesting a weak antiferromagnetic interaction. The magnetic moment experimentally determined change from $0,49\mu_B$ (at 76K) to $1,17\mu_B$ (at 303K) for 3,4- dimethoxy-
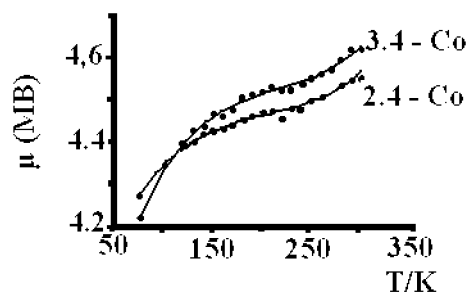

Figura 2. Relationship between μ vs T for 2,4- and 3,4-dimethoxybenzoates of Co(II).
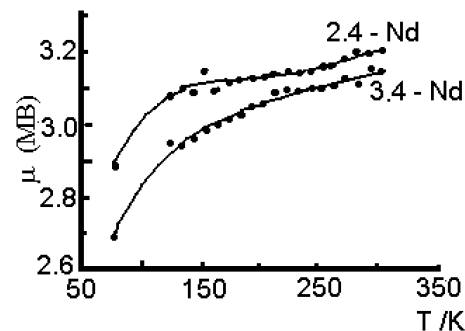

Figura 3. Dependence between μ vs T for 2,4- and 3,4-dimethoxybenzoates of Nd(III).

benzoates of Cu(II) and $0,64\mu_B$ (at 76K) to $1,57\mu_B$ (at 303K) for 2,4- dimethoxybenzoates of Cu(II) (Fig. 4). These values are lower than the d^9 spin-only magnetic moment $\Delta_{eff}=1,73\mu_B$. Such dependence is a typical behaviour for copper dimer [1,2,27,28]. Magnetic susceptibility measurements revealed the $\chi=f(T)$ relation course to be typical for copper(II) carboxylates, where the paramagnetic centers are antiferromagnetically coupled. Magnetic susceptibility is the highest at room temperature and decreases with the temperature lowering. This is related to the occupation of the triplet and singlet states. Occupation of the energetically lower singlet state increases with the temperature lowering [1,2,27,28-30].

From the comparison of the magnetic susceptibility and magnetic moment values for these two analysed series of dimethoxybenzoates of Cu(II), Co(II) and Nd(III) it follows that the various positions of -OCH_3 substituents in benzene ring do not influence their magnetic properties but effect the magnetic moment values. All complexes are paramagnetic compounds. The values of the
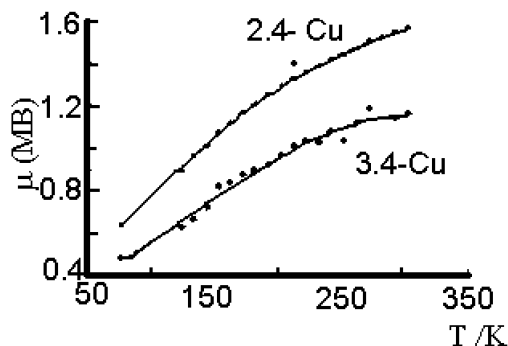
Figura 4. Relationship between m vs T for complexes of Cu(II).

Δ_{eff} calculated for the complexes in the range of 76-303K reveal the 2,4- dimethoxybenzoates of Cu(II) and Nd(III) to have the stronger paramagnetic properties than those for 3,4- dimethoxybenzoates. 3,4- Dimethoxybenzoate of Co(II) shows the greater values of magnetic moments compared to that of 2,4-dimethoxybenzoates.

Conclusions

The various positions of methoxy- groups in the benzene ring do not influence the metal : ligand ratio, magnetic properties and colours of complexes, but effect the magnetic moment values and the modes of the carboxylate group coordinations. These differences result from the various influence of an inductive, mesomeric and steric effects of the -OCH$_3$ substituent positions on the electron density in the benzene ring. When –OCH$_3$ group is in the *ortho*- position in benzene ring the steric effect is stronger than in its *meta*- position in which it clearly reveals the mesomeric one.

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