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Complexes of 3,4-dimethoxybenzoic acid anion with Cu(II), Co(II), La(III), and Nd(III)

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Abstract: Physico-chemical properties of 3,4-dimethoxybenzoates of Co(II), Cu(II), La(III) and Nd(III) were studied. The complexes were obtained as hydrated or anhydrous polycrystalline solids with a metal ion–ligand mole ratio of 1 : 2 for divalent ions and of 1 : 3 in the case of trivalent cations. Their colours depend on the kind of central ion: pink for Co(II) complex, blue for Cu(II), white for La(III) and violet for Nd(III) complexes. The carboxylate groups in these compounds are monodentate, bidentate bridging or chelating and tridentate ligands. Their thermal decomposition was studied in the range of 293–1173 K. Hydrated complexes lose crystallization water molecules in one step and form anhydrous compounds, that next decompose to the oxides of respective metals. 3,4 – Dimethoxybenzoates of Co(II) is directly decomposed to the appropriate oxide and that of Nd(III) is also ultimately decomposed to its oxide but with the intemediate formation of $Nd_2O_2CO_3$. The magnetic moment values of 3,4–dimethoxybenzoates determined in the range of 76–303 K change from 4.22 μ_B to 4.61 μ_B for Co(II) complex , from 0.49 μ_B to 1.17 μ_B for Cu(II) complex , and from 2.69 μ_B to 3.15 μ_B for Nd(III) complex.

Keywords: 3,4 – dimethoxybenzoates; thermal stability; magnetic properties; Cu(II); Co(II); La(III); Nd(III); IR spectra.

Introduction

3,4–Dimethoxybenzoic acid is a white solid sparingly soluble in cold water but very good soluble in the hot one. Its melting point is equal to 181ºC [1–3]. It plays an important role in bioinorganic chemistry and in medicine for producing antibiotics and various dyes [4,5]. From the survey of literature it follows that there are papers on the compounds of 3,4–dimethoxybenzoic acid anion with the following cations: Na^+, Ag^+, Ba^{2+} and some of light and heavy lanthanides(III) [1,6,7]. The complexes of 3,4-dimethoxybenzoates of La(III) and Nd(III) were synthesized as tetrahydrates and some of their properties were studied. The preparation and investigations of 3,4–dimethoxybenzoates of Co(II), Cu(II), La(III) and Nd(III) are presented in this paper, because on one hand, the carboxylates have the significant positions in inorganic and bioinorganic chemistry, and then again many metal cations in a great number of various biological processes, especially six – membered ring system, are components of several vitamins and drugs [8,9]. 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 electric materials, and they may have applications as precursors in superconducting ceramic and magnetic material productions. They may form various magnetic nanostructures that induced by current

may by used as magnetic switch in spin valve. According to literature survey compounds of various organic ligands have been studied. Therefore, there are papers that deal with their complexes with *d* and *4f* metal ions [10-18]. The complexes described in the above-mentioned papers were synthesized and characterized by elemental analysis and IR spectra. Their thermogravimetric studies, X-ray diffraction and magnetic measurements were also presented.

This time, as a continuation of our research on the compounds of methoxybenzoic acids [6, 7, 16] we decided to synthesize and investigate the complexes of 3,4–dimethoxybenzoic acid anion with Co(II), Cu(II), La(III) and Nd(III). These types of compounds may find the application in medicine as components of drugs or they may be used in technique as magnetic materials depending on their magnetic properties. The complexes of Co(II) and Cu(II) have not been investigated so far but those of La(III) and Nd(III) have been previously synthesized and studied by us [6]. We decided to prepare them again in order to verify the repeatibility of the synthesis condition of these complexes, to check their compositions, to study some of their properties and to compare them with those of 3d electron metal ion which have not been studied so far.

The physico-chemical properties of 3,4–dimethoxybenzoates of Co(II), Cu(II), La(III) and Nd(III) were determined by thermal stability in air atmosphere during heating to 1173 K , IR spectral data, X-ray powder investigations and magnetic properties. Thermal stability investigations give information about the ways of complex decompositions and the endo- or exo- effects connected with such processes as: dehydration, melting, polymorphic changes, crystallization, oxidation or reduction. The magnetic properties of 3,4–dimethoxybenzoates of Co(II), Cu(II) and Nd(III) were investigated in the range of 76–303 K in order to study the kind of coordination of central ions and ligands. If the effective magnetic moment μ_{eff} is known, the number of unpaired electrons can be calculated. This may also give information on the oxidation state of the metal ion or the central atom of a complex, on the electron configuration and, hence, on the nature of the bonding between the metal and the ligands. The determination of the number of unpaired electrons of the central atom allows to establish whether the complex investigated is of low or high spin and whether the ligand field is strong or weak.

Experimental details

For the preparation of the complexes the following chlorides of d-block elements were used: $CoCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ (REAGENTS – Chemical Enterprise in Lublin (Poland)). The 3,4–dimethoxybenzoic acid, Nd_2O_3, and La_2O_3 used for preparation were produced by Aldrich Chemical Company. In the experiments the solution of NH_3aq (25 %) produced by Polish Chemical Reagents in Gliwice (Poland) was also used.

The C and H analysis was performed using a CHN 2400 Perkin-Elmer analyzer. The contents of M(II) metals were calculated from TG curves and were established gravimetrically. The contents of Nd^{3+} and La^{3+} were determined by oxalic acid method.

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_μ radiation. The measurements were made within the range $2\theta = 4 - 80^o$ by means of the Debye–Scherrer–Hull method.

The thermal stability and decomposition of Co(II), Cu(II), La(III) and Nd(III) complexes

Table 1. Elemental analysis data of Co(II), Cu(II), La(III) and Nd(III) 3,4-dimethoxybenzoates.

Complex $L=C_9H_9O_4^-$	C / %		H / %		M / %	
	calcd.	found	calcd.	found	calcd.	found
$LaL_3 \cdot H_2O$	44.03	44.18	4.48	4.45	18.87	18.68
NdL_3	47.14	47.14	3.93	3.86	20.99	20.54
$CuL_2 \cdot 2H_2O$	46.80	47.05	4.51	4.35	13.76	14.58
CoL_2	51.07	52.44	4.26	4.55	13.93	13.69

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

Complex $L^- = C_9H_9O_4$	ν / cm^{-1}				
	$\nu_{C=O}$	$\nu_{as\ COO^-}$	$\nu_{s\ COO^-}$	$\Delta\nu_{\ COO^-}$	$\nu_{\ M-O}$
$LaL_3 \cdot H_2O$	—	1590	1380	210	580
NdL_3	—	1600	1380	220	580
			1420	180	
$CuL_2 \cdot 2H_2O$	—	1600	1380	220	420
CoL_2	—	1600	1360	240	460
			1380	220	
NaL	—	1612	1384	228	—
HL	1700	—	—	—	—

were studied in air using a Q–1500D derivatograph with Derill converter recording TG, DTG and DTA curves. The measurements were made at heating rate of 10 K · cm^{-1}. The samples (100 mg) were heated in platinum crucibles in static air to 1173 K with a sensitivity of TG–100 mg. DTA and DTG sensitivities were regulated by the Derill computer programme. The products of decompositions were calculated from the TG curves and verified by the diffraction pattern registration.

Magnetic susceptibilities of polycrystalline samples of 3,4-dimethoxybenzoates of Co(II), Cu(II), La(III) and Nd(III) were measured by the Gouy method using a sensitive Cahn RM-2 electrobalance. 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 [19]. Magnetic moments were calculated from the the equations (1) and (1*):

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

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

Complexes

The complexes of the 3,4 – dimethoxybenzoic acid anion with Co^{2+}, Cu^{2+}, La^{3+} and Nd^{3+} were obtained by the addition of equivalent quantities of 0.1 M ammonium 3,4 – dimethoxybenzoate (pH ~ 5) to a hot solution containing the chlorides of respective metal ions and crystallizing at 293 K. The solids were filtred off,

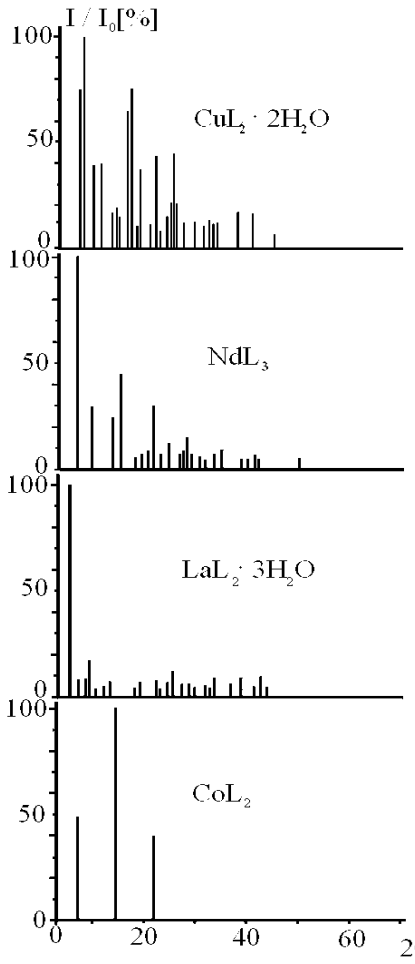

Figure 1. Dependence of I / I_0 vs 2θ for 3,4 – dimethoxybenzoates of Cu(II), Co(II), La(III) and Nd(III).

Table 3. Temperature range of thermal stability of Co(II), Cu(II), La(III) and Nd(III) 3,4 – dimethoxybenzoates in air

Complex $L^- = C_9H_9O_4$	ΔT_1 / K	Mass loss %		n	ΔT_2 / K	Mass loss %		IDP	ΔT_3 / K	Mass loss %		Residue %		Final product of decomposition in solid state
		calcd	found			calcd	found			calcd	found	calcd	found	
$LaL_3 \cdot 3H_2O$	346-391	7.34	7.38	3	501-959	75.00	75.50	$La_2O_2CO_3$	963-1025	77.87	78.00	22.13	22.00	La_2O_3
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
$CuL_2 \cdot 2H_2O$	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	Co_3O_4

ΔT_1= temperature range of dehydration process; n= number of crystallization water molecules lost in one endothermic step; ΔT_2= temperature range of decomposition of anhydrous complex; ΔT_3= temperature range of decomposition of oxycarbonates of La(III) and Nd(III); IDP= Intermediate decomposition product

Table 4. Magnetic data for the studied compounds of Co(II), Cu(II) and Nd(III).

$CuL_2 \cdot 2H_2O$			CoL_2			NdL_3	
T / K	$\chi_M \cdot 10^6$ $cm^3 \cdot mol^{-1}$	μ_{eff} / MB	T / K	$\chi_M \cdot 10^6$ $cm^3 \cdot mol^{-1}$	μ_{eff} / MB	T / K	$\chi_M \cdot 10^6$ $cm^3 \cdot mol^{-1}$
76	392	0.49	76	29236	4.22	76	11902
123	405	0.63	123	19580	4.39	123	8817
133	418	0.67	133	18383	4.43	133	8134
143	457	0.72	143	17187	4.44	143	7645
153	547	0.82	153	16270	4.47	153	7281
163	534	0.84	163	15249	4.46	163	6894
173	560	0.88	173	14463	4.48	173	6564
183	560	0.91	183	13835	4.50	183	6256
193	560	0.93	193	13171	4.51	193	6017
203	586	0.98	203	12542	4.52	203	5755
213	599	1.01	213	12010	4.53	213	5596
223	599	1.03	223	11460	4.52	223	5368
233	573	1.03	233	10953	4.52	233	5129
243	599	1.08	243	10560	4.53	243	4936
253	534	1.04	253	10202	4.55	253	4742
263	599	1.12	263	9862	4.56	263	4583
273	650	1.19	273	9556	4.57	273	4481
283	586	1.15	283	9294	4.59	283	4287
293	560	1.15	293	9076	4.61	293	4241
303	560	1.17	303	8771	4.61	303	4093

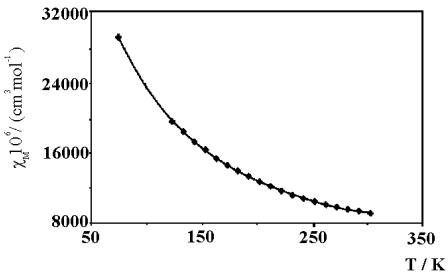

Figure 2. Dependence between χ_M vs T for 3,4 – dimethoxybenzoate of Co(II).

washed with hot water to remove ammonium ions and dried to constant mass at 303 K.

Results and Discussion

The complexes of 3,4-dimethoxybenzoates of Cu(II), Co(II) La(III) and Nd(III) were obtained as polycrystalline products with a metal ion to ligand ratio of 1 : 2 and the general formula $M(C_9H_9O_4)_2 \cdot nH_2O$ for divalent ions, where M(II)

= Cu, Co, and n = 2 for Cu(II), and n = 0 for Co(II). For Nd(III) and La(III) complexes a metal ion to ligand ratio is 1 : 3 and the general formula $M(C_9H_9O_4)_3 \cdot nH_2O$, where n = 3 for La(III), and n = 0 for Nd(III) complex (Table 1). Their colours are following: pink for Co (II) complex, light blue for - Cu(II), white for - La(III) and violet for Nd compound. In Cu(II) and Co(II) compounds the $d \rightarrow d$ and in Nd(III) complex the $f \rightarrow f$ electron transitions of the central ions are those of the lowest energy and the absorption occurs at relatively high wavelengths that depends on the nature of the metal ion [11,17,18].

The complexes were characterized by elemental analysis (Table 1). The compounds exihibit similar solid state IR spectra. Some of the results are presented in Table 2. The band at 1700 cm^{-1} originating from COOH stretching vibration, in the spectrum of the acid, is replaced in the spectra of complexes, by two bands at 1590-1600 cm^{-1} and 1380-1420 cm^{-1}, which can be ascribed to the asymmetric and symmetric vibrations of $–COO^-$ groups, respectively [20]. The bands attributed to asymmetric and symmetric C-H stretching modes of the CH_3 groups are observed at 2920-2970 cm^{-1} and 2820-2840 cm^{-1}, respectively. The bands with the maxima at 3450-3460 cm^{-1} in the spectra of 3,4-dimethoxybenzoates of Cu(II) and La(III) are characteristic for ν(OH) vibrations [20, 21] The bands of ν(C-C) ring vibrations appear at 1450-1500 cm^{-1} and 770-880 cm^{-1}, and those corresponding to M-O stretching occur at 420-580 cm^{-1}.

The Table 2 presents the values of the two band frequencies of asymmetrical and symmetrical vibrations of carboxylate group for 3,4-dimethoxybenzoates of Cu(II), Co(II), La(III), Nd(III) and Na(I). The difference in the values, $\Delta\nu_{OCO}$, between the frequencies ν_{asOCO} and ν_{sOCO} in the complexes are higher and lower (180-240 cm^{-1}) than in the sodium salt ($\Delta\nu$ = 228 cm^{-1}). In the case of anhydrous complexes of Co(II) and Nd(III) two bands of symmetrical carboxylate groups, $\nu_{sOCO,}$ occur, which indicates their various positions in the analysed compounds. According to the spectroscopic criteria [20, 22] the carboxylate ions appear to be monodentate, bidentate bridging or chelating and even tridentate groups.

In order to estimate the crystalline forms of the 3,4–dimethoxybenzoates the X-ray powder diffraction measurements were done. The analyses suggest them to be polycrystalline compounds with various degrees of crystallinity (Fig. 1) [23].

The thermal stability of analysed 3,4 –dimethoxybenzoates was studied in air at 293-1173K (Table 3). The results obtained from their thermal decomposition support their assignment as anhydrous, di- and trihydrates, in agreement with data of elemental analyses (Table 1). When heated to 1173K Cu(II) dihydrate releases two water molecules in one step and form anhydrous salt that next is decomposed to CuO which is the final product of its decomposition. The found weight loss being equal to 6.9% corresponds to the release of two water molecules (calculated value is 7.8%). The intermediate compounds formed in the range of 501-745K may contain Cu and Cu_2O that are next oxidized to CuO. The found weight loss is equal to 82.50%, while the calculated value 82.70%. The residue mass determined from TG curve is 17.50% (theoretical value is 17.30%). The final mass of complex decomposition was confirmed by elemental analysis, IR spectra and X-ray powder diffractogram. The dehydrated process in this case, is connected with an endothermic effect seen on DTA curve, while the combustion of the organic ligand is accompanied by exothermic one.

The hydrated 3,4 – dimethoxybenzoate of La(III) releases at 346-391K three water molecules in one step and forms anhydrous complex. The mass loss estimated from TG curve is equal to 7.38% and that theoretically calculated is 7.34%. The anhydrous complex at 501-939K is decomposed to $La_2O_2CO_3$. The loss of mass is equal to 75.50% and calculated 75.00%. The $La_2O_2CO_3$ is next decomposed to La_2O_3 which is the residue of complex decomposition. It calculated from TG curve is equal to 22.00% (theoretical value is 22.13%). This worth corresponds to the La_2O_3 formation that was identified by IR spectra and X-ray powder diffractogram. The dehydration process is connected with the endothermic effect seen on DTA curve. Considering the temperature at which the dehydration process of complex 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 [23-26]. From the comparison of thermal stability it appears that Cu(II) complex is more thermally stable (362K) than that of La(III) (346K).

During heating in air to 1173K the anhydrous 3,4-dimethoxybenzoate of Co(II) decomposes to Co_3O_4, which is the final product of its decomposition with intermediate formations of Co and Co_2O_3. The final mass calculated from TG curve is equal to 19.00% while the theoretically calculated value is 19.10%. The formation of Co_3O_4 was confirmed by IR spectra and X-ray powder diffraction. The mass calculated from TG curve is 81% and calculated value 80.9%.

The anhydrous Nd(III) complex in the range of 495-1005K is decomposed to Nd_2O_3 that is the final product of decomposition with the intermediate formation of $Nd_2O_2CO_3$. The found loss of mass is equal to 75.20% and calculated 75.60%. The $Nd_2O_2CO_3$ is next decomposed to Nd_2O_3. The found residue mass is equal to 24.80% (calculated value is 24.40%).This worth corresponds to the Nd_2O_3 formation that was identified by IR spectra and X-ray powder diffraction. Comparison of the thermal stabilities of Co(II) and Nd(III) complexes reveals the complex of Co(II) to be more thermally stable than that of Nd(III).

The final and intermediate products of all analysed complex decompositions were identified by X-ray powder diffraction measurements and IR spectra analysis.

The magnetic susceptibility of analysed complexes was measured over the range of 76 – 303 K (Table 4, Fig. 2). The complexes of Co(II) and Nd(III) obey the Curie – Weiss law (Fig. 2) suggesting a weak ferromagnetic interaction. The magnetic moment values experimentally determined at 76 – 303 K for Co(II), and Nd(III) 3,4 – dimethoxybenzoates change from 4.22 μ_B to 4.61 μ_B for Co(II) complex, and from 2.69 μ_B to 3.15 μ_B for Nd(III) 3,4 – dimethoxybenzoate. The magnetic moment data are very close to the spin only values for the 3,4 – dimethoxybenzoate 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 magnetic moment value calculated at room temperature for Co(II) ion is equal to 3.88 μ_B. For Co^{2+} ion the magnetic moment may be lower than the spin – only value or the same compared to it. This is due to the fact that the vectors *L* and *S* are aligned by the strong field of the heavy atom in opposite directions and this diminishes the resultant magnetic moment. The experimental data suggest that the compound of Co(II) seems to be high – spin complexes with probably weak ligand field [21].

The value of the Weiss constant, θ, is negative for Nd(III) 3,4–dimethoxybenzoate (θ = -25), which may be caused by small antiferromagnetic spin interactions in the complex that are higher at room temperatures than at lower ones or a crystal field splitting of the paramagnetic spin state [27–29]. 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 3,4–dimethoxybenzoate of Nd(III) obeys the Curie–Weiss law. The values of μ_{eff} determined for Nd^{3+} in the range of 76–303 K (2.69–3.15 μ_B ; 3.70 μ_B theoretical value at 293 K) are close to those calculated for Nd(III) ion by Hund (3.62 μ_B), and van Vleck (3.68 μ_B) [21]. The experimental data suggest that 3,4–dimethoxybenzoate of Nd(III) seems high–spin complex. The magnetic susceptibility values of 3,4–dimethoxybenzoate of Cu(II) incrase with rising temperature suggesting a weak antiferromagnetic interaction. The magnetic moment values experimentally determined change from 0.49 μ_B (at 76 K) to 1.17 μ_B (at 303 K). These values are lower than the d^9 spin – only magnetic moment μ_{eff} = 1.73 μ_B. Such dependence is a typical behaviour for copper dimer (Table 4) [27, 30–32]. Magnetic susceptibility measurements revealed the χ_{Cu} = f(T) relation course to be typical for copper (II) carboxylates, where the paramagnetic centres 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.

The observed magnetic properties are typical for dimer systems in which exists the magnetic superexchange between the Cu(II) centres [33 – 38]. The suggested formula for the Cu(II) complex is $Cu_2L_4(H_2O)_4$.

From the obtained results it appears that in 3,4–dimethoxybenzoates of Cu(II), Co(II), La(III) and Nd(III) the coordination numbers may be equal to 5, 6 and 9 depending on the dentates of carboxylate group and the position of water molecules in the complex. The coordination numbers of individual ions could be established on the basis of the complete crystal structure determination of monocrystals but they have not been obtained. Therefore, according to the Cu(II) complex we can only suppose that each copper(II) atom may show a fivefold coordination in the form of a square pyramid with four oxygen atoms of the bridging dimethoxybenzoate anions in the basal plane and one oxygen atom of the inner sphere water molecule at the apex [38]. In the cases of Co(II) and Nd (III) 3,4–dimethoxybenzoates the ligands behave as a monodentate and bidentate chelating groups, but it is difficult to estimate the coordination number of central ions in analysed complexes without full data of single crystal structure determinations. Probably it may be equal to 6 while for La(III) ion it is 9. In its coordination there are six oxygen atoms of three bidentate carboxylate groups and three oxygen atoms of water molcules. As it was indicated by thermal analysis data the water molecules in this complex were supposed to be lattice water because they were released below 423 K [25, 26], but their position in the complex coordination sphere was not precisely determined. However, taking into account the dentates of carboxylate groups and the coordination numbers of central ions, we can suggest them to be coordination water, that is released at the temperature typical generally for lattice water.

Conclusion

One the basis of the results obtained it appears that 3,4–dimethoxybenzoates of Cu(II), Co(II), La(III) and Nd(III) were synthesized as hydrated or anhydrous complexes. Their colours are following: white for La(III), light blue for Cu(II), pink for Co(II) and violet for Nd(III) compounds. 3,4–Dimethoxybenzoates of analysed cations are crystalline and on heating in air to 1173 K they decompose in various ways: Cu(II) in two steps, La(III) in three ones, Co(II) and Nd(III) in one step. In the first step the hydrates release the water molecules and form anhydrous complexes that next decompose to the oxides of the appropriate metals. The values of the μ_{eff} calculated for analysed complexes in the range of 76–303 K reveal that the Nd(III) and Co(II) complexes are high – spin and that of Cu(II) forms dimer. Lanthanum 3,4–dimethoxybenzoate is a diamagnetic.

In this case under the same condition of synthesis the obtained complexes of Nd(III) and La(III) have different compositions compared to those previously prepared. Therefore the complex compositions were appeared not to be repeatable.

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