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THERMAL, SPECTRAL AND MAGNETIC PROPERTIES OF 3,5-DIMETHOXYBENZOATES OF Co(II), Ni(II) AND Cu(II)

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The complexes of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) have been synthesized as hydrated polycrystalline solids and characterized by elemental analysis, IR, FIR and electronic spectroscopy, magnetic studies and X-ray diffraction measurements. They possess colours typical of the *M*(II) ions: Cu-blue, Ni-green, Co-pink. The carboxylate groups bind as monodentate or a symmetrical, bidentate chelating or bridging ligands. The thermal stabilities were determined in air. When heated they dehydrate to form anhydrous salts which are decomposed to the oxides of respective metals. The magnetic susceptibilities of the complexes were measured over the range 77–300 K and the magnetic moments were calculated. The results reveal the complexes of Ni(II) and Co(II) to be high-spin complexes and that of Cu(II) to form dimer.

Keywords: *3,5-dimethoxybenzoates, electronic spectra, magnetic properties of Co(II), Ni(II) and Cu(II) 3,5-dimethoxybenzoates, thermal stability*

Introduction

According to literature survey the compounds of various metal ions with different carboxylic acid anions have been scarcely studied. However, for instance, there are papers on the complexes of rare earth elements with 2,4-, 3,4-dimethoxy-, 4-chloro-2-nitro- and 4-chloro-3-nitrobenzoic acid anions [1–6].

The compounds of 3,5-dimethoxybenzoic acid anion with various cations are rather little known. Papers exist on its complexes with the following cations as: Cu(II), Ag(I), Zn(II) and Pb(II). The complexes were obtained as solids or were investigated in solution [7, 8]. The 3,5-dimethoxybenzoate of Cu(II) was isolated in the solid-state and its thermal stability was studied [7] while those of Ag(I), Zn(II) and Pb(II) were only investigated in solution [8].

There are also informations about the solid-state properties of complexes of 3,5-dimethoxybenzoates of rare earth elements [9] but no about those of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II). Therefore it was decided to synthesize them as solids and to examine some of their properties such as thermal stability in air and nitrogen, solubility in water at room temperature, IR spectral characteristic and crystalline form in order to determine whether they are crystalline or amorphous compounds. Their magnetic properties were also studied in the range 77–300 K. The thermal stability investigations enabled the evaluation of the mechanism of the complex decomposition. The determination of the solubility is valuable because it gives information about the practical use of the acid for the separation of the elements by extraction or ion-exchange chromatographic methods. Magnetic properties of analysed complexes were investigated in order to study the kinds of the way of coordination of the central ions and the nature of the bonding between central ions and ligands. If the magnetic moment 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 complex, on the electron configuration and hence, on the nature of the bonding between the metal and the ligands. On the other hand, when the number of unpaired electrons in the complexes is known, the spin only moment can be calculated. The deviation of the measured magnetic moment from the spin only permits the drawing of conclusions on the symmetry of the complex in certain cases. In coordination compounds the number of unpaired electrons on the central atom is determined by its oxidation state on the ligand-field strength. The determination of the number of unpaired electrons on the central atom establishes whether the compound investigated is of low or high spin complex and whether the ligand field is strong or weak.

Experimental

The complexes of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) were prepared by the addition of

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equivalent quantities of 0.1 M ammonium 3,5-dimethoxybenzoate (pH≈5) to a 0.1 M hot aqueous solution containing the nitrates of these ion metals and crystallizing at 293 K. The solids were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303 K to a constant mass. The contents of carbon and hydrogen in the complexes were determined by elemental analysis using a CHN 2400 Perkin-Elmer analyser. The contents of M^{2+} metal ions were established by ASA method with the use of ASA 880 spectrophotometer (Table 1).

The IR and FIR spectra of complexes were recorded over the ranges 4000–400 and 600–100 cm^{-1}, respectively, using a FTIR 1725X Perkin-Elmer spectrometer and a Nicolet MAGNA FIR 760 spectrometer. The samples for the FTIR spectra measurements were prepared as KBr discs and those for the FIR spectra with polyethylene of masses from 0.8 to 1.0 mg. Some of the results are presented in Table 2.

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 $2\theta=4$–80° by means of the Debye–Scherrer–Hull method. The relationships between I/I_0 and 2θ for these complexes are presented in Fig. 1.

The thermal stability and decomposition of the complexes were determined by Paulik–Paulik–Erdey Q-1500 D derivatograph with Derill converter, recording TG, DTG and DTA curves (Figs 2–4). The measurements were made at a heating rate of 10 K min^{-1} with a full scale. The samples (100 mg) were heated in platinum crucibles in static air to 1173 K with a sensitivity of TG–100 mg. DTG and DTA sensitivities were regulated by a Derill computer program. The products of decomposition were calculated from TG curves and verified by the diffraction pattern registration. The results are presented in Table 3. The nature of the solid products of decomposition was established from the TG curves and confirmed by IR and X-ray spectra.

Magnetic susceptibilities of polycrystalline samples of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) were measured by the Gouy method using a sensitive Cahn RM-2 balance. Measurements were carried out at a magnetic field strength of 9.9 KOe. $Hg[Co(SCN)_4]$ with the magnetic susceptibility [10] of $1.644\cdot10^{-5}$ cm^3 g^{-1} was employed as calibrant. The correction of diamagnetism of the constituent atoms was calculated by using Pascal's constants [11]. The magnetism of the samples was found to be field independent. Their magnetic moments, μ_{eff}, were calculated and presented in Table 4.

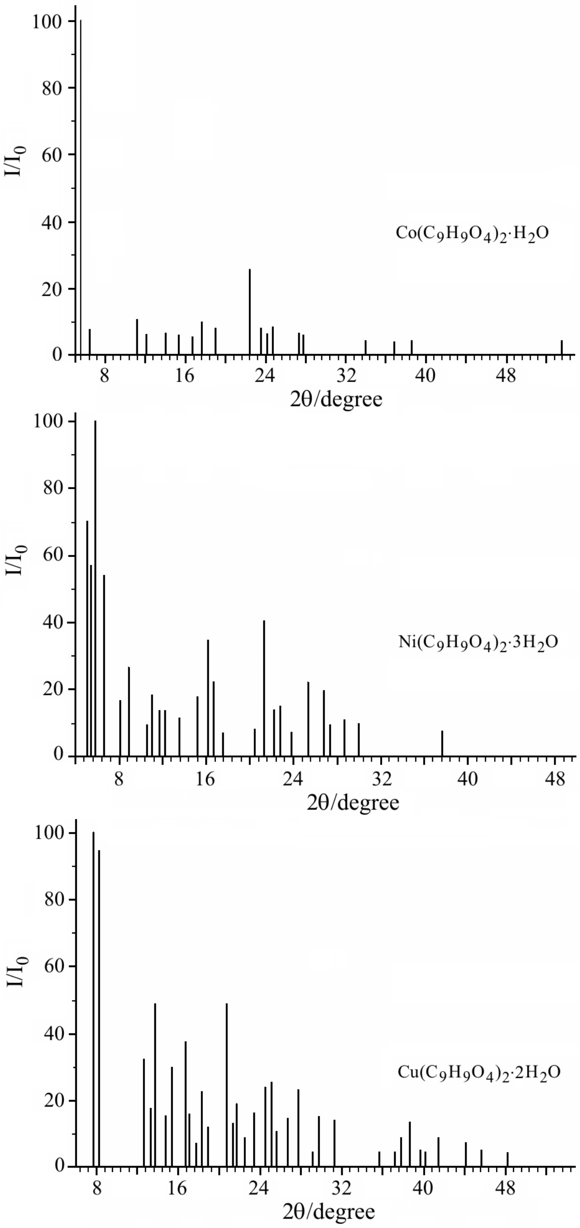

Fig. 1 Relationships between I/I_0 and 2θ for Co(II), Ni(II) and Cu(II) 3,5-dimethoxybenzoates

Table 1 Elemental analysis of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II)

Complex $L=C_9H_9O_4^-$	C/%		H/%		M/%		Solubility/mol dm^{-3}
	calcd.	found	calcd.	found	calcd.	found	
$CoL_2\cdot2H_2O$	47.27	46.73	4.81	4.60	12.89	12.59	$1.5\cdot10^{-3}$
$NiL_2\cdot3H_2O$	45.50	44.86	5.05	4.66	12.36	12.18	$5.4\cdot10^{-4}$
$CuL_2\cdot2H_2O$	46.75	47.45	4.95	4.43	14.85	14.63	$2.5\cdot10^{-5}$

$L=C_6H_3(OCH_3)_2COO^-$

Table 2 Frequencies of the absorption bands of COO^- vibrations for 3,5-dimethoxybenzoates of Co(II), Ni(II), Cu(II) and sodium and that of C=O for non-coordinated 3,5-dimethoxybenzoic acid (cm^{-1})

Complex $L=C_9H_9O_4^-$	ν(C=O)	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu(COO^-)$	ν(M–O)
$CoL_2{\cdot}2H_2O$	–	1598	1401 1428	197 170	208
$NiL_2{\cdot}3H_2O$	–	1582	1392 1426	190 156	409 228
$CuL_2{\cdot}2H_2O$	–	1581	1392 1428	189 153	496 278
HL	1684	–	–	–	–
NaL	–	1580	1385	195	–

Table 3 Data of thermal decomposition processes for 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) in air atmosphere

Complex $L=C_9H_9O_4^-$	ΔT/K	Mass loss/%		Product of decomposition in solid-state
		calcd.	found	
$CoL_2{\cdot}2H_2O$	376–468	7.88	8.0	CoL_2
CoL_2	546–924	87.10	87.0	Co
Co	942–973	82.43	82.6	Co_3O_4
Co_3O_4	1161–1221	83.60	84.1	CoO
$NiL_2{\cdot}3H_2O$	334–440	11.37	11.0	NiL_2
NiL_2	578–835	87.78	85.1	Ni
Ni	859–921	84.40	83.6	NiO
$CuL_2{\cdot}2H_2O$	325–442	7.79	7.0	CuL_2
CuL_2	521–848	74.90	74.2	CuO

ΔT – temperature range of decomposition processes

The electronic spectra of the complexes of Co(II), Ni(II) and Cu(II) and their chlorates(VII) used as standards were recorded using UV-VIS Specord spectrometer. The chlorates(VII) of these elements were used as standards because they practically do not form complexes. Measurements were made in the diluted (ca. 0.1 M) aqueous solutions of chlorates(VII) and 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II). The obtained data are presented in Table 5.

Results and discussion

The complexes of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) were obtained as polycrystalline products with a metal ion to ligand ratio of 1:2 and the general formula $M(C_9H_9O_4)_2{\cdot}nH_2O$, where M(II)=Co, Ni, Cu and n=2 for Co(II) and Cu(II) and n=3 for Ni(II). Their colours are those typical for the appropriate divalent ions (Cu-blue, Ni-green, Co-pink). In these complexes the $d\rightarrow d$ electron transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wavelengths that depends on the nature of the metal ion.

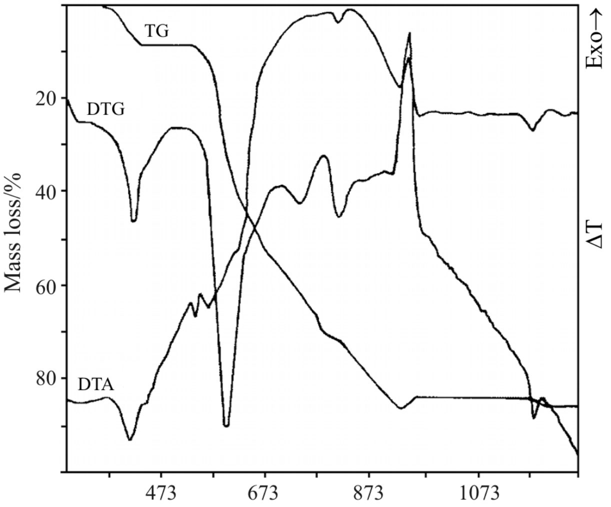

Fig. 2 TG, DTG and DTA curves for Co(II) 3,5-dimethoxybenzoate in air

The compounds were characterized by elemental analysis (Table 1), FTIR and FIR spectra (Table 2). The 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) exhibit similar solid-state IR spectra. The band at 1684 cm^{-1} originating from the RCOOH group, presented in the spectrum of acid, is replaced in the spectra of complexes by two bands at 1598–1581 and

1428–1382 cm^{-1}, which can be ascribed to the asymmetric and symmetric vibrations of COO^- group, respectively [12–15]. The bands attributed to asymmetric and symmetric C–H stretching modes of the CH_3 groups are observed at 2968–2937 and 2840–2839 cm^{-1}, respectively. The bands with the maxima at 3606–3392 cm^{-1} in the spectra of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) are characteristic for ν(OH) vibration [13-15]. Additionally, in the spectra of complexes there are bands at 900 and 700 cm^{-1} that may confirm the presence of molecules of water of crystallization in the inner sphere of coordination. The bands of ν(C–C) ring vibrations appear at 1455–1428, 1308–1288, 993–992 and 678–645 cm^{-1}. The bands corresponding to metal ion-oxygen stretching appear at 497, 228 and 208 cm^{-1}. Table 2 presents the values of the two band frequencies of asymmetrical and symmetrical vibrations for carboxylate group of Co(II), Ni(II) and Cu(II) 3,5-dimethoxybenzoates. The separations of the $\nu_{as(OCO^-)}$ and $\nu_{s(OCO^-)}$ modes of the complexes, $\Delta\nu_{(OCO^-)}$, are greater, smaller or the same than that of the sodium salt ($\Delta\nu_{(OCO^-)}$=195 cm^{-1}). It indicates the different participations of ionic bonds in the analysed complexes compared to that of the sodium salt. For the complexes the shifts of the frequencies of bands of $\nu_{as(OCO^-)}$ and $\nu_{s(OCO^-)}$ are higher or practically the same and higher, respectively, than those for sodium 3,5-dimethoxybenzoate. Accordingly taking into account the spectroscopic criteria [13, 15, 16] the carboxylate ions appear to be bidentate, chelating and bridging.

In order to estimate the crystalline forms of the 3,5-dimethoxybenzoates the X-ray powder diffraction measurements were done. The diffractogram analysis suggests them to be polycrystalline compounds with various degrees of crystallinity [17].

The thermal stability of Co(II), Ni(II) and Cu(II) 3,5-dimethoxybenzoates was studied in air (Table 3, Figs 2–4). When heated to 1173 K the complex of Co(II) is gradually decomposed to CoO with the intermediate formations, at first, of CoL_2, next Co and finally Co_3O_4. The Co is oxidized to Co_3O_4 (Fig 2). The found mass loss is equal to 84.1 and calculated value 83.6 %. In the temperature range 1161–1221 K the Co_3O_4 is reduced to CoO which is the final product of decomposition. This process of reduction is connected with the endoeffect while that of oxidation with exothermic one. The decomposition process of 3,5-dimethoxybenzoate of Co(II) may be presented by the following scheme:

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

where L=$C_9H_9O_4^-$.

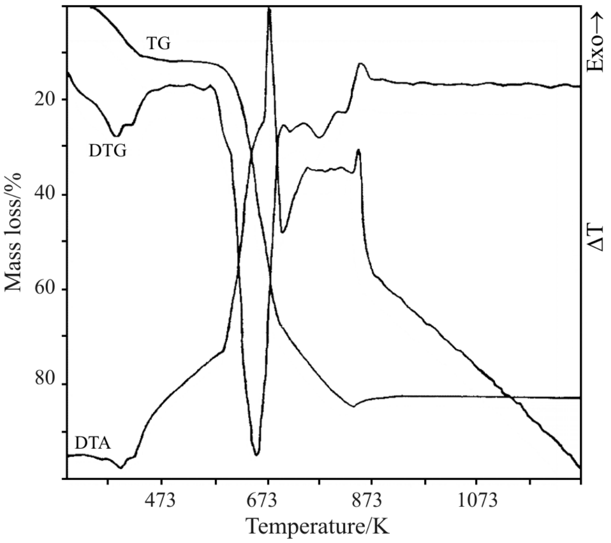

Fig. 3 TG, DTG and DTA curves of Ni(II) 3,5-dimethoxybenzoate in air

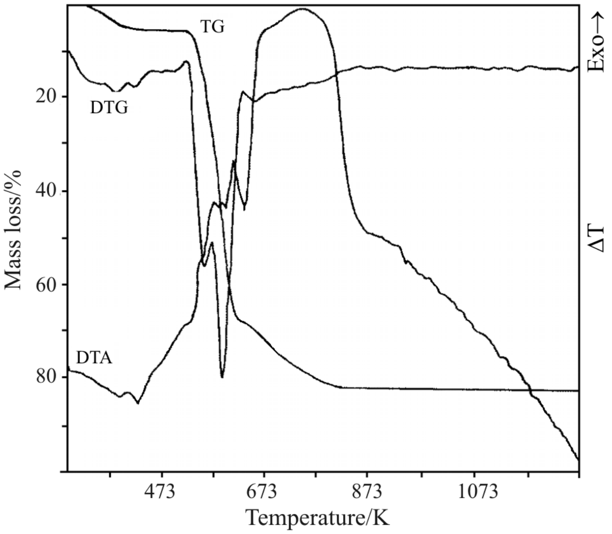

Fig. 4 TG, DTG and DTA curves for Cu(II) 3,5-dimethoxybenzoate in air

The trihydrate of 3,5-dimethoxybenzoate of Ni(II) dehydrates in one step in the range 334–440 K losing three molecules of water and it forms the anhydrous complex. The mass loss calculated from TG curve being equal to 11% corresponds to the loss of three water molecules (theoretical value is 11.37%). The anhydrous 3,5-dimethoxybenzoate of Ni(II) in the temperature range 578–835 K is decomposed to form Ni that next is oxidized (859–921 K) to NiO which is the final product of thermal decomposition. The mass losses calculated from TG curve are equal to 85.0% which corresponds to the Ni formation (calculated value is 87.78%) and to 83.6% (theoretical value is 84.40%) in the case of NiO formation. The dehydration

Table 4 Values of μ_{eff} for 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II)

$CoL_2 \cdot 2H_2O$			$NiL_2 \cdot 3H_2O$			$CuL_2 \cdot 2H_2O$		
T/K	$\chi_M \cdot 10^6$	μ_{eff}/BM	T/K	$\chi_M \cdot 10^6$	μ_{eff}/BM	T/K	$\chi_M \cdot 10^6$	μ_{eff}/BM
77	30294	4.33	103	15000	3.54	77	462	0.67
101	26273	4.63	114	13196	3.50	91	508	0.75
104	25405	4.62	121	11772	3.41	101	554	0.81
109	24308	4.60	131	11060	3.44	109	600	0.87
113	23349	4.61	143	10063	3.43	117	646	0.92
119	22480	4.65	157	9398	3.48	125	693	0.98
123	21932	4.67	168	8591	3.44	136	831	1.09
128	21430	4.71	178	7879	3.40	143	924	1.16
133	20881	4.74	188	7357	3.38	147	970	1.20
138	20104	4.74	198	6693	3.37	152	1016	1.25
143	19647	4.77	207	6313	3.29	155	1062	1.28
148	19328	4.81	217	6076	3.31	161	1108	1.33
153	19053	4.86	228	5981	3.37	170	1155	1.39
158	18505	4.86	238	5648	3.35	176	1201	1.43
163	18003	4.87	248	5506	3.37	182	1247	1.48
173	17089	4.89	258	5316	3.38	189	1247	1.51
183	15992	4.87	269	5126	3.40	198	1293	1.57
193	15306	4.90	277	1841	3.35	208	1293	1.61
203	14666	4.92	287	4746	3.38	217	1293	1.64
214	13936	4.92	298	4462	3.35	228	1339	1.68
221	13159	4.86				237	1293	1.72
227	12794	4.86				245	1247	1.75
236	12565	4.91				255	1247	1.76
245	12337	4.96				262	1247	1.78
251	11925	4.94				272	1201	1.79
260	11651	4.97				280	1108	1.76
271	11194	4.97				287	1108	1.76
281	10966	5.01				298	1016	1.75
297	10555	5.06						

$L=C_9H_9O_4^-$

and reduction processes are connected with an endothermic effects seen in DTA curve while the combustion of the organic ligand and the oxidation of Ni to NiO with the exothermic ones (Fig. 3). The decomposition process of 3,5-dimethoxybenzoate of Ni(II) may proceed in the following way:

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

where $L=C_9H_9O_4^-$.

Considering the temperature at which the dehydration process of the complex takes place and the way by which it proceeds it is possible to assume that the water molecules are also in the outer sphere of complex coordination [18–21]. The peaks seen on the DTG curve correspond to the loss of masses seen in the TG curve. The molecules of crystallization water in the analysed complexes may be in the inner coordination spheres of complexes. When heated the hydrated complexes form anhydrous compounds and then in the central ion spheres the methoxy- or changing their dentates carboxylate groups may occur in order to fill their inner coordination spheres.

During heating to 1173 K the dihydrate of Cu(II) 3,5-dimethoxybenzoate dehydrates in one step (Fig. 4). In the temperature range 325–442 K it losses two water molecules and forms anhydrous complex. The loss of mass calculated from TG curve is equal to 7.0% (the theoretical value is 7.79%). The anhydrous complex in the range 521–848 K is decomposed to CuO. The loss of mass calculated from TG curve is

Table 5 Values of the maximum of absorption bands for Co(II), Ni(II) and Cu(II) ions in the solution of chlorate(VII) samples and 3,5-dimethoxybenzoates

Complex of 3,5-dimethoxybenzoates	Range of measurements $1/\lambda\cdot 10^3$/cm^{-1}	Maximum of absorption bands of M^{2+} ions in the solutions of		$\Delta 1/\lambda\cdot 10^3$/cm^{-1}
		sample	chlorate(VII)	
Co(II)	25–15	19.57	19.32	0.25
Ni(II)	15.3–12.3 28–22	13.92 25.54	13.75 25.03	0.17 0.51
Cu(II)	14.5–11.5	13.93	12.14	1.79

equal to 74.2% (theoretical value is 74.9%). The thermal decomposition of 3,5-dimethoxybenzoate of Cu(II) may proceed according to the scheme:

$$CuL_2\cdot 2H_2O\rightarrow CuL_2\rightarrow CuO$$

where $L=C_9H_9O_4^-$.

The final products of decompositions of Co(II), Ni(II) and Cu(II) 3,5-dimethoxybenzoates were identified roentgenographically.

The solubilities of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) were measured (Table 1). They are in the orders of 10^{-5}–10^{-3} mol dm^{-3}. The Co(II) 3,5-dimethoxybenzoate is the most soluble salt while that of Cu(II) the least soluble one.

The magnetic susceptibility of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) was measured over the range 77–300 K (Table 4). The values of the magnetic susceptibilities for the complexes of Co(II) and Ni(II) obey the Curie–Weiss law while those for Cu(II) 3,5-dimethoxybenzoate do not accomplish it because they increase with the rise of temperature. At lower temperature range for dimers only the lowest levels are occupied. That may be followed on the example of the course of $\chi_{Cu}=f(T)$ for the copper(II) dimers, with states S=1 and S=0. Electron population in both levels is combined with the Boltzmann contribution law and is temperature dependent. At the higher temperatures and for the relatively high exchange parameters $|J|$ (J<0) both states are occupied (triplet state is dominating) and the magnetic moment has the values close to the pure spin (1.73 BM) but usually lower. With temperature lowering the population of the triplet decreases and within the lowest temperature ranges only the singlet state is occupied (S=0) and μ=0 (BM).

In the case of 3,5-dimethoxybenzoates of Co(II) and Ni(II) the values of magnetic moments are lower than those close to the pure spins only [22]. These values indicate that the complexes have the octahedral symmetry.

The experimental data reveal that the magnetic moments of 3,5-dimethoxybenzoate of Ni(II) are connected with a spin-only moment. This indicates that in the solid-state the nickel(II) cation exists in the octahedral triplet ground state with molecules of water and probably with bidentate chelating or bridging carboxylate groups coordinated to it. This was confirmed by the IR spectral analysis (Table 2). The ground state configuration of the nickel(II) ion in a regular octahedral field is ${}^3A_{2g}$ ($t_{2g}^6\, e_g^2$) 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.

The electronic spectra of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) and their chlorates(VII) as standards were recorded in the UV and VIS ranges from 200 to 900 nm in order to observe only the changes in the positions of the recorded absorption bands. The data obtained for the absorption bands in the spectra recorded for these complexes and the standards in the ranges 25000–15000 cm^{-1} for Co(II), 14500–11500 cm^{-1} for Cu(II) and 28000–22000 and 15300–12300 cm^{-1} for Ni(II) are presented in Table 5. The values of frequencies selectively presented show the maxima of the bands of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) and their standards. The absorption bands characteristic for Co^{2+}, Ni^{2+} and Cu^{2+} ions in the aqueous solutions of 3,5-dimethoxybenzoates change to the shorter waves yielding the hypsochromic shift which depends on the character and stability of metal ion-ligand bond to be connected with the kind of ligand, hydration degree of central ions and with the kind of solvents. It also depends on the character of interaction between central ion and the group of atoms in its surroundings. The oxygen atoms of COO^- groups, of water molecules and of the $-OCH_3$ substituents may variously influence the *d* orbitals of central ions because the COO^- ions and $-OCH_3$ groups have different values of inductive and mesomeric effects. Therefore the values of excitation energy are changed causing the movements of absorption bands. With the rise of the complex stabilities the maxima of absorption bands characteristic for the vibrations caused by metal ions are moved to the shorter waves of higher frequencies. When the complex has the greater stability, the stronger bonding between central ion and ligand bonding is. The observed hypsochromic replacements of absorption bands in the electronic spectra, in the comparison with their positions in the corresponding spectra of standards, are indicative of the greater stability of central ion-ligand bonding in the analysed complexes. On the basis of this displacement it is not possible to determine the covalency of bonding because this replacement depends on the coordination number of central ion, its ion radius and oxidation degree. From the obtained results it follows that the values of movements of absorption bands of Co(II), Ni(II) and Cu(II) are changed with the increase of atomic number of element, similarly as the values of stability constants of these elements in the Irving–Williams sequence [23].

The smallest value of change of absorption band was observed for 3,5-dimethoxybenzoate of Ni(II) in the range 15300–12300 cm^{-1}. It is indicative of the small stability of metal ion-ligand bonding in the solution and of its strong hydration degree. The composition of coordination sphere for central ion is similar to that of high-spin aquation for those elements for which it is equal to 6 and with octahedral coordination.

The colours of 3,5-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) are typical for M^{2+} of those element ions (pink for Co^{2+}, green for Ni^{2+} and blue for Cu^{2+}). It is indicative of the coordination of these element ions with the oxygen atoms and the octahedral coordination with the high spin character of the complex.

Acknowledgements

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