Magnetic, thermal and spectral properties of Ni(II) 2,3- , 3,5- and 2,6-dimethoxybenzoates

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Abstract: Complexes of Ni(II) 2,3-, 3,5- and 2,6-dimethoxybenzoates have been synthesized, their physico-chemical properties have been compared and the influence of the position of $-OCH_3$ substituent on their properties investigated. The analysed compounds are crystalline, hydrated salts with green colour. The carboxylate ions show a bidentate chelating or bridging coordination modes. The thermal stabilities of Ni(II) dimethoxybenzoates were investigated in air in the range of 293-1173 K. The complexes decompose in three steps, yelding the NiO as the final product of decomposition. Their solubilities in water at 293 K are in the order of 10^{-2}-10^{-4} mol·dm^{-3}. The magnetic susceptibilities for the analysed dimethoxybenzoates of Ni(II) were measured over the range of 76-303 K and the magnetic moments were calculated. The results reveal that the complexes are the high-spin ones and the ligands form the weak electrostatic field in the octahedral coordination sphere of the central Ni(II) ion. The various position $-OCH_3$ groups in benzene ring cause the different steric, mesomeric and inductive effects on the electron density in benzene ring.

Keywords: dimethoxybenzoates; magnetic moments; Ni(II) complexes; thermal stability; FTIR spectra.

Introduction

The literature survey shows that, in principle, there is no information about the complexes of 2,3-, 3,5- and 2,6-dimethoxybenzoic acids with various cations. Papers exist only on their compounds with rare earth elements in solution and solid state [1-3]. 2,3-, 3,5- and 2,6-Dimethoxybenzoic acids are crystalline solids sparingly soluble in cold water [4-8].

At present we decided to synthesize the complexes of Ni(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 [9-12] 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 Ni(II) complexes in order to investigate the influence of substituent positions on their properties.

Experimental details

2,3-, 3,5- and 2,6-Dimethoxybenzoates of Ni(II) were prepared by addition of equivalent

quantities of 0.1 M ammonium 2,3-, 3,5- and 2,6-dimethoxybenzoates (pH 5) to warm 0.1 M aqueous solutions containing the nitrates (V) of Ni(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 Ni^{2+} 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 and Fig. 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 $2\Theta=4-80°$ by means of the Debye-Scherrer-Hull method. The relationships between I/I_0 and 2Θ for these complexes are presented in Fig. 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 $K\cdot min^{-1}$. The 100 mg samples were heated in platinum crucibles in static air to 1173 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 $mm\cdot min^{-1}$ and Al_2O_3 was used as a standard. The decomposition products were calculated from the TG curves and verified by powder diffraction analysis.

Table 1. Frequencies of the OCO^- absorption bands for Ni(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-dimethobenzoic acids (cm^{-1})

	Complex $L=C_9H_9O_4^-$	ν C=O	$\nu_{as}OCO$	$\nu_s OCO$	$\Delta\nu OCO$	νM-O	Solubility ($mol\cdot dm^{-3}$)
2,3-	$NiL_2\cdot H_2O$	-	1629	1436	192	440	$2.1\cdot10^{-4}$
			1579	1448	131		
	NaL	-	1604	1396	208		
	HL	1686	-	-	-		
3,5-	$NiL_2\cdot 3H_2O$	-	1582	1392	190	409	$5.4\cdot10^{-4}$
				1426	156		
	NaL	-	1580	1385	195		
	HL	1684	-	-	-		
2,6-	$NiL_2\cdot 4H_2O$	-	1596	1400	196	432	$1.4\cdot10^{-2}$
	NaL	-	1608	1408	200		
	HL	1712	-	-	-		
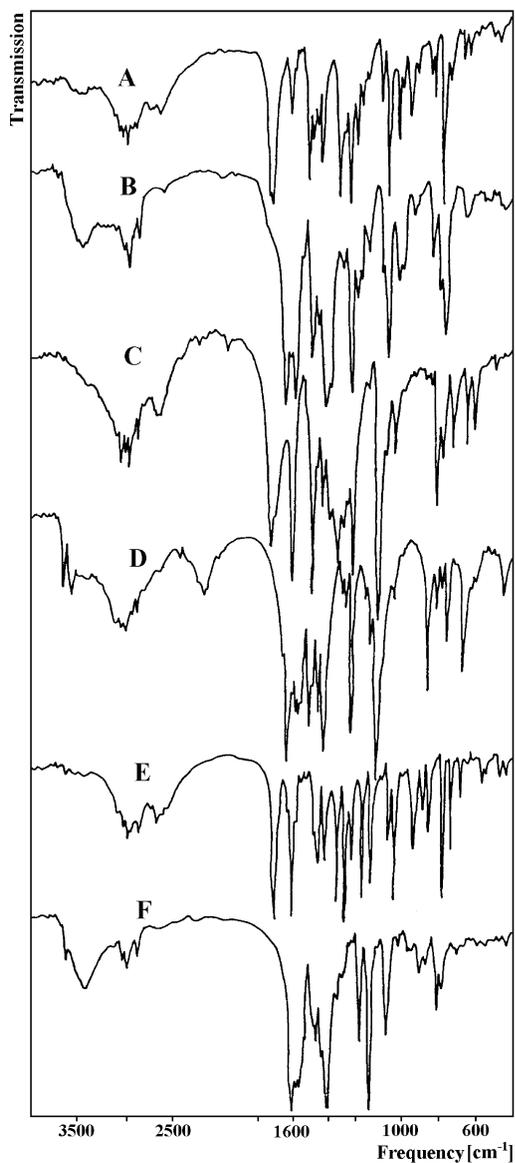
Figure 1. IR spectra of 2,3-dimethoxybenzoic acid (A); 2,3-dimethoxybenzoate of Ni(II) (B); 2,6-dimethoxybenzoic acid (C); 2,6-dimethoxyben-zoate of Ni(II) (D); 3,5-dimethoxybenzoic acid (E); 3,5-dimethoxybenzoate of Ni(II) (F).

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

Magnetic susceptibilities of polycrystalline samples of 2,3-, 3,5- and 2,6-dimethoxybenzoates of Ni(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 asummed to be $1.644 \cdot 10^{-5}$ cm$^3 \cdot$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)

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

The solubilities of 2,3-, 3,5- and 2,6-dimethoxybenzoates of Ni(II) in water were measured at 293 K. Saturated solution of the

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

Complex L=$C_9H_9O_4^-$		Temperature decomp.range (K)	Mass loss (%)		Water molecule n	Intermediate and final products of decomp.
			Calcd.	Found		
2,3-	$NiL_2 \cdot H_2O$	331-398	4.11	3.70	1	NiL_2
	NiL_2	463-871	86.62	86.40	-	Ni
	Ni	880-911	82.97	84.60	-	NiO
3,5-	$NiL_2 \cdot 3H_2O$	334-440	11.37	11.00	3	NiL_2
	NiL_2	578-835	87.78	85.10	-	Ni
	Ni	859-921	84.40	83.60	-	NiO
2,6-	$NiL_2 \cdot 4H_2O$	335-382	3.65	3.60	1	$NiL_2 \cdot 3H_2O$
	$NiL_2 \cdot 3H_2O$	388-438	14.61	14.90	3	NiL_2
	NiL_2	458-888	84.84	83.70	-	NiO

obtained compounds were prepared under isothermal conditions. The contents of Ni(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 Ni(II) were obtained as polycrystalline green solids with a metal to ligand ratio of 1:2 and the general formula $Ni(C_9H_9O_4)_2 \cdot nH_2O$, where n=1 for 2,3-dimethoxybenzoate, n=3 for 3,5-dimethoxybenzoate and n=4 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 1628-1579 cm-1 and 1448-1392 cm-1, respectively for analysed complexes [15-21]. The bands due to ν(M-O) appear in the range of 440-409 cm-1. The magnitudes of the separation ΔνOCO- (where ΔνOCO- = $ν_{as}$OCO- - $ν_s$OCO-), which characterize the type of metal ion-oxygen bond change from 196 to 131 cm-1. According to spectroscopic criteria and especially with regard to Nakamoto [17, 20, 21], the carboxylate groups in the analysed complexes show different modes of coordination. In the 2,3- and 3,5-dimethoxybenzoates of Ni(II) they may function as bidentate chelating or bridging groups and in the 2,6-dimethoxybenzoate only as bidentate bridging.

The X-ray diffraction patterns of the 2,3-, 3,5- and 2,6-dimethoxybenzoates of Ni(II) were recorded. The analysis of the diffractograms suggest 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.

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

NiL$_2$·H$_2$O 2,3-dimethoxybenzoate			NiL$_2$·3H$_2$O 3,5-dimethoxybenzoate			NiL$_2$·4H$_2$O 2,6-dimethoxybenzoate		
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	17280	3.28	103	15000	3.54	76	7513	2.14
103	14210	3.44	114	13196	3.50	123	5989	2.43
112	12807	3.41	121	11772	3.41	133	5660	2.46
117	11973	3.37	131	11060	3.44	143	5370	2.48
127	11359	3.26	143	10063	3.43	153	5133	2.51
127	11052	3.38	157	9398	3.48	163	4909	2.53
132	10526	3.37	168	8591	3.44	173	4711	2.55
137	10043	3.35	178	7879	3.40	183	4527	2.58
143	9517	3.33	188	7357	3.38	193	4382	2.60
148	9254	3.35	198	6693	3.37	203	4158	2.60
153	9035	3.36	207	6313	3.29	213	4039	2.62
157	8772	3.36	217	6067	3.31	223	3881	2.63
164	8289	3.34	228	5981	3.37	233	3749	2.65
173	7763	3.32	238	5648	3.35	243	3631	2.66
180	7324	3.29	248	5506	3.37	253	3539	2.68
190	7193	3.35	258	5316	3.38	263	3433	2.69
199	6754	3.33	269	5126	3.40	273	3354	2.71
208	6359	3.31	277	1841	3.35	283	3302	2.74
221	6052	3.33	287	4746	3.38	293	3222	2.75
229	5833	3.33	298	4462	3.35	303	3143	2.76
237	5526	3.30						

L = C$_9$H$_9$O$_4^-$

The thermal stability of Ni(II) 2,3-, 3,5- and 2,6-dimethoxybenzoates was studied in air. All the details concerning their thermal decomposition were described in our previous papers [8-12]. Accordingly, in this paper only some selected results obtained for their thermal stability in air are presented (Table 2). The 2,3-, 3,5- and 2,6-dimethoxybenzoates of Ni(II) are stable up to 331-335 K. The hydrated complexes lose water molecules in one or two steps and form the anhydrous compounds. The dehydration processes are associated with an endothermic effect on the DTA curves. The anhydrous Ni(II) dimethoxybenzoates decompose to NiO, (with intermediate formation of Ni in the case of 2,3- and 3,5-dimethoxybenzoates), which is the final product of complex decompositions. The thermal stability of hydrated dimethoxybenzoates increases in the following order: 2,3- < 3,5- < 2,6-, while that of the anhydrous ones in the sequence: 2,6- < 2,3- < 3,5-. From the comparison of the decomposition way results it appears that the various position of -OCH$_3$ substituents in benzene ring influences the decomposition process being connected with various participations of the inductive, and mesomeric effects of *methoxy-* groups in the electron density of the system.

The ways of the thermal decomposition of Ni(II) dimethoxybenzoates are as follows:

NiL$_2$·H$_2$O → NiL$_2$ → Ni·→ NiO ; for 2,3-dimethoxybenzoate of Ni(II)

NiL$_2$·3H$_2$O → NiL$_2$ → Ni·→ NiO ; for 3,5-dimethoxybenzoate of Ni(II)

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

	Central ion
	Ni^{2+}
Number of d electrons	8
Number of unpaired electrons	2
Spin-only moment (BM)	2.83
Magnetic moment (BM) for	2,3-dimethoxybenzoate: 3.28-3.44 3,5-dimethoxybenzoate: 3.29-3.54 2,6-dimethoxybenzoate: 2.14-2.76

$NiL_2 \cdot 4H_2O \rightarrow NiL_2 \cdot 3H_2O \rightarrow NiL_2 \rightarrow NiO$; for 2,6-dimethoxybenzoate of Ni(II)

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 Ni(II) 2,3-, 3,5- and 2,6-dimethoxybenzoates in water at room temperature were determined (Table 1). They are of the order of 10^{-4}-10^{-2} mol·dm^{-3}. 2,6-Dimethoxybenzoate of Ni(II) is the best soluble salt while that of 2,3-dimethoxybenzoate the least one. The values of solubilities increase in the order: 2,3- < 3,5- < 2,6-. The changes in the values presented above are connected with the various influences of inductive, mesomeric and steric effects of *methoxy-* groups in 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 of 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 decrease with rising temperature. The effective magnetic moment values of the 2,3-, 3,5- and 2,6-dimethoxybenzoates of Ni(II) change from 3.28 BM (at 77 K) to 3.30 BM (at 237 K) for 2,3-dimethoxybenzoate, from 3.54 BM (at 103 K) to 3.35 BM (at 298 K) for 3,5-dimethoxybenzoate, and from 2.14 BM (at 76 K) to 2.76 BM (at 303 K) for 2,6-dimethoxybenzoate of Ni(II). The complexes show paramagnetic properties and they obey the Curie-Weiss law. The values of the Weiss constant, Θ, for all the complexes were found to be negative, which probably arises from a crystal field splitting of the paramagnetic spin state [9-12, 29-32]. The paramagnetic dependences of values of the magnetic susceptibility as a function of temperatures are given in Table 3. They give informations about the magnetic interaction between paramagnetic centers. As a rule, if the χ_M values 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-, 3,5- and 2,6-dimethoxybenzoates of Ni(II) show a gradual decrease with increasing temperature. This indicates a tendency of ferromagnetic interaction between the metal ions. In the case of the 2,3-, 3,5- and 2,6-dimethoxybenzoates of Ni(II), the effective magnetic moments are equal to 3.28-3.30 BM, 3.35-3.54 BM and 2.14-2.76 BM (Table 3). The magnetic moments measured for the Ni(II) complexes are 3.30, 3.35 and 2.76 BM at room temperature. These values differ from that of the spin-only moment, which amounts to 2.83 BM (Table 4). This difference between the measured and calculated values results from spin-orbital coupling [33] in the case of 2,3- and 3,5-dimethoxybenzoates of Ni(II), while in the 2,6-dimethoxybenzoate of Ni(II) they are connected with a spin-only moment. It indicates that in the solid state the nickel cation exists in an octahedral triplet ground state with molecules of water and bidentate carboxylate groups coordinated to Ni(II) ion. This was confirmed by the IR spectral analysis (Table 1). The ground state configuration of Ni(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 experimental data suggest that the 2,3-, 3,5- and 2,6-dimethoxybenzoates of Ni(II) are high-spin complexes with weak electrostatic ligand fields and octahedral coordination of Ni(II) ions in which there are four oxygen atoms of carboxylate groups and oxygen atoms of water molecules.

Differences in the magnetic properties are obviously evidenced by differences in their molecular and crystal structures [34]. The main difference in the structures is connected with the geometry of the octahedral coordination spheres. The ways of coordinations of central ions of Ni(II) in the analysed compounds could be established on the basis of the complete crystal structure determinations of monocrystals but they

have not been obtained. In the case of 2,6-dimethoxybenzoate of Ni(II) the magnetic moment values change from 2.76 BM at 303 K to 2.14 BM at 76 K. The reason for this could be the second order spin-coupling which splits the $^3A_{2g}$ ground state of Ni(II) ion, on perhaps this effect combined with an antiferromagnetic super-change interaction [35-37].

Conclusions

From the obtained results it appears that 2,3-, 3,5- and 2,6- dimethoxybenzoates of Ni(II) were synthesized as hydrated complexes with green colours. They are crystalline compounds and on heating in air to 1173 K the complexes decompose in three steps and form NiO, which is the final product of decomposition. The solubility of the complexes in water at 293 K is of the order of 10^{-2}-10^{-4} mol·dm^{-3}. The values of μ_{eff} calculated for analysed complexes in the range of 76-303 K reveal that the Ni(II) complexes are high-spin with octahedral coordination and weak ligand field.

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