

Magnetic, thermal and spectral characterization of 2,6-dimethoxybenzoates of Co(II), Ni(II) and Cu(II)

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Abstract: The complexes of 2,6-dimethoxybenzoic acid anion with ions of Co(II), Ni(II), and Cu(II) have been synthesized as polycrystalline solids, and characterized by elemental analysis, spectroscopy, magnetic studies, and also by X-ray diffraction and thermogravimetric measurements. The analysed complexes have following colours: pink for Co(II), green for Ni(II), and blue for Cu(II) compounds. The carboxylate group binds as monodentate, and bidentate bridging and chelating ligands. On heating in air to 1173 K the complexes decompose in four, three or two steps. At first, they dehydrate in one or two steps to anhydrous salts, that next decompose to oxides of the respective metals. The solubility of the investigated dimethoxybenzoates in water at 293 K is of the order of 10^{-2} mol/dm³. Their magnetic moments were determined in the temperature range of 76-303 K. The results reveal the compounds of Co(II) and Ni(II) to be high-spin complexes and that of Cu(II) to form dimer.

Keywords: 2,6-dimethoxybenzoates; thermal stability; magnetic properties of Co(II), Ni(II) and Cu(II); IR spectra.

Introduction

The carboxylates play an important role in inorganic and bioinorganic chemistry. Many metal cations in a great number of various biological processes are a component of several vitamins and drugs [1, 2]. The carboxylates of d- and 4f ion elements may be used as electric materials in the modern branches of techniques and technology, and they may have applications as precursors in superconducting ceramic and magnetic field productions.

According to literature survey compounds of various organic ligands, also chloromethoxy- and methoxybenzoic acids have been prepared and studied. There are papers that deal with their complexes with d- and mainly 4f metal ion elements [3-15]

The compounds of 2,6-dimethoxybenzoic acid anion with following cations: Cu(II), Mn(II), Co(II), Ni(II), Zn(II) and some of Ln(III) have been obtained in solids or studied in solution [16-18].

2,6-Dimethoxybenzoic acid is a white solid sparingly soluble in water [19]. It crystallizes from water in the plate form. Its dissociation constants were determined in the solutions of various water – dioxan ratios [20]. The pKa value of 2,6-dimethoxybenzoic acid and its thermodynamic parameter values were determined potentiometrically but only in the aqueous solution [16]. Its pKa is equal to 8.49.

As a continuation of our study on carboxylates we decided to synthesize 2,6-dimethoxybenzoates of Co(II), Ni(II) and Cu(II)

and to study some of their properties not to be investigated so far, such as magnetic properties in the range of 77-300 K, thermal stability in air at 293-1173 K, solubility in water at 293 K and to record their FTIR spectra.

Thermal stability investigations give informations about the process of dehydration and the ways of decompositions, and the magnetic susceptibility measurements let study the kinds of the way of coordination of the central ions, and the nature of bonding between central ions and ligands. The determination of the solubility is valuable because it informs about the practical use of the acid for separation of transition metal ions by extraction or ion-exchange chromatographic methods.

Experimental details

The 2,6-dimethoxybenzoates of Co(II), Ni(II), and Cu(II) were prepared by adding the equivalent quantities of 0.1 M ammonium 2,6-

dimethoxybenzoate (pH \approx 5) to a hot solution containing the 0.1 M Co(II), Ni(II), and Cu(II) nitrate(V) and crystallizing at 293 K (1 h). The solid formed 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 M²⁺ metal ions were established gravimetrically, and by ASA method with the use of ASA 880 spectrophotometer (Varian) (Table 1).

The IR spectra of complexes were recorded over the range of 4000-400 cm⁻¹ using an FTIR 1725 X Perkin-Elmer spectrometer. The samples for the FTIR spectra measurements were prepared as KBr discs. 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 $2\theta = 4-80^\circ$ by

Table 1. Elemental analysis data of Co(II), Ni(II), and Cu(II) 2,6-dimethoxybenzoates, and their solubilities in water at 293 K.

H / %		C / %		M / %	
calcd.	found	calcd.	found	calcd.	found
5.27	4.90	43.82	41.88	11.95	12.73
5.27	5.19	43.84	43.88	11.91	12.73
4.51	4.42	48.70	48.68	14.32	13.57

Table 2. Wavenumbers (cm⁻¹) of COO⁻ bands in the analysed complexes of Co(II), Ni(II), Cu(II), and Na(I), and of the COOH band in 2,6-dimethoxybenzoic acid.

Complex	$\nu_{as} \text{COO}^-$	$\nu_s \text{COO}^-$	$\Delta\nu_{\text{COO}^-}$	$\nu_{\text{M-O}}$	$\nu_{\text{C=O}}$
CoL ₂ ·4H ₂ O	1600	1392	208	424	-
NiL ₂ ·4H ₂ O	1596	1400	196	432	-
CuL ₂ ·H ₂ O	1596	1412	184	472	-
NaL	1608	1408	200	-	-
HL	-	-	-	1712	-

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 of the complexes were determined by Paulik-Paulik-Erday Q-1500D derivatograph with Derill converter, recording TG, DTG, and DTA curves (Fig. 2). The measurements were made at a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ with a full scale. The samples (60 mg and 100 mg) were heated in platinum crucibles in static air to 1173 K with a sensitivity of TG 60-100 mg. DTG, and DTA sensitivities were regulated by a Derill computer program. The products of decompositions were calculated from the TG

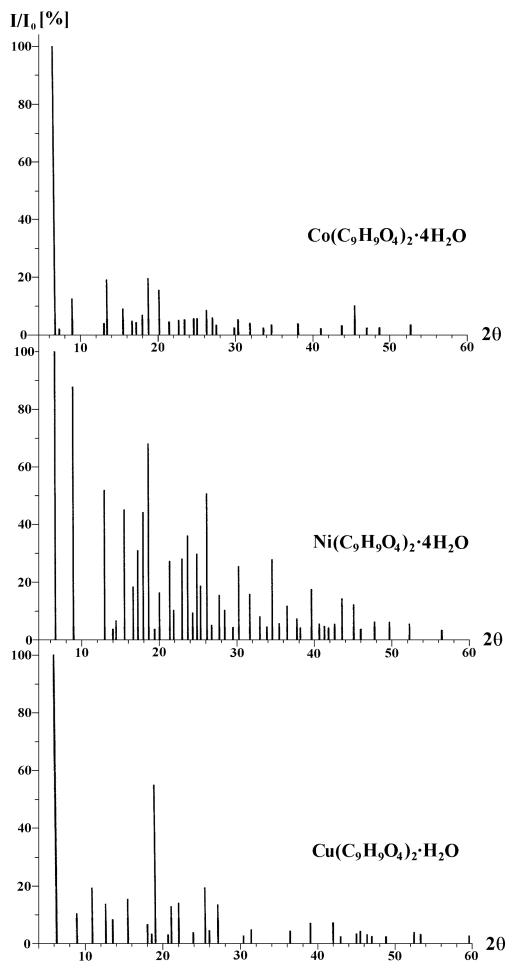


Figure 1. Dependence of I/I_0 vs 2θ for Co(II), Ni(II), Cu(II) 2,6-dimethoxybenzoate.

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 2,6-dimethoxybenzoates of Co(II), Ni(II), and 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 $\text{Hg}[\text{Co}(\text{SCN})_4]$ for which the magnetic susceptibility was assumed to be $1,644 \cdot 10^{-5}\text{ cm}^3 \cdot \text{g}^{-1}$. Correction for diamagnetism of the calibrant atoms was calculated by the use of Pascal's constants [21, 22]. Magnetic moments were calculated from Eq. (1):

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

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

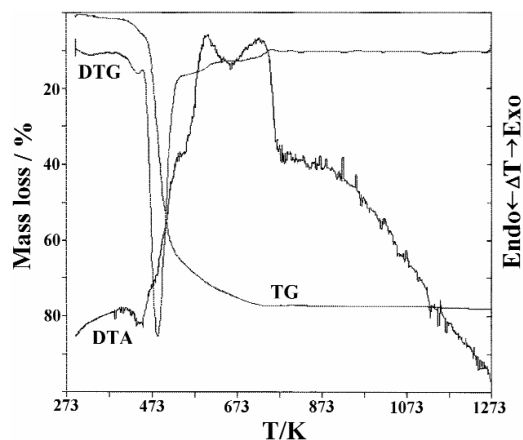


Figure 2. TG, DTG and DTA curves for Cu(II) 2,6-dimethoxybenzoate.

Table 3. Temperature range of thermal stability of Co(II), Ni(II), and Cu(II) 2,6-dimethoxybenzoates in air.

Complex $L=C_9H_9O_4^-$	ΔT^a / K	Mass loss / %		n^b	Final product of decomp. in solid state
		Calcd.	Found		
$CoL_2 \cdot 4H_2O$	331-426	14.61	14.40	4	CoL₂
CoL₂	467-858	88.05	87.80	-	Co
Co	871-905	83.72	83.10	-	Co₃O₄
Co₃O₄	1146-1188	84.97	85.80	-	CoO
$NiL_2 \cdot 4H_2O$	335-382	3.65	3.60	1	$NiL_2 \cdot 3H_2O$
$NiL_2 \cdot 3H_2O$	388-438	14.61	14.90	3	NiL₂
NiL₂	458-888	84.84	83.70	-	NiO
$CuL_2 \cdot H_2O$	398-433	4.05	3.40	1	CuL₂
CuL₂	448-742	82.07	82.40	-	CuO

ΔT^a = temperature range of decomposition processes,

n^b = number of water molecules lost in the dehydration process

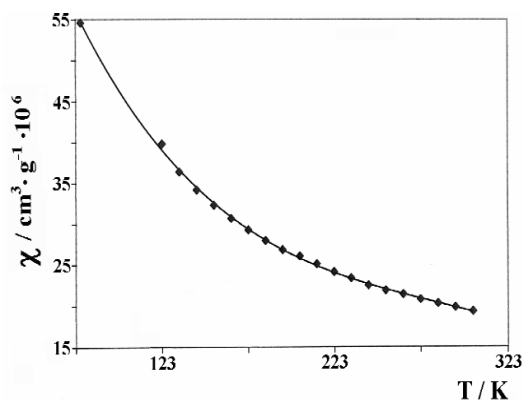


Figure 3. Dependence between magnetic susceptibility values vs temperatures for 2,6-dimethoxybenzoate of Co(II).

Results and Discussion

The complexes of 2,6-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 $M(II)=Co, Ni, Cu$,

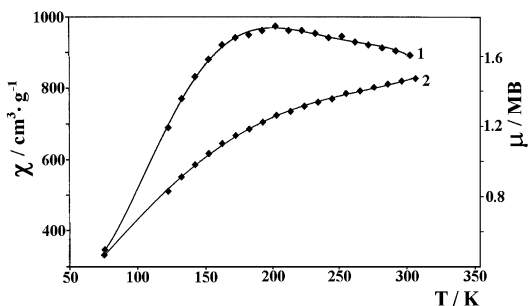


Figure 4. Dependence between magnetic susceptibility (1) and magnetic moment (2) values vs temperature for 2,6-dimethoxybenzoate of Cu(II).

and $n=4$ for Co(II) and Ni(II), and $n=1$ for Cu(II). Their colours are following: pink for Co(II), green for Ni(II), and blue for Cu(II) complexes. In these compounds 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 [15, 23, 24].

The compounds were characterized by elemental analysis (Table 1), and FTIR spectra. The

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

CoL ₂ ·4H ₂ O L=C ₉ H ₉ O ₄ ⁻			NiL ₂ ·4H ₂ O			CuL ₂ ·H ₂ O		
T / K	χ _M ·10 ⁶	μ _{eff} / μ _B	T / K	χ _M ·10 ⁶	μ _{eff} / μ _B	T / K	χ _M ·10 ⁶	μ _{eff} / μ _B
76	23208	3.76	76	7513	2.14	76	346	0.46
123	16999	4.09	123	5989	2.43	123	688	0.82
133	15552	4.07	133	5660	2.46	133	770	0.91
143	14617	4.09	143	5370	2.48	143	831	0.98
153	13826	4.12	153	5133	2.51	153	880	1.04
163	13142	4.14	163	4909	2.53	163	921	1.10
173	12554	4.17	173	4711	2.55	173	941	1.14
183	12004	4.19	183	4527	2.58	183	949	1.18
193	11531	4.22	193	4382	2.60	193	961	1.22
203	11204	4.27	203	4158	2.60	203	974	1.26
213	10799	4.29	213	4039	2.62	213	961	1.28
223	10394	4.31	223	3881	2.63	223	961	1.31
233	10075	4.34	233	3749	2.65	233	953	1.33
243	9709	4.35	243	3631	2.66	243	941	1.35
253	9449	4.38	253	3539	2.68	253	945	1.38
263	9246	4.41	263	3433	2.69	263	929	1.40
273	8986	4.43	273	3354	2.71	273	921	1.42
283	8774	4.46	283	3302	2.74	283	913	1.44
293	8581	4.49	293	3222	2.75	293	904	1.46
303	8369	4.51	303	3143	2.76	303	892	1.47

2,6-dimethoxybenzoates of Co(II), Ni(II), and Cu(II) exhibit similar solid state IR spectra. Some of results are presented in Table 2. The band at 1712 cm⁻¹ originating from the RCOOH group, presented in the acid spectrum, is replaced in the spectra of complexes by two bands at 1600-1596 cm⁻¹, and 1412-1392 cm⁻¹, which can be ascribed to the asymmetric and symmetric vibrations of COO⁻ group, respectively [25-28]. The bands attributed to asymmetric and symmetric C-H stretching modes of the -CH₃ groups are observed at 2944-2936 cm⁻¹, and 2840-2832 cm⁻¹, respectively. The bands with the maxima at 3670-3552 cm⁻¹ in the spectra of 2,6-dimethoxybenzoates of Co(II), Ni(II), and Cu(II) are characteristic for ν(OH) vibration [26-28]. The bands of ν(C=C) ring vibrations appear at 1480-1432 cm⁻¹, 1304-1288 cm⁻¹, and 644-640 cm⁻¹, and those corresponding to M-O stretching appear at 472-424

cm⁻¹. Table 2 presents the values of the two band frequencies of asymmetrical and symmetrical vibrations for carboxylate group of analysed complexes. The separations of the ν_{as}(OCO⁻), and ν_s(OCO⁻) modes in the compounds, Δν(OCO⁻), are greater or smaller than that of the sodium salt (ΔνOCO⁻ = 200 cm⁻¹). It indicates the different participations of ionic bonds in 2,6-dimethoxybenzoates compared to that of the sodium salt. For the complexes the shifts of the frequencies of bands of ν_{as}(OCO⁻), and ν_s(OCO⁻) are lower, and lower, and higher, respectively, than those for sodium 2,6-dimethoxybenzoate. Accordingly, taking into account the spectroscopic criteria [26, 28, 29] the carboxylate ions appear to be monodentate and bidentate bridging or chelating groups.

In order to estimate the crystalline forms of the 2,6-dimethoxybenzoates the X-ray powder diffraction measurements were done. The diffrac-

togram analyses suggest them to be polycrystalline compounds with various degrees of crystallinity [30]. The complexes of Co(II), and Ni(II) seem to be isostructural compounds (Fig. 1).

The thermal stability of Co(II), Ni(II), and Cu(II) 2,6-dimethoxybenzoates was studied in air at 293-1173 K (Table 3, Fig. 2). When heated to 1173 K the Co(II) complex is dehydrated in one step and next gradually decomposed to CoO with the intermediate formations, at first, of CoL_2 , next of Co, and Co_3O_4 . The found weight loss is equal to 83.10 %, and calculated value 83.72 %. In the range of 1146-1188 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 tetrahydrate of 2,6-dimethoxybenzoate of Ni(II) dehydrates in two steps at 335-382 K, and 388-438 K losing one and three molecules of water, respectively, and it forms the anhydrous complex. The mass losses calculated from TG curve being equal to 3.6 %, and 14.90 % correspond to the loss of one, and then three water molecules (theoretical values are equal to 3.65 %, and 14.61 %). The anhydrous 2,6-dimethoxybenzoate of Ni(II) at 458-888 K is decomposed to NiO, which is the final product of thermal decomposition. The mass loss calculated from TG curve is equal to 83.70 %, that corresponds to the NiO formation (calculated value is 84.84 %). The dehydration process is connected with an endothermic effect seen on DTA curve, while the combustion of the organic ligand is accompanied by exothermic one. 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 may be also in the outer sphere of complex coordination [31-34].

During heating to 1173 K the monohydrate of Cu(II) 2,6-dimethoxybenzoate dehydrates in one step (Fig. 2). In the temperature range of 398-433 K it losses one water molecule, and forms anhydrous complex. The loss of mass calculated from TG curve is equal to 3.40 % (the theoretical value is 4.05 %). The anhydrous complex at 448-742 K is decomposed to CuO. The loss of mass calculated from TG curve is equal to 82.40 % (theoretical value is 82.07 %).

The final products of decompositions of Co(II), Ni(II), and Cu(II) complexes were identified by X-ray diffraction on the powder.

The solubility of analysed compounds was measured (Table 1). It is in the order of 10^{-2} mol·dm⁻³. The Co(II) 2,6-dimethoxybenzoate is the most soluble salt, while that of Cu(II) the least soluble one. These compounds are relatively readily soluble in water, and the order value is not sufficient to use 2,6-dimethoxybenzoic acid for the separation of some metal ions by ion-exchange chromatography method.

The magnetic susceptibility of 2,6-dimethoxybenzoates of Co(II), Ni(II), and Cu(II) was measured over the range of 76-303 K (Table 4). The measured values for Co(II), and Ni(II) complexes obey the Curie-Weiss law suggesting a weak ferromagnetic interaction (Fig. 3). The magnetic moment values experimentally determined at 76-303 K for Co(II), and Ni(II) compounds change from 3.76 μ_B (at 76 K) to 4.51 μ_B (at 303 K) for Co(II) complex, and from 2.14 μ_B (at 76 K) to 2.76 μ_B (at 303 K) for Ni(II) 2,6-dimethoxybenzoate. These magnetic moment data are very close to the spin only values for the respective ions calculated from the equation $\mu_{\text{eff}} = [4s(s+1)]^{1/2}$ in the absence of the magnetic interactions for present spin-system. The magnetic moment values calculated at room temperature for Co(II), Ni(II), and Cu(II) ions are equal to 3.88 μ_B , 2.83 μ_B and 1.73 μ_B , respectively. For Co(II), Ni(II), and Cu(II) ions the magnetic moment values may be different than the spin-only. In the case of Co(II) compound they are higher than the spin-only worth which results from a spin-orbital coupling. For Ni(II), and Cu(II) ions the magnetic moment are lower than the spin-only value. 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 compound of Ni(II) seems high-spin complex with octahedral symmetry and probably weak ligand field [34-39].

The magnetic susceptibility values of 2,6-dimethoxybenzoate of Cu(II) increase with rising temperatures suggesting a weak antiferromagnetic interaction (Fig. 4). The magnetic moment values experimentally determined changed from 0.46 μ_B (at 76 K) to 1.47 μ_B (at 303 K). These values are

lower than the d^9 spin-only value of $\mu_{\text{eff}}=1.73 \mu_{\text{B}}$. Such dependence is a typical behaviour for copper dimer (Table 4, Fig. 4) [35-39]. Magnetic susceptibility measurements revealed the $\chi_{\text{Cu}}=f(T)$ relation course to be typical for the 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. The observed magnetic properties are typical for dimer systems in which exists the magnetic superexchange between the Cu(II) centers [39].

From the obtained results it appears that in 2,6-dimethoxybenzoates of Cu(II), Co(II) and Ni(II) the coordination numbers may be equal to 5 and 6 depending on the dentates of carboxylate group and the position of water molecules in the complex. The coordination numbers of Cu(II), Co(II) and Ni(II) ions could be established on the basis of the complete crystal structure determination of monocrystals but they have not been obtained. Therefore according to Cu(II) complex we can only suppose that each copper(II) ion may show a fivefold coordination in the form of a square pyramid with four oxygen atoms of bidentate 2,6-dimethoxybenzoate

anions in the basal plane and one oxygen atom of water molecule at the apex. In the 2,6-dimethoxybenzoates of Co(II) and Ni(II) the cations are presumably in octahedral coordination in which there are four oxygen atoms of two carboxylate groups, and two oxygen atoms of water molecules.

Conclusions

On the basis of the results it appears that 2,6-dimethoxybenzoates of Co(II), Ni(II) and Cu(II) were synthesized as hydrated complexes. Their colours are following: pink for Co(II), green for Ni(II) and blue for Cu(II) compounds. The complexes are crystalline compounds and on heating in air to 1173 K they decompose in various ways: Co(II) complex in four steps, Ni(II) in three stages and Cu(II) in two steps. In the first step they dehydrate in one or two steps to anhydrous salts that next decompose to the oxides of the appropriate metals. The values of μ_{eff} calculated for analysed complexes in the range of 76-303 K reveal that the Co(II) and Ni(II) complexes are high-spin and that of Cu(II) forms dimer.

Recebido em: 22/03/2006

Aceito em: 10/04/2006

W. Ferenc, A. Walków-Dziewulska, J. Sarzynski. Caracterização magnética, térmica e espectral de 2,6-dimetóxi benzoatos de Co(II), Ni(II) e Cu(II).

Resumo: Os anions complexos do ácido 2,6-dimetóxi benzóico com ions de Co(II), Ni(II) e Cu(II) foram sintetizados como sólidos policristalinos e caracterizados por análise elementar, espectroscopia, estudos magnéticos e também por medidas de difratometria de raios X e termogravimetria. Os complexos analisados apresentaram a seguinte coloração: rosa para os compostos de Co(II), verde para os compostos de Ni(II) e azul para os compostos de Cu(II). O grupo carboxilato se liga como monodentado, bidentado em ponte e ligantes quelatos. No aquecimento ao ar até 1173 K os complexos se decompõem em quatro, três ou duas etapas. Inicialmente, eles se desidratam para sais anidros em uma ou duas etapas, decompondo-se em seguida para os respectivos óxidos metálicos. A solubilidade em água a 293 K dos dimetoxibenzoatos analisados é em torno de 10^{-2} mol/dm³. Seus momentos magnéticos foram determinados no intervalo de temperaturas entre 76-303 K. Os resultados mostraram que os compostos de Co(II) e Ni(II) são complexos de spin elevado e que os compostos de Cu(II) formam dímeros.

Palavras-chave: 2,6-dimetoxibenzoatos; estabilidade térmica; propriedades magnéticas dos compostos de Co(II), Ni(II) e Cu(II); espectros de IV.

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