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New Complexes of 3,4-Dimethoxyphenylacetic Acid with Selected Transition Metal Ions: Spectral, Thermal, and Magnetic Properties[1]

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Abstract—3,4-Dimethoxyphenylacetates of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) of general formula $M(C_{10}H_{11}O_4)_2 \cdot nH_2O$, where n = 1, 2 or 4 depending on M(II) ions, are obtained. The complexes crystallize in monoclinic or triclinic systems. The carboxylate groups act as bidentate chelating or bridging ligands. On heating in the air (293–1173 K) they decompose in three steps finally forming oxides of the corresponding metals(II) or their mixtures. Magnetic moments of compounds were determined in the ranges of 76–303 and 4–300 K.

Keywords: 3,4-dimethoxyphenylacetic acid, transition metals, magnetic properties, thermal stability, powder diffraction

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INTRODUCTION

3,4-Dimethoxyphenylacetic acid (DMPA) (Fig. 1a) is a white or beige soluble in water solid with melting point 96–98°C. DMPA is a dopamine metabolite that inhibits brain mitochondrial respiration via monoamine oxidase. It is the main metabolite of 3,4-dimethoxyphenoxyethyl-amine [1, 2]. 3,4-Dimethylphenylamine and 3,4-dimethoxyphenylacetic acid are neurotoxins accompanying schizophrenia [3]. Their role in the Parkinson disease processes and the biochemical reactions are under study [4–6].

The detailed study of this acid and its complexes are of high importance for understanding the course of diseases with dopamine participation.

The carboxylic group in acid molecules connected with the aromatic ring by aliphatic chain can interact with metal ions affecting their biological activity. Activity of 3,4-dimethoxyphenylacetic acid is determined by two methoxy substituents in *meta* and *para* positions in the aromatic ring. Influence of the substituents on the reactions of aromatic compounds is described by Hammett's constant δ, the value of which depends on the substituent nature and its position in the aromatic ring. The greater its value, the stronger electrons are attracted by the given substituent. The δ values for $–O–CH_3$ substituent are $\delta_m = +0.280$ and $\delta_p = –0.268$ [7]. In presented acid molecules the $–O–CH_3$ groups in the *meta* and *para* positions of the ring influence upon its stabilization.

Biological activity of coordination compounds is modulated by many factors, such as nature of the substituent in the basic ligand, type of the metal and environment surrrounding the central metal ion, and also by a solution pH. Moreover, the title compound forms hydrogen bonds, that may generate mostly chain units rather than dimers in the crystal structure (Fig. 1b) [8–10].

The review of the available literature on DMPA and its derivatives demonstrated that there were no publications on their complexes, only the structure of DMPA was presented (Fig. 1a) [9, 10]. Some studies of heteroligand complexes of 3,4-dimethoxyphenylacetic acid anion and 1,10–phenanthroline with Ce(III), Pr(III), Nd(III), Gd(III), Yb(III), and Zn(II) by means of IR and X-ray spectra, elemental analysis and TG/DTA were carried out [11–14]. Crystal structure of the complex $[Zn(DMPA)_2(phen)] \cdot 6H_2O$ was determined by X-ray diffraction single crystal method (Fig. 1c) [14].

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[1] The text was submitted by the authors in English.

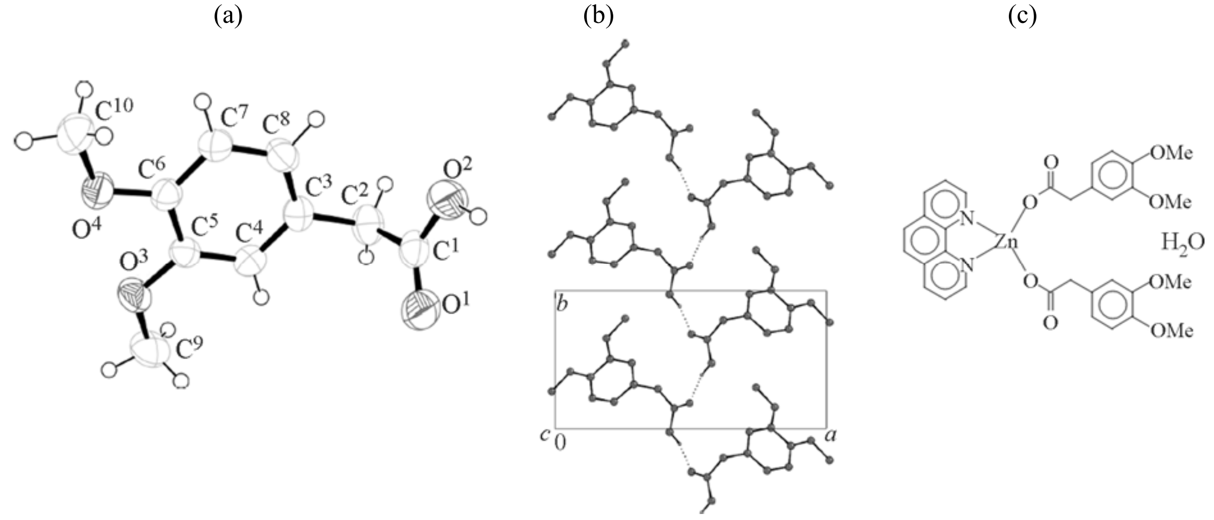


Fig. 1. (a) Molecular structure of 3,4-dimethoxyphenylacetic acid [8–10], (b) the hydrogen-bonded chains formed by acid molecules [10], and (c) chemical formula of Zn(II) with 3,4-dimethoxyphenylacetic acid and 1,10-phenanthroline complex [14].

Transition metal ions demonstrate important biochemical properties that may be used in metabolism investigations. Taking into account the above facts, studies of the structure, conditions of formation, physico-chemical properties, and biological activity of DMPA complexes with various metal ions were of considerable importance.

We synthesized some complexes of 3,4-dimethoxyphenylacetic acid anion with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) and studied their magnetic properties at 77–303 K and for some of them at 4–300 K, thermal stability in the air, and recorded their FT-IR and X-ray spectra in attempt to determine their structures.

EXPERIMENTAL

All chemicals and solvents used were commercially available reagent grade and applied without further purification. Ammonium 3,4-dimethoxyphenylacetate (pH~5) of 0.1 mol/L concentration was prepared by addition of 7.5 cm^3 of NH_3 (aq.) solution [25% pure, Polish Chemical Reagents in Gliwice (Poland)] to 19.62 g of 3,4-dimethoxyphenylacetic acid (99% pure, Aldrich Chemical Company) in water.

The complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with HL acid were prepared by addition of the equivalent quantity of 0.1 mol/L ammonium salt of HL acid (pH ~ 5) to warm solutions of those metals chlorides (0.8 g): $MnCl_2·4H_2O$, $CoCl_2·6H_2O$, $NiCl_2·6H_2O$, $CuCl_2·2H_2O$, and $ZnCl_2$ (analytically pure, Polish Chemical Reagents in Gliwice–Poland) (Scheme 1), and crystallized at 293 K. Volumes of 0.1 M ammonium 3,4-dimethoxyphenylacetate added to a suitable chloride, Mn(II), Co(II), Ni(II), Cu(II), or Zn(II), were equal to: 81, 68, 68, 94, and 118 cm^3, respectively. For reaching the equilibrium state the solids were constantly stirred in solutions for 1 h, then filtered off, washed with warm water to remove ammonium and chloride ions and dried at 303 K until gaining the constant mass. Sodium salt of HL acid was prepared by addition of the equivalent amount of 0.1 mol/L ammonium salt of HL acid (25 cm^3) to the solution of 0.1 g of NaOH (analytically pure, Polish Chemical Reagents in Gliwice–Poland) followed by crystallization.

$MnL_2·2H_2O$. Creamy crystals. Found, %: C 49.83; H 5.67; M 11.58. Calculated, %: C 49.9; H 5.45; M 11.41.

$CoL_2·4H_2O$. Pink crystals. Found, %: C 46.94; H 6.01; M 11.45. Calculated, %: C 46.06; H 5.81; M 11.30.

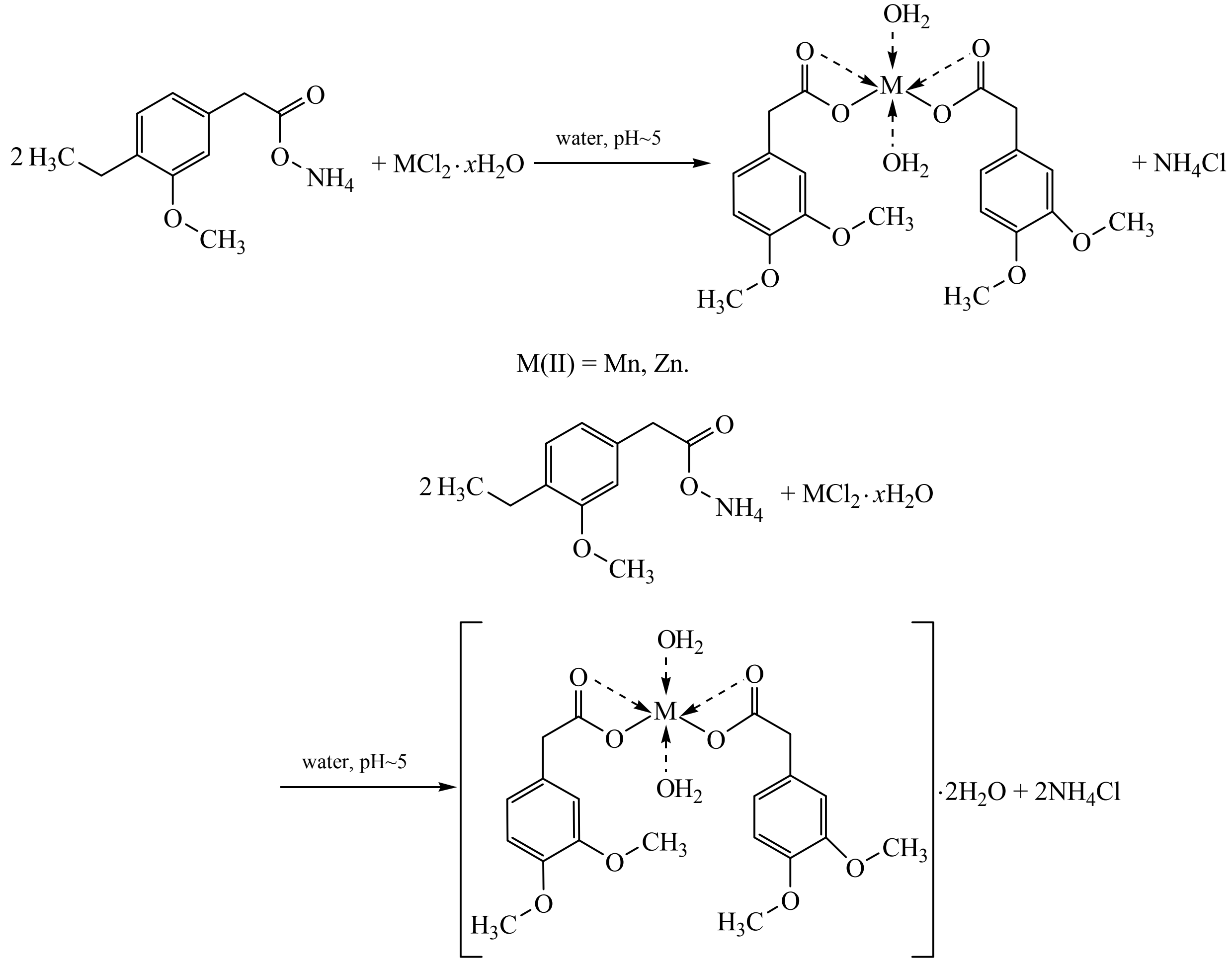
$NiL_2·4H_2O$. Green crystals. Found, %: C 47.02; H 5.9; M 11.68. Calculated, %: C 46.09; H 5.81; M 11.66.

$CuL_2·H_2O$. Blue crystals. Found, %: C 52.25; H 5.21; M 13.42. Calculated, %: C 50.89; H 5.14; M 13.46.

$ZnL_2·2H_2O$ (%). White crystals. Found, %: C 48.95; H 5.45; M 13.32. Calculated, %: C 48.84; H 5.34; M 13.29.

CH analysis was carried out on a CHN 2400 Perkin-Elmer analyzer. The amounts of M(II) metals were determined by X-ray fluorescence XRF method using a spectrophotometer of X-ray fluorescence with energy dispersion EDXRF-1510 (Canberra-Packard). FT-IR spectra (KBr discs) of complexes, products and decom-

Scheme 1. Synthesis of Mn(II), Ni(II), and Zn(II) 3,4-dimethoxyphenylacetates.



M(II) = Mn, Zn.

M(II) = Ni.

position residues were recorded over the range of 4000–400 cm^{-1} on a M-80 Perking-Elmer spectrophotometer.

X-ray diffraction patterns of compounds and the products of the final decomposition processes were measured on a HZG-4 (Carl-Zeiss, Jena) diffractometer with Ni filtered CuK_α radiation within the range of $2\theta = 4°–80°$ by means of the Bragg–Brentano method.

Thermal stability and decomposition of the complexes were studied in the air using a Setsys 16/18 (Setaram) TG, DTG and DSC instrument. The experiments were carried out under the air flow rate of 1 L/h in the temperature range of 297–1173 K at the heating rate of 5 K/min. The initial mass of samples of 3,4-dimethoxyphenylacetates of selected transition metals used changed from 4.74 to 3.38 mg. Samples of those compounds were heated in Al_2O_3 crucibles.

TG–FT-IR measurements were performed on a Q5000 TA apparatus coupled with a Nicolet 6700 spectrophotometer. The experiments were carried out under the dynamic nitrogen atmosphere at a heating rate of 10 deg/min in flowing nitrogen (20 mL/min) in an open platinum crucibles. The samples were heated up to 1000°C at the heating rate of 20 deg/min. The decomposition gaseous products were analyzed over the range of 4000–400 cm^{-1} on a Nicolet 6700 spectrophotometer.

Magnetic susceptibility of polycrystalline samples of 3,4-dimethoxyphenylacetates of selected transition metals were studied at 76–303 K and for some of them at 4–300 K. The measurements in the range of 76–303 K were carried out using the Gouy's method. Mass changes were measured on a Cahn RM-2 analytical balance. The calibrate employed was Hg[Co

Table 1. FT-IR bands (cm^{-1}) in the spectra of 3,4-dimethoxyphenylacetates of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)[a]

Assignment	HL, $L = C_{10}H_{11}O_4$	$MnL_2 \cdot 2H_2O$	$CoL_2 \cdot 4H_2O$	$NiL_2 \cdot 4H_2O$	$CuL_2 \cdot H_2O$	$ZnL_2 \cdot 2H_2O$
ν_{OH}	–	3160	3432	3420	3444	3128
$\nu_{as}(O–CH_3)$	2940	2940	2940	2940	2936	2940
$\nu_s(O–CH_3)$	2840	2840	2832	2832	2836	2840
$\nu(COOH)$	1720	–	–	–	–	–
$\delta(H_2O)$	–	1712	–	1712	1712	1684
ν_{Ar}	1582	1592		1576		1592
$\nu_{as}(COO^-)$	–	1516	1580	1516	1588	1516
$\delta(CH_2)$	1468	1468	1464	1464	1468	1468
$\delta(CH_2)$	1448	1424	1424	1424	1452	1444
$\nu_s(COO^-)$	–	1344	1384	1388	1408	1344
$\nu_{as}(C–O–C)$	1148	1192	1156	1156	1156	1160
$\nu_s(C–O–C)$	1024	1024	1024	1024	1024	1028
δ_{CH}	964	960	964	960	964	964
δ_{CH}	896	928	904	908	916	928
ν_{Ar}	800	788	816	816	804	788
δ_{CH}	764	764	760	760	764	764
δ_{CH}	692	732	708	712	716	732
ν_{Ar}	604	612	612	616	612	608
$\nu(M–O)$	–	552	556	452	468	552
$\nu(C–C)$	336	388	386	364	–	356

[a] Bands of CH_2 in plane scissoring vibrations $\delta(CH_2)$, bands of $C–C_{Ar}$ asymmetric valence vibrations of the aromatic ring, ν_{Ar}, bands of O–H bending vibrations ν_{OH} bands of C–O stretching vibrations [ν(C–O)], bands of O–C–O asymmetric deformation vibrations ν_{as}(O–C–O), bands of O–C–O symmetric deformation vibrations ν_s(O–C–O).

$(SCN)_4]$ with magnetic susceptibility assumed to be 1.644×10^{-5} cm^3/g. The measurements were made at a magnetic field strength of 9.9 kOe. Correction for diamagnetism of the constituent atoms was calculated using Pascal's constants [15].

The effective magnetic moment values were calculated from Eq. (1):

$$\mu_{eff} = 2.83(\chi_m T)^{1/2}, \quad (1)$$

where μ_{eff} is an effective magnetic moment, χ_m is a magnetic susceptibility per molecule and T is an absolute temperature.

Measurements in the range of 4–300 K were carried out on a Quantum Design SQUID–VSM magnetometer. The superconducting agent was generally operated at the field strength ranging from 0 to 7 T. Measurements of samples were made at magnetic field 0–1 T. A SQUID magnetometer was calibrated with the palladium rod sample.

RESULTS AND DISCUSSION

3,4-Dimethoxyphenylacetates of selected transition metal ions are coloured crystalline compounds [16, 17] of general formula: $ML_2 \cdot nH_2O$, where $L = C_{10}H_{11}O_4$, M(II) = Mn, Co, Ni, Cu, Zn, n = 1, 2 or 4, depending on M(II) ions.

IR spectra. 3,4-Dimethoxyphenylacetates of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) exhibited similar solid state IR spectral data (Table 1). The characteristic band of stretching vibrations of free carboxylic acid at 1720 cm^{-1} was not recorded in IR spectra of the complexes. Split into two peaks of asymmetric and symmetric vibrations bands of the COO^{-} group at 1588–1516 and 1408–1344 cm^{-1}, respectively, was recorded. The magnitudes of separations, $\Delta\nu_{OCO}$, between the frequencies assigned to ν_{asOCO} and ν_{sOCO} in the spectra of analysed compounds indicated that the carboxylate group acted as the bidentate chelating or bridging ligand [18–22]. Taking in account the Nakamoto criterion, magnitude of separation, $\Delta\nu_{OCO}$, of investtigated compounds and its sodium salt ($\Delta\nu_{OCO}$ = 1576–1384 = 192 cm^{-1}) indicated that the carboxylate group acted as the bidentate chelating in the cases of Mn(II) ($\Delta\nu_{OCO}$ = 172 cm^{-1}), Ni(II) ($\Delta\nu_{OCO}$ = 188 cm^{-1}), Cu(II) ($\Delta\nu_{OCO}$ = 180 cm^{-1}), and Zn(II) ($\Delta\nu_{OCO}$ = 172 cm^{-1}) complexes or, probably, bidentate bridging one in Co(II) compound ($\Delta\nu_{OCO}$ = 196 cm^{-1}).

With reference to the Manhas criterion, the carboxylate group of Ni(II) 3,4-dimethoxyphenylacetate acted as the bidentate chelating because the shifts of ν_{asOCO} and ν_{sOCO} bands were lower and higher (Table 1), respectively, compared to the bands recorded for the sodium salt. The carboxylate groups in Co(II) and Cu(II) compounds were bidentate bridging because the bands of ν_{asOCO} and ν_{sOCO} in the FT-IR spectra were shifted to higher wavenumbers or stayed in the same position compared with those for the sodium salt [19, 21].

The bands in the range of 3444–3128 cm^{-1} were characteristic for the OH group stretching vibrations and confirmed the presence of crystallization water molecules in the complexes [23, 24]. The bands at 556–452 cm^{-1} indicated the metal ion–oxygen stretching bond vibrations [25–31]. The separations of the ν_{asOCO} and ν_{sOCO} modes ($\Delta\nu_{OCO} = \nu_{asOCO} - \nu_{sOCO}$) could serve as the criterion for evaluation of nature of the metal–oxygen bond. The values for Mn(II), Ni(II), Cu(II), and Zn(II) complexes were smaller ($\Delta\nu_{OCO}$ = 188 – 172 cm^{-1}) than those of sodium salts ($\Delta\nu_{OCO}$ = 1576 – 1384 = 192 cm^{-1}) that indicated the lower degree of ionic character of the M–O bonds in the products compared to those of the corresponding sodium salts.

X-Ray powder diffraction. X-Ray powder diffraction of 3,4-dimethoxyphenylacetates of selected transition metal ions indicated those as crystalline compounds (Fig. 2). Attempts to grow single crystals suitable for X-ray experiments in various solvents (H_2O, alcohols, DMSO, DMF, and acetonitrile) were unsuccessful. Estimation of the unit cell parameters was carried out by applying the Dicvol 06 programme (Table 2) [32] using the X-ray powder diffraction data. According to the obtained results all analyzed complexes formed low symmetry compounds. 3,4-Dimethoxyphenylacetates of Mn(II) and Cu(II) crystallized in a triclinic system [32, 33] (Fig. 2).

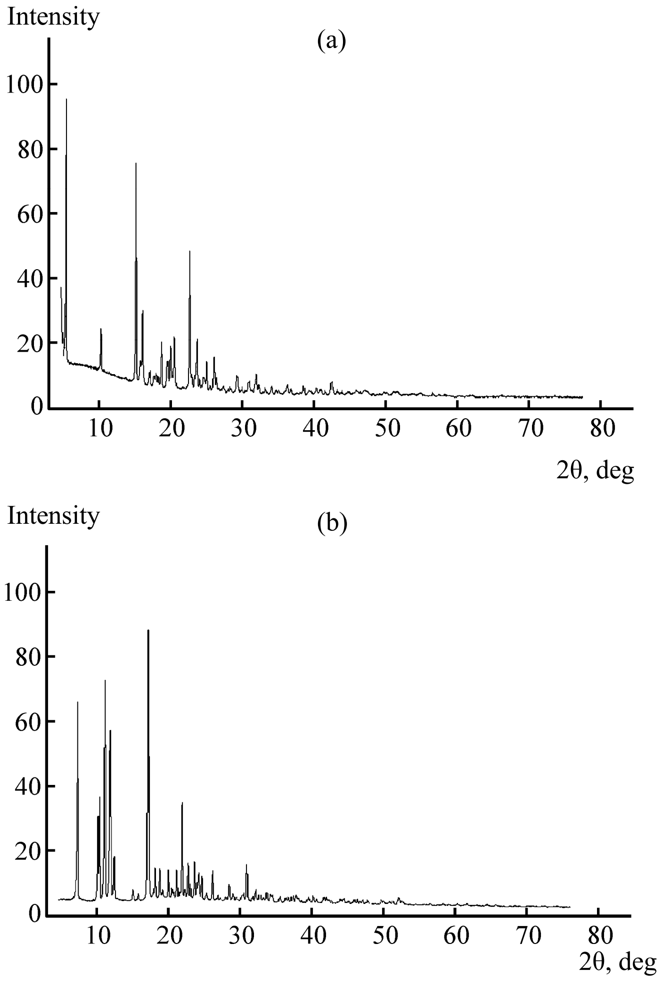


Fig. 2. X-ray diffractograms for (a) Mn(II) and (b) Ni(II) 3,4-dimethoxyphenylacetates.

Thermal analysis. Thermal stability of 3,4-dimethoxyphenylacetates was studied in the air in the range of 293–1173 K (Table 3). The TG, DTG, and DSC curves were recorded using the DSC/TG technique.

Upon heating to 1173 K the complex of Mn(II) dehydrated in one step (318–393 K) losing two molecules of water. The process of dehydration was related with the endothermic effect (DSC curve). The anhydrous compound above 650 K gradually decomposed to the mixture of Mn_2O_3 (23%) with Mn_3O_4 (77%) via the intermediate formation of Mn_2OCO_3 (610 K). The final product of decomposition was confirmed by X-ray diffraction patterns (Fig. 3). The

Table 2. Data of unit cell parameters (α, β, γ, *a, b, c*, and *V*) determined for analyzed 3,4-dimethoxyphenylacetates with the use of the Dicvol 06 program, (L = $C_{10}H_{11}O_4$)

Parameter	$MnL_2 \cdot 2H_2O$	$CoL_2 \cdot 4H_2O$	$NiL_2 \cdot 4H_2O$	$CuL_2 \cdot H_2O$	$ZnL_2 \cdot 2H_2O$
a, Å	17.8005	14.7220	7.2244	18.4081	17.9993
b, Å	5.8042	15.7820	15.7521	15.8125	5.8355
c, Å	5.5059	6.0447	14.9726	13.1073	16.1739
α, deg	106.106	90	90	74.508	90
β, deg	93.435	91.040	107.620	96.776	108.111
γ, deg	96.672	90	90	106.448	90
V, Å^3	540.30	1404.21	1679.23	3522.47	1614.65

Table 3. Temperature ranges of thermal stability for analyzed complexes in the air at 293–1173 K and their dehydration process, and enthalpy values[a]

Complex[b]	ΔT_1, K	Mass loss, %		n	ΔT_2, K	Mass loss, %		Residue mass, %		T_K, K	ΔH, kJ/mol	ΔH^0, kJ/mol
		calculated	found			calculated	found	calculated	found			
$MnL_2 \cdot 2H_2O$	318–393	6.54	5.64	2	403–683	90.05	89.89	9.95	10.11	698	46.06	23.03
$CoL_2 \cdot 4H_2O$	310–387	13.82	13.89	4	395–693	89.76	89.62	10.24	10.38	723	69.64	17.41
$NiL_2 \cdot 4H_2O$	310–413	13.83	12.87	4	418–698	87.97	88.34	12.03	11.66	723	109.88	27.47
$CuL_2 \cdot H_2O$	313–383	3.82	3.46	1	389–760	89.33	89.90	10.67	10.10	773	34.84	34.84
$ZnL_2 \cdot 2H_2O$	313–403	7.33	7.34	2	412–848	83.46	86.64	16.54	13.36	773	67.14	33.57

[a] (ΔT_1) temperature range of dehydration process, (n) number of water molecules lost in one step, (ΔT_2) temperature range of anhydrous complex decomposition, (T_K) final temperature of decomposition process, (ΔH^0) enthalpy value for one molecule of water.

[b] L = $C_{10}H_{11}O_4$.

oxidation process was related with the exothermic effect recorded on the DSC curve.

Tetrahydrate of Co(II) 3,4-dimethoxyphenylacetate in the course of heating dehydrated in one step in the range of 310–387 K (Fig. 4). Anhydrous Co(II) 3,4-dimethoxyphenylacetate upon heating in the range of 395–693 K gave the mixture of 33% of CoO + 67% of Co_3O_4 (above 600 K) (Fig. 3**)** with the transitional formation of Co_2OCO_3 at 543 K.

3,4-Dimethoxyphenylacetate of Ni(II) dehydrated at 310–413 K losing four molecules of water. The anhydrous complex gave finally NiO (418–698 K) via formation of the intermediate product Ni_2OCO_3 (583 K). The final residue of decomposition was identified by X-ray analysis. Above 723 K the TG curve reached a plateau indicating the end of decomposition process.

In the course of heating to 1173 K the complex of 3,4-dimethoxyphenylacetate with Cu(II) endothermically dehydrated at 313–383 K. The anhydrous compound at 389–760 K decomposed to CuO with the transitional formation of Cu_2OCO_3 (583 K). The final product of decomposition was identified roentgenographically (Fig. 3).

The dihydrate of Zn(II) 3,4-dimethoxyphenylacetate lost two molecules of water (313–403 K) and formed the anhydrous complex (Fig. 5). The dehydration process was accompanied by an endothermic effect (DSC curve). The small endothermic peak recorded at 443 K could be the result of the polymorphic change or melting process that occurred during heating of complex. The anhydrous Zn(II) compound at 412–848 K was ultimately decomposed to ZnO (the TG curve above 773 K reaches a plateau).

Energy effects accompanying the dehydration processes were also determined. Enthalpy values, Δ*H*, changed from 34.84 to 109.88 kJ/mol and from 17.41 to 34.84 kJ/mol per one molecule of water. The values

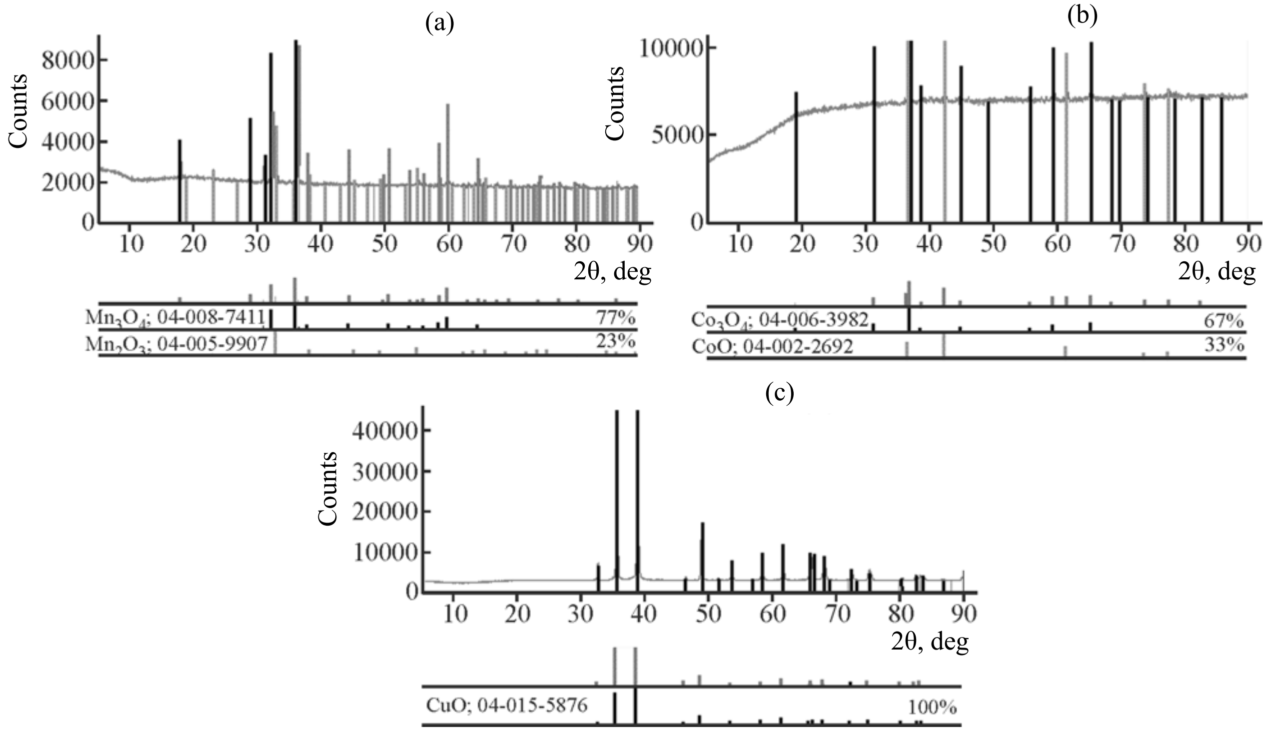


Fig. 3. X-Ray powder diffractograms of the final products of decomposition for (a) Mn(II), (b) Co(II), and (c) Cu(II) complexes.

could indicate that the water molecules were coordinated to a central ion with different strengths depending on their positions in the complex coordination spheres.

The water molecules in the analyzed 3,4-dimethoxyphenylacetates could be lattice or coordinated despite their loss at a low temperature [34–37]. The fact that the loss of water molecule proceeded in one step and at low temperature led us to conclusion that water could be in the outer sphere. However, if it acted as coordinated water being weekly bounded with central ion, its initial dehydration value could be also small.

TG-FT-IR analysis. The TG-FT-IR coupled technique was applied for analysis of complexes for identifying their gaseous decomposition products. For example, FT-IR spectra of volatile components evolved during the destruction of 3,4-dimethoxyphenylacetate of Ni(II) is presented in Fig. 6. Its analysis revealed that the molecules of H_2O, CO_2, CO, and hydrocarbons were released during heating of the

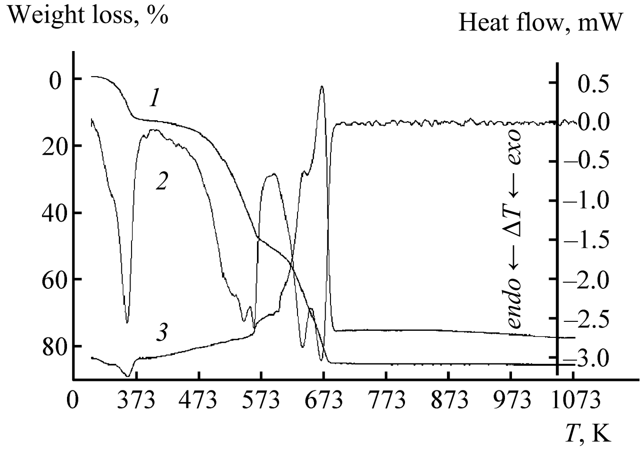


Fig. 4. (*1*) TG, (*2*) DTG, and (*3*) DSC curves for Co(II) 3,4-dimethoxyphenylacetate.

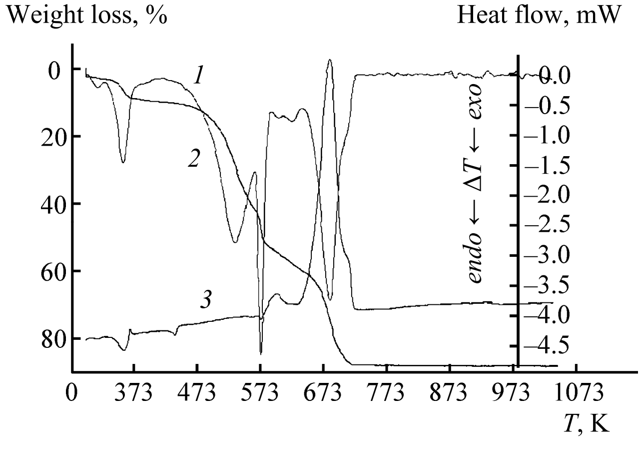


Fig. 5. (*1*) TG, (*2*) DTG, and (*3*) DSC curves for Zn(II) 3,4-dimethoxyphenylacetate.

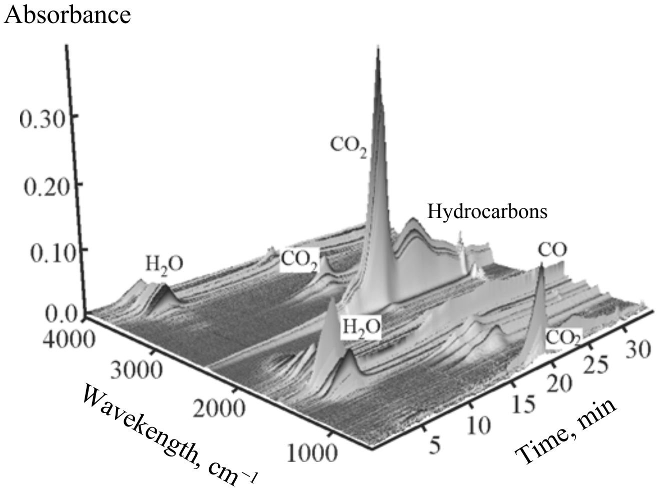


Fig. 6. FT-IR spectrum of gaseous products evolved during the decomposition of Ni(II) 3,4-dimethoxyphenylacetate.

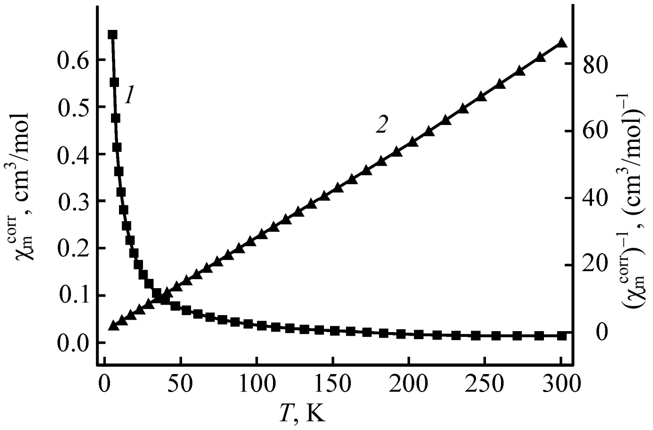


Fig. 7. Dependence of (*1*) χ_m^{corr} and (*2*) $(\chi_m^{corr})^{-1}$ values vs *T* for Mn(II) complex.

complex to 1173 K [18, 20, 25, 28, 30, 31]. At first, after 5 minutes of decomposition the molecules of water were lost in one step (338–406 K) which was confirmed by characteristic bands in the FT-IR spectrum in the regions of 3900–3750 and 1580–1350 cm^{-1}, that corresponded to stretching and deforma-tion vibrations, respectively, of the OH groups of water molecules [38]. The mass loss calculated from TG curve was equal to 13.75% (calculated 13.83%). At higher temperature, after 20 minutes of the anhydride decomposition, CO_2 and other gases began to evolve. Active liberation of CO_2 was observe in the range of 573–700 K as indicated by FTIR spectra in the ranges of 3800–3500, 2450–2400, and ca 700 cm^{-1}.

Magnetic properties. For determining the nature of metal to ligand bonding in analyzed complexes and the surrounding of coordination ions the magnetic susceptibility of Mn(II), Co(II), Ni(II), and Cu(II) compounds was measured in the temperature range of 76–303 K. The magnetic susceptibility for Mn(II) and Co(II) of 3,4-dimethoxyphenylacetates was also investigated between 4 and 300 K for determining whether the nature of atomic magnetic interactions was changed at low temperatures. The effective magnetic moment values experimentally determined in the range of 76–303 K changed from: 5.43 to 5.61 μ_B for Mn(II), 4.30 to 4.63 μ_B for Co(II), 2.76 to 2.84 μ_B for Ni(II), and 0.4, to 1.27 μ_B for Cu(II) complexes while those at 4–300 K varied from: 4.59 to 5.28 μ_B for Mn(II) and 3.75 to 4.67 μ_B for Co(II) of 3,4-dimethoxyphenylacetates. All analyzed compounds demonstrated paramagnetic properties and Mn(II), Co(II), and Ni(II) complexes obeyed the Curie–Weiss law since their magnetic susceptibility values decreased with increased temperature [39–44]. The dependences of magnetic susceptibility and its reciprocal values and also $\chi_m^{corr}T$ worths as a function of temperature for Mn(II), Co(II) and Cu(II) complexes are presented in Figs. 7–9. Magnetic moment values experimentally determined at 76–303 K and 4–300 K for described 3,4-dimethoxyphenylacetates seemed close to spin only values for the respective ions calculated from the equation: $\mu_{eff} = [4s(s + 1)]^{1/2}$, ($s = n/2$), in the absence of magnetic interactions for the present spin-system. These theoretical values calculated at room temperature for Mn(II), Co(II), Ni(II), and Cu(II) ions were equal to 5.9, 3.88, 2.83, and 1.73 μ_B, respectively.

The presented data indicated that there was no significant orbital contribution to the magnetic moments of the complexes [spin only for complexes of Mn(II) and Ni(II)], whereas its contribution was essential in case of complex of Co(II).

Values of μ_{eff} = 5.43–5.61 μ_B for Mn(II) 3,4-dimethoxyphenylacetate suggested that it was a high-spin compound with weak ligand field [39, 40, 44]. In the coordination sphere of Mn(II) ion there were probably two molecules of water and two carboxylate bidentate chelating groups (coordination number was probably equal to 6). This was confirmed by the IR spectroscopic data.

Magnetic properties of Mn(II) and Co(II) complexes were studied over the temperature range of 4–

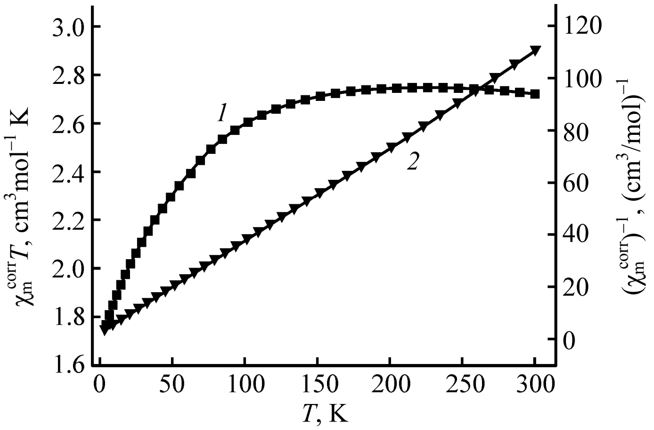


Fig. 8. Dependence of $\chi_m^{corr}T$ and $(\chi_m^{corr})^{-1}$ values vs T for Co(II) complex.

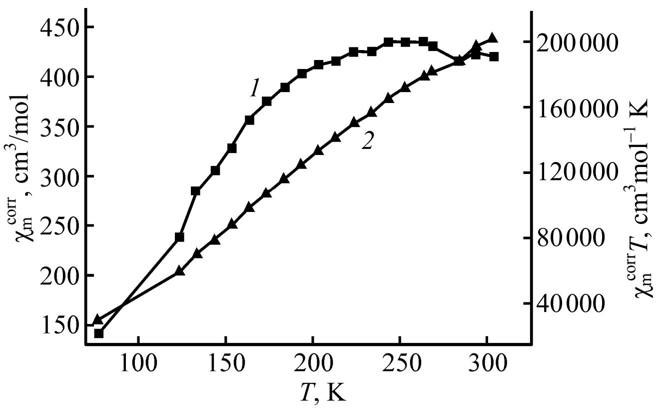


Fig. 9. Relationship of χ_m^{corr} and $\chi_m^{corr}T$ vs T for Cu(II) complex.

300 K. Plots of corrected molar magnetic susceptibility χ_m^{corr} and its reciprocal values versus T for Mn(II) complex (Fig. 7) demonstrated that the complex obeyed the Curie–Weiss law over the whole temperature range. According to the shape of χ_m^{corr} vs T curve it decreased with temperature rising in the range of 4–299 K. Between 4–50 K the χ_m^{corr} values decreased rapidly, changing their values from 0.6540 to 0.0709 cm^3/mol, while at 51.01–299 K they decreased slowly reaching the saturation paramagnetic state and gaining values of 0.0699 and 0.0116 cm^3/mol, respectively. The magnetic moment values of this complex changed from 4.59 to 5.37 μ_B in the range of 4.03 to 101.27 K and from 5.36 to 5.28 μ_B at 103.045–299.9 K. This could be due to the ferromagnetic and antiferromagnetic intermolecular interactions that indicated changes in the unpaired electrons order. On cooling in the range of 101.27 to 4.03 K the values of magnetic moments decreased due to antiferromagnetic inter-molecular interactions.

According to the Gouy's method the effective magnetic moment values calculated for the Co(II) complex were equal to 4.30–4.63 μ_B and their values determined by the SQUID method changed from 3.75 to 4.67 μ_B being higher than the spin–only worth that resulted from a spin–orbital coupling. The values could indicate that it was a complex with tetrahedral structure [39, 40, 44]. In the coordination sphere of Co(II) ion there were probably molecules of water and the bidentate bridging carboxylate group. Such character of carboxylate groups was also confirmed by the IR spectrum of the complex.

The relationship between $\chi_m^{corr}T$ and $(\chi_m^{corr})^{-1}$ and T values for Co(II) complex is shown in Fig. 8. From the $\chi_m^{corr}T$ vs T curve it appeared that the $\chi_m^{corr}T$ values decreased from 2.7297 to 1.7563 cm^3 mol^{-1} K at 289.88–4.03 K. In the range of 289.88–101.27 K they diminished very slowly showing the saturation paramagnetic state, while their radical decreased from 2.6031 to 1.7563 cm^3 mol^{-1} K was observed at 101.27–4.03 K. This drastic decrease indicated a negative θ value, hence, the antiferromagnetic intermolecular interactions. Therefore, the magnetic moment value of Co(II) complex was equal to 3.75 μ_B (4.03 K) and 4.57 μ_B (101.27 K). This parameter increased to 4.68 μ_B at 289.88 K.

For Ni(II) ion complex the magnetic moments were lower than the spin–only value and changed from 2.76 μ_B (76 K) to 2.84 μ_B (303 K). This was due to the fact that the vectors L and S were aligned with the strong field of the heavy atom in opposite directions and this diminished the resultanting magnetic moment. The ground state configuration of Ni(II) ion in a regular octahedral field was $^3A_{2g}(t_{2g}{}^6e_g{}^2)$ typical for paramagnetic structures with two unpaired electrons. The contribution to the magnetic susceptibility was presented by a spin-only term, second order spin–orbital coupling and the temperature independent paramagnetism. The experimental data suggested that Ni(II) compound seemed to be the high–spin complex with octahedral symmetry around central ion and the weak ligand field [39, 40, 44]. This indicated that in the solid state Ni(II) compound existed with two molecules of water and probably with two bidentate carboxylate groups coordinated to the cation. The IR spectrum of this complex revealed that the carboxylate groups were in fact bidentate chelating ones.

The magnetic susceptibility values of 3,4-dimethoxyphenylacetate of Cu(II) increased with rising temperatures in the range of 76–250 K, suggesting a weak antiferromagnetic interaction. The experimental magnetic moment values changed from 0.49 (at 76 K) to 1.27 μ_B (at 303 K) that were lower than the spin-only magnetic moment $\mu_{eff} = 1.73$ μ_B. Such dependence was a typical for copper dimer (Fig. 9) [45, 46].

According to the Manhas criterion, the carboxylate group acted in this complex as bidentate bridging which was confirmed by IR spectrum of this compound. The magnetic moment values of Cu(II) 3,4-dimethoxyphenylacetate decreased from 1.27 μ_B at 303 K to 0.49 μ_B at 76 K, as a consequence of depopulation of the excited triplet ($S = 1$) state. It is well-known that the interaction between two $S = 1/2$ metal atoms in a dimer leads to two molecular states: a spin singlet ($S = 0$) and a triplet ($S = 1$) separated by $2J$. The interaction would be antiferromagnetic ($J < 0$), if $S = 0$ was the ground state; on the contrary, if $S = 1$, the interaction would be ferromagnetic ($J > 0$).

The bidentate bridging coordination of carboxylate group in Cu(II) complex was confirmed by the Manhas criterion, whereas the Nakamoto criterion, based on the separation between the stretching modes of the carboxylate group, indicated its bidentate chelating mode. The violation of the Nakamoto and the Manhas rules could result from involvement of oxygen atoms of the carboxylate groups in hydrogen bonding with water molecules [47].

In 3,4-dimethoxyphenylacetates of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) the coordination number values could change from 4 to 6 depending on the dentate of the carboxylate group, kind of central ions and the position of water molecules in the complex sphere. For the ions under study they could be established on the basis of the complete crystal structure determination of monocrystals that have not been obtained so far.

CONCLUSIONS

3,4-Dimethoxyphenylacetates of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) were characterized by elemental analysis, thermal stability in the air, IR spectra, X-ray powder study and magnetic properties. According to the obtained data, the selected transition metal 3,4-dimethoxyphenylacetates were prepared as mono-, di- and tetrahydrates. The carboxylate groups act as bidentate chelating or bridging ligands. The compounds crystallize in monoclinic or triclinic systems. On heating in the air to 1173 K they decompose in three steps. At first they dehydrate to form anhydrous complexes, that are further decomposed to the oxides of the corresponding Metals(II) or the mixtures of their oxides with the intermediate formation of oxycarbonates of those metals [except Zn(II) complex]. The enthalpy values of dehydration processes were in the range of 34.84 to 109.88 kJ/mol and 17.41 to 36.63 kJ/mol per one molecule of water. The dominating volatile products of thermal decomposition of complexes are: water, carbon oxides and hydrocarbons. The complexes of Mn(II), Co(II) and Ni(II) with 3,4-dimethoxyphenylacetic acid anion obey the Curie–Weiss law, since the values of their magnetic susceptibility decrease with rising temperature. The obtained μ_{eff} values for Mn(II) and Ni(II) complexes suggest that they are high-spin complexes with octahedral coordination and with the weak ligand fields. The magnetic susceptibility of Cu(II) compound increases with rising temperature and the magnetic moments values indicate it as a dimer. The effective magnetic moment values found for the Co(II) complex indicate that it may be a complex with the tetrahedral structure.

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