Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 2, 377–383

THERMAL, SPECTRAL AND MAGNETIC BEHAVIOUR OF 2,3,4-TRIMETHOXYBENZOATES OF Mn(II), Co(II), Ni(II) AND Cu(II)

Wiesława Ferenc[1*], *Beata Bocian*[1] *and J. Sarzyński*[2]

[1]Faculty of Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Poland
[2]Institute of Physics, Maria Curie-Skłodowska University, 20-031 Lublin, Poland

Four new complexes of 2,3,4-trimethoxybenzoic acid anion with manganese(II), cobalt(II), nickel(II) and copper(II) cations were synthesized, analysed and characterized by standard chemical and physical methods. 2,3,4-Trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) are polycrystalline compounds with colours typical for M(II) ions. The carboxylate group in the anhydrous complexes of Mn(II), Co(II) and Ni(II) is monodentate and in that of Cu(II) monohydrate is bidentate bridging one. The anhydrous complexes of Mn(II), Co(II) and Ni(II) heated in air to 1273 K are stable up to 505–517 K. Next in the range of 505–1205 K they decompose to the following oxides: Mn_3O_4, CoO, NiO. The complex of Cu(II) is stable up to 390 K, and next in the range of 390–443 K it loses one molecule of water. The final product of its decomposition is CuO. The solubility in water at 293 K is of the order of 10^{-3} mol dm^{-3} for the Mn(II) complex and 10^{-4} mol dm^{-3} for Co(II), Ni(II) and Cu(II) complexes. The magnetic moment values of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions in 2,3,4-trimethoxybenzoates experimentally determined in the range of 77–300 K change from 5.64–6.57 μ_B (for Mn^{2+}), 4.73–5.17 μ_B (for Co^{2+}), 3.26–3.35 μ_B (for Ni^{2+}) and 0.27–1.42 μ_B (for Cu^{2+}). 2,3,4-Trimethoxybenzoates of Mn(II), Co(II) and Ni(II) follow the Curie–Weiss law, whereas that of Cu(II) forms a dimer.

Keywords: *complexes of Mn(II), Co(II), Ni(II), Cu(II), IR spectra, magnetic moments, thermal stability, 2,3,4-trimethoxybenzoates*

Introduction

2,3,4-Trimethoxybenzoic acid having formula $(CH_3O)_3C_6H_2CO_2H$ is a white crystalline solid, sparingly soluble in cold water. Its solubility in water increases with the rise of temperature [1]. Recently, we have synthesized 2,3,4-trimethoxybenzoates of lanthanides(III) and yttrium(III) and investigated some of their physico-chemical properties [2–10]. In order to study more intensely the properties of 2,3,4-trimethoxybenzoates of trivalent and divalent metal ions, as a continuation of our earlier work, four new complexes of general formula $M(C_{10}H_{11}O_5)_2{\cdot}nH_2O$ (where *M*=Mn, Co, Ni and Cu and *n*=1 for Cu(II)) have been prepared and examined.

Physico-chemical properties of these new coordination compounds were characterized by thermal stability in air during heating to 1273 K, IR spectral data, X-ray powder investigations, solubility in water at room temperature and magnetic properties. Thermal stability investigations give information about the mechanism of complex decomposition and the endo- or exo-effects connected with such processes as: dehydration, melting, polymorphic changes, crystallization, oxidation or reduction. The magnetic properties of obtained complexes of Mn(II), Co(II), Ni(II) and Cu(II) were investigated in the range of 77–300 K in order to study the kind of coordination of central ions and the nature of bonding between central ions and ligands. If the effective magnetic moment μ_{eff} is known, the number of unpaired electrons can be calculated. This may also give information on the oxidation state of the metal ion or the central atom of a complex, on the electron configuration and, hence, on the nature of the bonding between the metal and the ligands. 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 of the central atom is determined by its oxidation state on the ligand-field strength. The determination of the number of unpaired electrons of the central atom allows establishing whether the complex investigated is of low or high spin and whether the ligand field is strong or weak.

Experimental

Sample preparation

The complexes of the 2,3,4-trimethoxybenzoic acid anion with cations of Mn(II), Co(II), Ni(II) and Cu(II) were obtained by the addition of equivalent quantities of 0.1 M ammonium 2,3,4-trimethoxybenzoate (pH≈5)

* Author for correspondence: wetafer@hermes.umcs.lublin.pl

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

to a hot solution containing the nitrates(V) of these metal ions and crystallizing at 293 K. The solids were filtered off, washed with hot water and ethanol to remove ammonium ions and dried at 303 K.

Analytical techniques used

The C, H analysis was performed using a CHN 2400 Perkin-Elmer analyser.

The IR spectra of complexes were recorded over the range 4000–400 cm^{-1} using M-80 spectrophotometer (Carl-Zeiss, Jena). Samples for IR spectra measurements were prepared as KBr discs.

The X-ray powder diffraction were taken on a HZG-4 (Carl Zeiss-Jena) diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range 2θ=4–80° by means the Debye–Scherrer–Hull method.

The thermal stability and decomposition of the complexes were studied in air using a Setsys 16/18 TG, DTA instrument. The experiments were carried out under air flow in the temperature range of 297–1273 K. Samples ranging between 6.76 and 8.44 mg were heated in Al_2O_3 crucibles.

Magnetic susceptibilities of polycrystalline samples of 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) were investigated in the temperature range of 76–303 K. The measurements were carried out using the Gouy method. Mass changes were obtained from Cahn RM-2 electrobalance. The calibrant employed was $Co[Hg(SCN)_4]$ for which the magnetic susceptibility was assumed to be $1.644 \cdot 10^{-5}$ cm^{-3} g^{-1}. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [11, 12]. Magnetic moments were calculated according to Eqs (1) and (2).

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

$$\mu_{eff}=2.83[\chi_M (T-\theta)]^{1/2} \quad (2)$$

where θ is the Weiss constant.

Solubility of Mn(II), Co(II), Ni(II) and Cu(II) complexes in water was measured at 293 K. Saturated solutions of the obtained compounds were prepared under isothermal conditions. The contents of Mn(II), Co(II), Ni(II) and Cu(II) were determined by using ASA 880 spectrophotometer (Varian).

Results and discussion

2,3,4-Trimethoxybenzoates of manganese(II), cobalt(II), nickel(II) and copper(II) were obtained as polycrystalline solids with a metal ion to ligand ratio of 1:2 (Table 1) and a general formula $M(C_{10}H_{11}O_5)_2 \cdot nH_2O$ (where *M*=Mn, Co, Ni, Cu and *n*=1 for Cu) Their colours are typical for the corresponding divalent ions (Mn(II)-slightly pink, Co(II)-pink, Ni(II)-green, Cu(II)-blue).

Some of the results of IR spectra analysis are presented in Table 2. The infrared spectrum of 2,3,4-trimethoxybenzoic acid shows the following absorption bands: a strong band of COOH at 1680 cm^{-1}, the bands assigned to asymmetric and symmetric vibrations of the OCH_3 groups occurring at 2944 and 2840 cm^{-1}, respectively. The bands of ring vibrations appear at 1592,

Table 1 Elemental analysis data of Mn(II)-, Co(II)-, Ni(II)- and Cu(II)-2,3,4-trimethoxybenzoates

Complex $L=C_{10}H_{11}O_5^-$	H/%		C/%		*M*/%	
	calcd.	found	calcd.	found	calcd.	found
ML_2	4.61	4.62	50.28	50.32	11.50	14.34
CoL_2	4.57	4.56	49.86	49.69	12.24	13.47
NiL_2	4.57	4.57	49.89	49.50	12.20	12.28
$CuL_2 \cdot H_2O$	4.76	4.78	47.63	47.77	12.62	12.78

Table 2 Wavenumbers (cm^{-1}) of COO^- bands in 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II), in sodium salt of ligand and the COOH band in 2,3,4-trimethoxybenzoic acid

Complex $L=C_{10}H_{11}O_5^-$	ν(C=O)	$\nu_{as(COO^-)}$	$\nu_{s(COO^-)}$	$\Delta\nu_{COO^-}$
ML_2	–	1620	1380	240
CoL_2	–	1628	1370	258
	–	1620		250
NiL_2	–	1628	1370	258
$CuL_2 \cdot H_2O$	–	1560	1400	160
HL	1680	–	–	–
NaL	–	1610	1390	220

1500–1420, 1176 and 1020 cm^{-1} and the bands of C–H deformation vibrations, δ(C–H), are observed in the region 1144–1100 cm^{-1}. The –C–O–C– symmetric vibration bands, ν_s(COC), occur at 1020–1035 cm^{-1}. The bands observed at 940–650 cm^{-1} are associated with out-of-plane deformation ring vibrations, φ(CC), and the C–H wagging vibrations, γ(C–H). The bands at 830–800 cm^{-1} have been assigned to the γ(C–H) vibrations (in 1,2,3,4 substituted ring) [2–4, 13–25].

In the IR spectra of 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) the band at 1680 cm^{-1} disappears, which indicates that COOH group is not present in the analysed complexes. In their spectra there are two bands arising from asymmetric and symmetric vibrations of the COO^- group occurring at 1628–1560 and 1400–1370 cm^{-1}, respectively. The bands assigned to asymmetric and symmetric vibrations of the OCH_3 groups, $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$, are observed at the 2944–2936 and 2840 cm^{-1}, respectively. The bands of ν(C=C) ring vibrations appear at 1600, 1568, 1500–1404, 1290, 1100 cm^{-1}. The symmetric vibration of –C–O–C– group bands, ν_s(COC), occur at 1032–1028 cm^{-1}. The bands observed at 940–650 cm^{-1} are associated to out-of-plane deformation ring vibration, φ(CC), and out-of-plane C–H bond vibrations, γ(C–H). The bands at 800 cm^{-1} have been assigned to the γ(C–H) vibrations (in 1,2,3,4 substituted ring). The weak band at 420 cm^{-1} results from ν(M–O) stretching vibration [2–4, 13–25]. Table 2 presents the maximum at frequencies for absorption bands of asymmetric and symmetric vibrations of the COO^- group for 2,3,4-trimethoxybenzoates of manganese(II), cobalt(II), nickel(II), copper(II) and sodium. The magnitudes of the separation, $\Delta\nu_{COO^-}$, between the frequency values of $\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}$ in complexes of Mn(II), Co(II), Ni(II) are higher ($\Delta\nu_{COO^-}$=258–240 cm^{-1}) and in the complex of Cu(II) are lower ($\Delta\nu_{COO^-}$=160 cm^{-1}) than in the sodium 2,3,4-trimethoxybenzoate ($\Delta\nu_{COO^-}$= 220 cm^{-1}). For 2,3,4-trimethoxybenzoates of Mn(II), Co(II) and Ni(II) the shifts of the frequencies of $\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}$ are higher and lower, respectively, than those for sodium 2,3,4-trimethoxybenzoate. Accordingly, the carboxylate ion in the analysed coordination compounds appears to be monodentate group. On the other hand, for the Cu(II) complex the shifts of the frequencies of $\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}$ are lower and higher, respectively, than those for the sodium salt. Therefore the carboxylate ion in this compound appears to be a bidentate, bridging group [25, 26].

In order to evaluate, if the 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) are crystalline or amorphous compounds, their X-ray powder diffraction measurements were carried out. The analysis of the diffractograms suggests that the obtained complexes are polycrystalline compounds (Fig. 1). The structures of the compounds of Mn(II), Co(II), Ni(II) and Cu(II) have not been determined, because single crystals have not been obtained.

In order to verify the compositions of the complexes, to determine the temperature ranges of their thermal stability and decomposition during heating in air, to estimate the intermediate and final products of their decomposition and to evaluate the type of processes that occur during heating, the thermal stability of 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II)

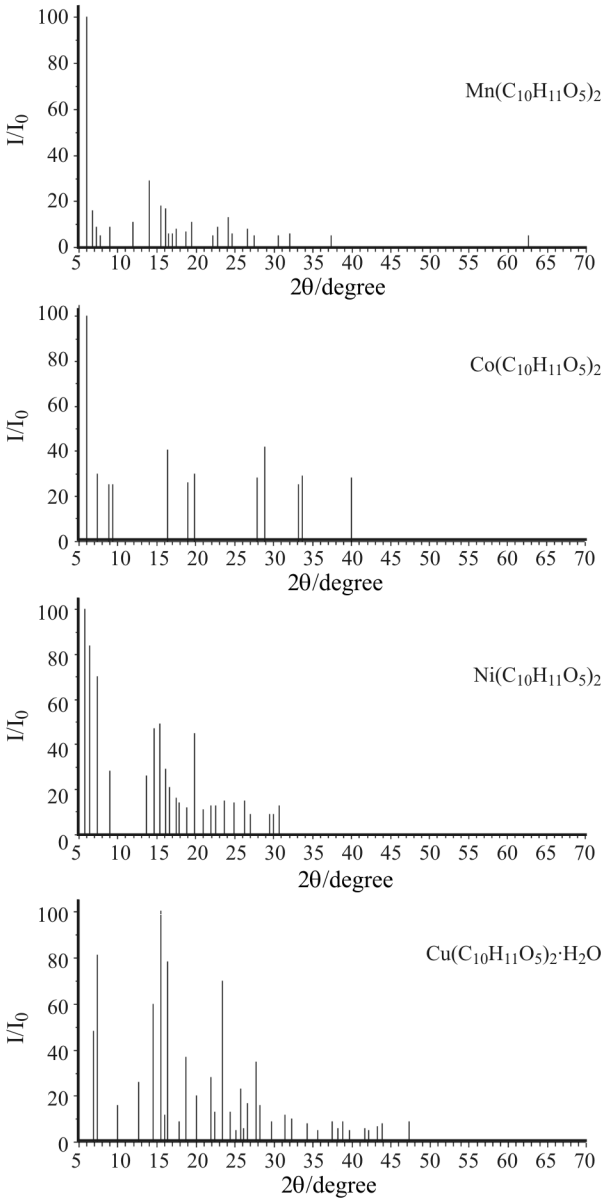

Fig. 1 Relationships between I/I_0 and 2θ for 2,3,4- trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II)

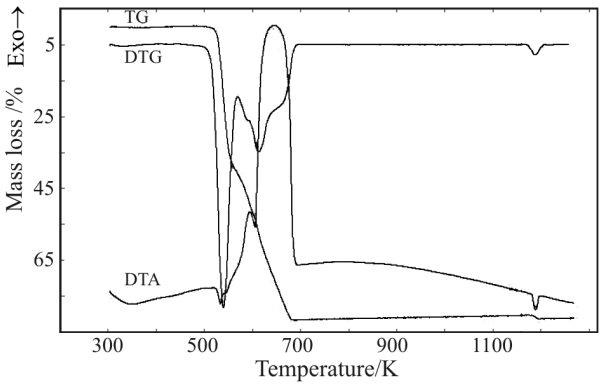

Fig. 2 TG and DTA curves of 2,3,4-trimethoxybenzoate of Co(II)

and Cu(II) was studied in the temperature range of 293–1273 K. Some results are presented in Table 3 and Fig. 2. The results reveal that the complexes of Mn(II), Co(II) and Ni(II) are anhydrous compounds, while that of Cu(II) is monohydrate. These results were also confirmed by the elemental analysis (Table 1) and the IR spectra. The anhydrous 2,3,4-trimethoxybenzoates of Mn(II), Co(II) and Ni(II) heated in air to 1273 K are stable up to 505–517 K. Having various stability, they decompose in the temperature range of 505–1205 K. The mass losses calculated from TG curves are equal to 80.1, 80.4 and 83.6%, respectively (the theoretical values are 84.0, 84.4 and 83.4%). The differences between calculated and theoretical values result from the apparatus errors. The combustion of the organic ligands is accompanied by strong exo-effect which can be seen in the DTA curve. 2,3,4-Trimethoxybenzoates of Mn(II) and Ni(II) decompose directly to the oxides: Mn_3O_4 and NiO, while the complex of Co(II) (Fig. 2) to CoO with intermediate formation of Co_3O_4. The process of Co_3O_4 reduction to CoO is connected with endo-effect to be seen in DTA curve [27–29]. The oxides of respective metals are the final products of the complex decompositions. The monohydrate of Cu(II) 2,3,4-trimethoxybenzoate is stable up to 390 K. Next, in the temperature range of 390–443 K being dehydrated it forms an anhydrous compound. The mass loss calculated from TG curve being equal to 3.5% corresponds to the loss of 1 molecule of crystallization water (theoretical value is 3.6%). The dehydration process is connected with an endothermic effect seen on DTA curve. In the temperature range of 443–813 K the anhydrous 2,3,4-trimethoxybenzoate of Cu(II) is being further decomposed to CuO.

The obtained results indicate that the thermal decomposition of 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) in air proceeds in the following steps:

$$Mn(C_{10}H_{11}O_5)_2 \xrightarrow{505-989\ K} Mn_3O_4$$

$$Co(C_{10}H_{11}O_5)_2 \xrightarrow{517-1168\ K} Co_3O_4 \xrightarrow{1168-1205\ K} CoO$$

$$Ni(C_{10}H_{11}O_5)_2 \xrightarrow{507-906\ K} NiO$$

$$Cu(C_{10}H_{11}O_5)_2\cdot H_2O \xrightarrow{390-443\ K} Cu(C_{10}H_{11}O_5)_2 \xrightarrow{443-813\ K} CuO$$

The solubility of 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) in water at 293 K was measured (Table 3). Its values amount to: $2.8\cdot10^{-3}$ mol dm^{-3} (for Mn(II) complex), $7.2\cdot10^{-4}$ mol dm^{-3} (for Co(II) complex), $7.5\cdot10^{-4}$ mol dm^{-3} (for Ni(II) complex) and $2.2\cdot10^{-4}$ mol dm^{-3} (for Cu(II) complex). The manganese(II) 2,3,4-trimethoxybenzoate is the most soluble salt while that of copper(II) is the least soluble one.

The magnetic susceptibility of the 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) was measured in the temperature range of 76–300 K (Table 4). The anhydrous 2,3,4-trimethoxybenzoates of Mn(II), Co(II) and Ni(II) follow the Curie-Weiss law, since the values of the magnetic susceptibility decrease with increasing temperature. The paramagnetic dependences of magnetic susceptibility values of the complexes as a function of temperatures are presented in Table 4 and those only for Co(II) 2,3,4-trimethoxybenzoate in Fig. 3. The effective magnetic moment values experimentally determined for 2,3,4-trimethoxybenzoates of Mn(II) and Ni(II) change from 5.64 (at 76 K) to 6.57 μ_B (at 303 K) and from 3.26 to 3.35 μ_B for those of two appropriate complexes, respectively. The experimental data reveal that the magnetic mo-

Table 3 Decomposition data for 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II) in air atmosphere and their solubility in water at 293 K

Complex L=$C_{10}H_{11}O_5^-$	ΔT_1/K	T_{max}/K	Mass loss/%		n	ΔT_2/K	Mass loss/%		Solubility/mol dm^{-3}
			calcd.	found			calcd.	found	
MnL_2	–	–	–	–	–	505–989	84.0	80.9	$2.8\cdot10^{-3}$
CoL_2	–	–	–	–	–	517–1205	84.4	80.4	$7.2\cdot10^{-4}$
NiL_2	–	–	–	–	–	507–906	83.4	83.6	$7.5\cdot10^{-4}$
$CuL_2\cdot H_2O$	390–443	413	3.6	3.5	1	443–813	84.2	84.0	$2.2\cdot10^{-4}$

ΔT_1 – temperature range of dehydration process; T_{max} – temperature of the maximum of the endothermic effect in the DTA curve; n – number of crystallization water molecules being lost in one endothermic step; ΔT_2 – temperature range of complex decomposition

ments of Ni^{2+} and Mn^{2+} ions in the complexes are connected with spin-only moments. Their theoretical values at room temperature are equal to 5.92 μ_B for the Mn^{2+} ion (d^5) and 2.83 μ_B for the Ni^{2+} ion (d^8), respectively. In the case of 2,3,4-trimethoxybenzoate of Co(II) the effective magnetic moments of cobalt ion determined in the range of 76–300 K are equal to 4.73–5.17 μ_B (Table 4, Fig. 3). The magnetic moment measured for the Co^{2+} ion is equal to 5.17 μ_B (at room temperature). This value differs from that of the spin-only moment which amounts to 3.88 μ_B. The relatively large difference between measured and calculated values results from a spin-orbital coupling [30, 31]. Figure 4 presents the χ_M^{-1} values with rising temperature for Co(II) 2,3,4-trimethoxybenzoate. The experimental data suggest that the Mn^{2+}, Co^{2+} and Ni^{2+} ions in the analysed complexes are in the high-spin state forming octahedral coordination and in weak field of ligands. The magnetic susceptibility of Cu^{2+} ions in 2,3,4-trimethoxybenzoate complex (Table 4) displays a minimum at 76 K (Fig. 5) and it increases reaching maximum at room temperature. Such dependence is a typical behaviour of copper dimers. The room temperature magnetic moment per Cu (μ_{eff}=1.42 μ_B) is similar to those observed for other dinuclear Cu(II) compounds [32–35] and is lower than the d^9 spin-only magnetic moment, μ_{eff}=1.73 μ_B. This observation is consistent with antiferromagnetic exchange between

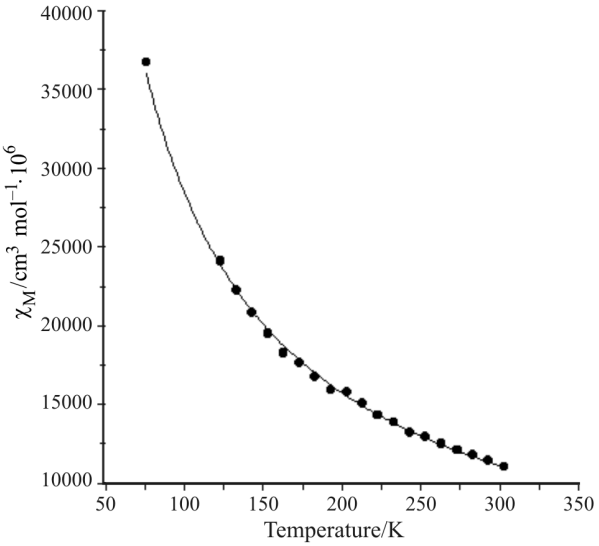

Fig. 3 Dependence of magnetic susceptibility values *vs.* temperature for 2,3,4-trimethoxybenzoate of Co(II)

Table 4 Values of μ_{eff} for 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Cu(II)

MnL_2			CoL_2			NiL_2			$CuL_2 \cdot H_2O$		
C=3.8·10^{-3}/K cm^3 g^{-1} θ=55/K			C=4.4·10^{-3}/K cm^3 g^{-1} θ=61/K			C=2.28·10^{-3}/K cm^3 g^{-1} θ=75/K			C=4.74·10^{-3}/K cm^3 g^{-1} θ=–18.9/K		
T/K	χ_M^{corr}·10^6	μ_{eff} (μ_B)	T/K	χ_M^{corr}·10^6	μ_{eff} (μ_B)	T/K	χ_M^{corr}·10^6	μ_{eff} (μ_B)	T/K	χ_M^{corr}·10^6	μ_{eff} (μ_B)
76	52092	5.64	76	36560	4.73	77	17280	3.26	76	158	0.27
123	36109	5.98	123	23919	4.87	122	11360	3.25	123	226	0.63
133	33909	6.02	133	22103	4.87	132	10527	3.38	133	318	0.73
143	31062	5.98	143	20664	4.89	143	9517	3.33	143	348	0.78
153	29703	6.05	153	19302	4.98	153	9036	3.34	153	409	0.85
163	28279	6.09	163	18091	4.88	164	8289	3.32	163	470	0.92
173	27049	6.14	173	17485	4.95	173	7763	3.32	173	501	0.97
183	25367	6.12	183	16577	4.95	183	7324	3.29	183	531	1.02
193	25820	6.34	193	15744	4.96	193	7194	3.32	193	562	1.07
203	23879	6.25	203	15593	5.06	199	6754	3.33	203	592	1.12
213	23231	6.32	213	14912	5.07	208	6359	3.31	213	605	1.15
223	20967	6.14	223	14155	5.06	221	6052	3.33	223	623	1.20
233	20902	6.27	233	13701	5.09	237	5527	3.30	233	635	1.23
243	19802	6.23	243	13057	5.07	247	5263	3.29	243	641	1.26
253	19672	6.34	253	12754	5.12	256	5043	3.28	253	623	1.27
263	19478	6.43	263	12300	5.12	263	5000	3.31	263	635	1.31
273	18896	6.45	273	11922	5.14	273	4956	3.35	273	647	1.34
283	18442	6.49	283	11619	5.17	283	4824	3.36	283	666	1.38
293	17990	6.53	293	11241	5.17	303	4117	3.35	293	641	1.39
303	17602	6.57	303	10862	5.17				303	653	1.42

L=$C_{10}H_{11}O_5^-$

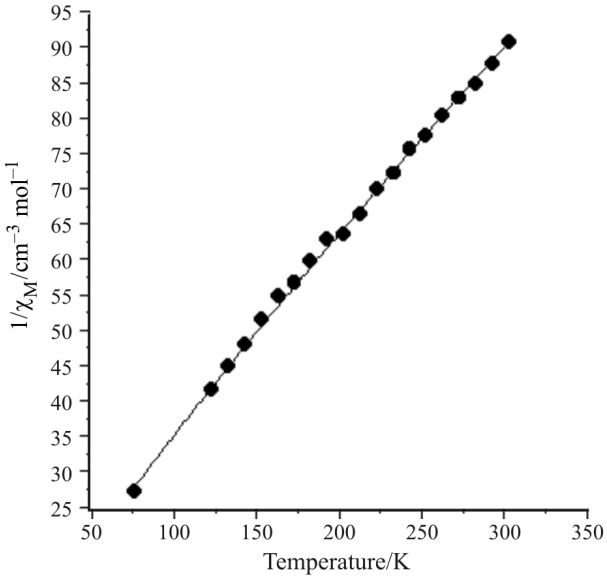

Fig. 4 Dependence of $1/\chi_M$ values *vs*. temperature for Co(II) 2,3,4-trimethoxybenzoate

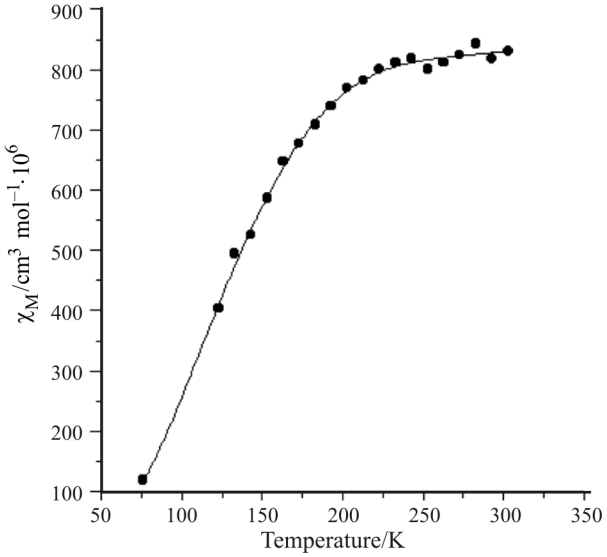

Fig. 5 Dependence of magnetic susceptibility values *vs*. temperature for 2,3,4-trimethoxybenzoate of Cu(II)

the two Cu(II) ions. The variable temperature magnetic results for 2,3,4-trimethoxybenzoate of Cu(II) are plotted in Fig. 5 and given in Table 4. The magnetic moment values of the Cu(II) complex decrease from 1.42 μ_B at 303 K to 0.27 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 will be antiferromagnetic (J<0) if S=0 is the ground state; on the contrary, if S=1, the interaction will be ferromagnetic (J>0) [34–41].

Conclusions

On the basis of the obtained results it appears that 2,3,4-trimethoxybenzoates of Mn(II), Co(II), Ni(II) are anhydrous compounds while that of Cu(II) is hydrate. The final products of their decomposition are following oxides: Mn_3O_4, CoO, NiO and CuO, respectively. The solubility of the coordination compounds of Mn(II), Co(II), Ni(II) and Cu(II) is of the order of 10^{-3}–10^{-4} mol dm^{-3}. The complexes of Mn^{2+}, Co^{2+} and Ni^{2+} with of 2,3,4-trimethoxybenzoate acid anion obey the Curie–Weiss law, since the values of their magnetic susceptibility decrease with rising temperature. 2,3,4-Trimethoxybenzoate of copper(II) whose effective magnetic moment value is equal to 1.42 μ_B (at the room temperature) forms a dimer.

References

1 Beilsteins Handbuch der organischen Chemie, Bd. X, Springer, Berlin 1922.
2 W. Ferenc, B. Bocian and A. Walków-Dziewulska, J. Serb. Chem. Soc., 69 (2004) 195.
3 W. Ferenc, B. Bocian and M. Chudziak, J. Therm. Anal. Cal., 58 (1999) 639.
4 W. Ferenc and B. Bocian, J. Therm. Anal. Cal., 60 (2000) 131.
5 W. Ferenc and A. Walków-Dziewulska, J. Therm. Anal. Cal., 61 (2000) 923.
6 W. Ferenc and A. Walków-Dziewulska, J. Therm. Anal. Cal., 63 (2001) 865.
7 W. Ferenc and A. Walków-Dziewulska, J. Therm. Anal. Cal., 70 (2002) 949.
8 W. Ferenc and A. Walków-Dziewulska, J. Therm. Anal. Cal., 71 (2003) 375.
9 W. Ferenc and A. Walków-Dziewulska, J. Therm. Anal. Cal., 74 (2003) 511.
10 W. Ferenc, A. Walków-Dziewulska, and B. Bocian, J. Therm. Anal. Cal., 79 (2005) 145.
11 B. N. Figgs and R. S. Nyholm, J. Chem. Soc., (1958) 4190.
12 E. König, Magnetic Properties of Coordination and Organometallic Transition Metal Compounds, Springer Verlag, Berlin 1966.
13 J. Janczak, Polish. J. Chem., 73 (1999) 437.
14 R. M. Silverstein and G. C. Bassler, Spektroskopowe metody identyfikacji związków organicznych, PWN, Warszawa 1970 (in Polish).
15 R. M. Silverstein, G. C. Bassler and T. C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley and Sons, Inc., New York 1991.
16 L. A. Kazicyna and N. B. Kupletska, Metody spektroskopowe wyznaczania struktury związków organicznych, PWN, Warszawa 1976 (in Polish).
17 W. Lewandowski and H. Barańska, Vibr. Spectr., 2 (1991) 211.
18 K. Bajdor, P. Koczoń, E. Więckowska and W. Lewandowski, Intern. J. Quan. Chem., 4 (1997) 385.
19 W. Lewandowski, J. Mol. Str., 101 (1983) 93.

20 K. Burger, Coordination Chemistry, Experimental Methods, Akadémiai Kiadó, Budapest 1973.
21 E. Pretsch, T. Clerc, J. Seibl and W. Simon, Tables of Spectral Data for Structure Determination of Organic Compounds, Springer Verlag, Berlin 1989.
22 L. J. Bellamy, The Infrared Spectra of Complex Molecules, Chapman & Hall Ltd., London 1975.
23 G. Varsányi, Assignments for Vibrational Spectra of 700 Benzene Derivatives, Akadémiai Kiadó, Budapest 1973.
24 Praca zbiorowa pod redakcją A. Rajcy, Spektroskopowe metody badania struktury związków organicznych, Skrypt Politechniki Śląskiej w Gliwicach Nr 1659, Gliwice 1991 (in Polish).
25 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, Toronto 1997.
26 S. Manhas and A.K. Trikha, J. Indian. Chem. Soc., 59 (1982) 315.
27 J. Garcia-Oricain and A. Fuster Camps, J. Thermal Anal., 29 (1984) 793.
28 D. Dollimore and D. L. Griffiths, J. Thermal Anal., 2 (1970) 229.
29 D. Czakis-Sulikowska, A. Malinowska and J. Radwańska-Doczekalska, Polish. J. Chem., 74 (2000) 607.
30 S. F. A. Keetle, Fizyczna chemia nieorganiczna, PWN, Warszawa 1999 (in Polish).
31 A. Earnshaw, L. F. Larkworthy and K. C. Patel, Proc. 9th Int. Conf. Coordination Chem., St.-Moritz Bad 1966.
32 Y. R. Morgan, P. Turner, B. J. Kennedy, T. W. Hambley, P. A. Lay, J. R. Biffin, H. L. Regtop and B. Warwick, Inorg. Chim. Acta, 324 (2001) 150.
33 J. E. Weder, T. W. Hambley, B. J. Kennedy, P. A. Lay, D. MacLachlan, R. Bramley, Ch. D. Delfs, K. S. Murray, B. Moubaraki, B. Warwick, J. R. Biffin and H. L. Regtop, Inorg. Chem., 38 (1999) 1736.
34 J. Casanova, G. Aluzet, J. LaTorre and J. Borras, Inorg. Chem., 36 (1997) 2052.
35 R. J. Doedens, Prog. Inorg. Chem., 21 (1976) 209.
36 J. Mroziński, M. Janik and T. Nowakowski, Zeszyty Naukowe Politechniki Śląskiej, seria Chemia Z., 119, 1988 (in Polish).
37 Kokot and R. L. Martin, Inorg. Chem., 3 (1964) 1306.
38 B. N. Figgis and R. L. Martin, J. Chem. Soc., (1956) 3837.
39 C. C Hadjikostas, G. A. Katsoulos, M. P. Sigalas, C. A. Tsipis and J. Mroziński, Inorg. Chim. Acta, 167 (1990) 165.
40 J. Casanova, G. Alzuet, J. Latorre and J. Borrás, Inorg. Chem., 36 (1997) 2052.
41 O. Kahn, Angew. Chem., Int. Ed. Engl., 24 (1985) 834.

Received: January 25, 2005
Accepted: March 21, 2005
OnlineFirst: January 11, 2006

DOI: 10.1007/s10973-005-6854-x