

## Crystal structures of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II) and Zn(II)

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**Abstract:** The crystal and molecular structures of [bis(5-chloro-2-methoxybenzoate)tetraaquamanganese(II)], [pentaqua(5-chloro-2-methoxybenzoato)cobalt(II)] (5-chloro-2-methoxybenzoate), [pentaqua(5-chloro-2-methoxybenzoato)nickel(II)] (5-chloro-2-methoxybenzoate) and [aquabis(5-chloro-2-methoxybenzoate)zinc(II)] monohydrate were determined by a single-crystal X-ray analysis. Mn(H<sub>2</sub>O)<sub>4</sub>L<sub>2</sub> (where L = C<sub>8</sub>H<sub>6</sub>ClO<sub>3</sub>) crystallizes in the monoclinic system, space group *P21/c*. [Co(H<sub>2</sub>O)<sub>5</sub>L]L and [Ni(H<sub>2</sub>O)<sub>5</sub>L]L both are isostructural, space group *P212121*. The crystals of [Zn(H<sub>2</sub>O)L<sub>2</sub>] H<sub>2</sub>O are monoclinic, space group *Pc*. Mn(II) ion is positioned at the crystallographic symmetry center. Mn(II) and Co(II) ions adopt the distorted octahedral coordination but Zn(II) tetrahedral one. The carboxylate groups in the complexes with M(II) cations function as monodentate, bidentate and/or free COO-groups. The ligands exist in the crystals as aquaanions. The complexes of 5-chloro-2-methoxybenzoates with Mn(II), Co(II) and Zn(II) form bilayer structure.

**Keywords:** crystal structure; 5-chloro-2-methoxybenzoates; magnetic moment;

### Introduction

5-Chloro-2-methoxybenzoic acid having formula C<sub>8</sub>H<sub>7</sub>ClO<sub>3</sub> is a white crystalline solid sparingly soluble in cold water, that is stable up to 199°C after which it decomposes with the melting point temperature [1].

The complexes of 5-chloro-2-methoxybenzoic acid with Mn(II), Co(II), Ni(II) and Zn(II) were obtained and some of their physico-chemical properties such as: thermal stability in air and nitrogen atmospheres and magnetic properties in the range of 80–300 K were studied. The results of elemental and thermal analyses suggest that these complexes are di-, tetra- and pentahydrates, and the water molecules are released only in one step with the rise of temperature. The FTIR and FIR spectra analysis reveals the carboxylate group to be monodentate and bidentate ligands. The magnetic measurement results suggest, that the Mn(II), Co(II) and Ni(II) are high-spin complexes. The ligands form the weak electrostatic field in the coordination sphere of the central ions. The Zn(II) complex is

diamagnetic as may be expected from Zn(II) closed shell electronic configuration and the absence of unpaired electrons [2-5].

In order to explain the physico-chemical properties of the complexes, to elucidate the ways of coordinations of Mn(II), Co(II), Ni(II) and Zn(II) ions with 5-chloro-2-methoxybenzoate ligand and to determine the positions of water molecules in the crystal lattice their structures were determined by single-crystal X-ray analysis.

### Experimental details

#### Preparation of complexes

The 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), and Zn(II) were prepared by the addition of equivalent quantities of 0.1M ammonium 5-chloro-2-methoxybenzoate (pH~5) to a hot solution containing the nitrates(V) of those elements and crystallizing at 293K. The solids were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303K to a constant mass. Suitable crystals of the title compounds for X-ray diffraction were grown by

the recrystallization process evaporating an aqueous solution of the salts at 293 K. The contents of carbon and hydrogen in complexes were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser and the content of chlorine by Schöniger method. The contents of  $M^{2+}$  metals were established by ASA method and TG curves. *Anal. Calcd.* for  $C_{16}H_{20}Cl_2O_{10}Mn$  ( $M_r = 498$ ): C, 38.56; H, 4.02; Cl, 14.06; Mn 11.03%; found: C, 38.85; H, 3.96; Cl, 14.61; Mn 10.95%. *Calcd.* for  $C_{16}H_{22}Cl_2O_{11}Co$  ( $M_r = 519.9$ ): C, 36.93; H, 4.23; Cl, 13.46; Co 11.33%; found: C, 37.25; H, 4.13; Cl, 13.71; Co 11.43%. *Calcd.* for  $C_{16}H_{22}Cl_2O_{11}Ni$  ( $M_r = 519.7$ ): C, 36.95; H, 4.23; Cl, 13.66; Ni, 11.29%; found: C, 37.03; H, 4.09; Cl, 13.30; Ni, 11.40%. *Calcd.* for  $C_{16}H_{16}Cl_2O_8Zn$  ( $M_r = 472$ ): C, 40.64; H, 3.39; Cl, 14.82; Zn 13.84%; found: C, 40.67; H, 3.32; Cl, 14.12; Zn 13.86%.

#### X-ray structure determination

X-ray diffraction data for title compounds were measured at 100 K on a KM4 CCD

diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.710073\text{\AA}$ ). The data were corrected for empirical absorption. The crystal and experimental data are collected in Table 1.

The atomic coordinates of non-hydrogen atoms with their isotropic temperature factors after the final refinement are given in Table 2.

Crystal structure was solved by direct method, using the SHELXS-97 program [6] and refined by full matrix least-squares method on  $F^2$  using the SHELXL-97 program [7]. The non-hydrogen atoms were refined with anisotropic displacement parameters. Positions of ligand H-atoms were calculated from the geometry assuming the trigonal or tetragonal configuration of respective non-H atoms, while that of water molecules were located in difference maps. H-atoms were given isotropic factors of  $1.2U_{eq}$  and their positions are refined.

**Table 1.** Crystal data and details of the structure refinement.

	$Mn(H_2O)_4L_2$	$[Co(H_2O)_5L]L$	$[Ni(H_2O)_5L]L$	$[Zn(H_2O)_6L_2]\cdot H_2O$
Empirical formula	$C_8H_{10}ClO_3Mn_{0.5}$	$C_{16}H_{22}Cl_2O_{11}Co$	$C_{16}H_{22}Cl_2O_{11}Ni$	$C_{16}H_{16}Cl_2O_8Zn$
Formula weight	249.08	520.17	519.94	472.56
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$Pc$
Volume ( $\text{\AA}^3$ )	969	2057	2065	931
Unit cell dimensions ( $\text{\AA}$ , $^\circ$ )				
<i>a</i>	14.600(4)	7.164(2)	7.145(3)	4.924(2)
<i>b</i>	9.432(3)	8.226(3)	8.302(5)	6.817(3)
<i>c</i>	7.047(3)	34.889(5)	34.82(2)	27.731(7)
$\beta$	92.88(3)			91.18(3)
<i>Z</i>	4	4	4	2
Density ( $\text{g cm}^{-3}$ )	1.707	1.680		1.686
$\mu$ ( $\text{mm}^{-1}$ )	1.011	1.152		1.648
<i>F</i> (000)	510	1068		480
Crystal size (mm)	0.30 × 0.20 × 0.02	0.50 × 0.12 × 0.12		0.45 × 0.1 × 0.1
$\theta$ range for data collection ( $^\circ$ )	3.53 - 28.46	3.50 - 28.44		3.71 - 28.30
Index ranges	-17 ≤ <i>h</i> ≤ 19 -12 ≤ <i>k</i> ≤ 11 -9 ≤ <i>l</i> ≤ 8	-9 ≤ <i>h</i> ≤ 9 -10 ≤ <i>k</i> ≤ 10 -39 ≤ <i>l</i> ≤ 44		-6 ≤ <i>h</i> ≤ 6 -8 ≤ <i>k</i> ≤ 9 -36 ≤ <i>l</i> ≤ 35
Reflections collected	6069	13382		7118
Independent reflections	2265, [ $R_{int} = 0.0407$ ]	4756, [ $R_{int} = 0.0342$ ]		3422, [ $R_{int} = 0.0297$ ]
Absorption correction: $T_{min}$ ; $T_{max}$	0.7514; 0.9801	0.5966; 0.8741		0.536; 0.887
Data parameters	146	359		242
Goodness-of-fit on $F^2$	1.198	1.072		1.092
Final R indices [ $I > 2\sigma(I)$ ]	<i>R</i> = 0.0649 <i>wR</i> = 0.1255	<i>R</i> = 0.0248 <i>wR</i> = 0.0515		<i>R</i> = 0.0281 <i>wR</i> = 0.0644
R indices (all data)	<i>R</i> = 0.0788 <i>wR</i> = 0.1307	<i>R</i> = 0.0297 <i>wR</i> = 0.0554		<i>R</i> = 0.0300 <i>wR</i> = 0.0660
$\Delta\rho_{max}$ ; $\Delta\rho_{min}$ ( $e \text{\AA}^{-3}$ )	0.70; -0.53	0.27; -0.38		0.31; -0.48

**Table 2.** Atomic coordinates ( $\times 10^4$ ) of non-hydrogen atoms and their equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ).

Atom	x	y	z	$U_{eq}$
<b>Mn(H<sub>2</sub>O)<sub>2</sub>L<sub>2</sub></b>				
Mn	0	0	0	12(1)
O1w	-1025(2)	-1060(3)	1789(4)	17(1)
O2w	551(2)	1095(3)	2626(4)	16(1)
O1	967(2)	-1615(3)	500(4)	18(1)
O2	938(2)	-3967(3)	397(4)	16(1)
O3	2419(2)	-5262(3)	-746(4)	18(1)
C1	2299(3)	-2753(4)	-502(5)	13(1)
C2	2828(3)	-3960(4)	-908(6)	16(1)
C3	3727(3)	-3810(4)	-1437(6)	16(1)
C4	4105(3)	-2473(4)	-1633(6)	15(1)
C5	3583(3)	-1285(4)	-1306(6)	15(1)
C6	2688(3)	-1412(4)	-732(5)	14(1)
C7	1326(3)	-2793(4)	174(5)	13(1)
C8	2932(3)	-6487(4)	-1285(7)	23(1)
C11	4041(1)	405(1)	-1582(2)	20(1)
<b>[Co(H<sub>2</sub>O)<sub>2</sub>L]<sub>2</sub></b>				
Co	2511(1)	-425(1)	2834(1)	9(1)
O1w	2450(3)	-2783(2)	3070(1)	19(1)
O2w	2207(2)	1903(2)	2571(1)	11(1)
O3w	11(2)	-222(2)	3130(1)	14(1)
O4w	1093(2)	-1298(2)	2355(1)	14(1)
O5w	5042(2)	-683(2)	2504(1)	11(1)
O1A	4015(2)	504(2)	3286(1)	15(1)
O2A	6653(2)	1333(2)	3006(1)	13(1)
O3A	9050(2)	2946(2)	3466(1)	14(1)
C1A	6369(3)	1546(2)	3694(1)	12(1)
C2A	8054(3)	2377(2)	3770(1)	12(1)
C3A	8622(3)	2614(3)	4151(1)	16(1)
C4A	7538(4)	2058(2)	4455(1)	16(1)
C5A	5882(3)	1265(2)	4378(1)	14(1)
C6A	5305(3)	1014(2)	4005(1)	14(1)
C7A	5637(3)	1122(2)	3298(1)	11(1)
C8A	10901(3)	3541(3)	3538(1)	16(1)
C11A	4496(1)	549(1)	4755(1)	20(1)
O1B	5503(2)	5445(2)	3211(1)	14(1)
O2B	8226(2)	6754(2)	3171(1)	16(1)
O3B	9816(2)	7638(2)	3810(1)	19(1)
C1B	6861(3)	6347(2)	3792(1)	12(1)
C2B	8291(3)	7091(2)	4005(1)	14(1)
C3B	8122(3)	7232(3)	4403(1)	18(1)
C4B	6576(3)	6637(3)	4594(1)	20(1)
C5B	5176(3)	5885(3)	4383(1)	16(1)
C6B	5310(3)	5739(2)	3988(1)	13(1)
C7B	6877(3)	6171(2)	3360(1)	12(1)
C8B	11177(3)	8582(3)	4011(1)	23(1)
C11B	3203(1)	5137(1)	4620(1)	24(1)
<b>[Zn(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O</b>				
Zn	5000	8834(1)	5000	12(1)
O1w	3976(5)	6042(3)	5089(1)	18(1)
O2w	-285(5)	4207(4)	4690(1)	18(1)
O1A	12659(4)	9704(3)	4463(1)	14(1)
O2A	8860(4)	8808(3)	4817(1)	12(1)
O3A	6328(5)	6726(3)	4045(1)	15(1)
C1A	8737(6)	9689(5)	3972(1)	12(1)
C2A	6807(6)	8376(5)	3779(1)	12(1)
C3A	5566(7)	8760(5)	3336(1)	16(1)
C4A	6246(7)	10423(5)	3077(1)	17(1)
C5A	8222(7)	11683(5)	3261(1)	16(1)
C6A	9491(7)	11321(5)	3703(1)	14(1)
C7A	10142(6)	9375(4)	4453(1)	11(1)
C8A	4241(7)	5413(5)	3872(1)	18(1)
C11A	9165(2)	13756(1)	2932(1)	21(1)
O1B	4693(5)	9766(3)	5662(1)	16(1)
O2B	5931(5)	12506(3)	5306(1)	16(1)
O3B	8065(5)	15129(3)	5939(1)	17(1)
C1B	4997(7)	12595(5)	6148(1)	15(1)
C2B	6393(7)	14351(5)	6273(1)	13(1)
C3B	6037(7)	15164(5)	6731(1)	16(1)
C4B	4253(7)	14326(5)	7054(1)	17(1)
C5B	2870(7)	12638(5)	6924(1)	17(1)
C6B	3238(7)	11772(5)	6478(1)	14(1)
C7B	5264(6)	11608(5)	5671(1)	13(1)
C8B	9611(8)	16840(5)	6076(1)	21(1)
C11B	618(2)	11567(1)	7327(1)	22(1)

## Magnetism

The magnetic susceptibilities of samples of 5-chloro-2-methoxybenzoates of Mn(II), Co(II) and Ni(II) at 4.4–294 K were measured using an AC Lake Shore 7225 magnetometer. The magnetic susceptibilities of these complexes were also determined by Gouy method using a sensitive Cahn RM-2 balance. The measurements were made at a magnetic field strength of 9.9 kQe. The calibrant employed was  $\text{Hg}[\text{Co}(\text{SCN})_4]$  for which the magnetic susceptibility of  $1.644 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1}$  was taken and then the effective magnetic moment values were calculated for 5-chloro-2-methoxybenzoates of Mn(II), Co(II) and Ni(II). Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [8].

## Results and Discussions

The complexes of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II) and Zn(II) were obtained as crystalline products with a metal to ligand ratio of 1:2 and a general formula  $\text{M}(\text{C}_8\text{H}_6\text{ClO}_3)_2 \cdot n\text{H}_2\text{O}$ , where M = Mn, Co, Ni, Zn and n=4 for Mn(II), n=5 for Co(II), Ni(II), and n=2 for Zn(II). The colour of the complexes is typical of the particular divalent ion salts, i.e., is slightly pink in the case of Mn(II), pink for Co(II), green for Ni(II), and white for Zn(II) and originates from d-d electronic transitions of the central ions.

### Molecular and crystal structure

#### Structure of 5-chloro-2-methoxybenzoate aquaanion

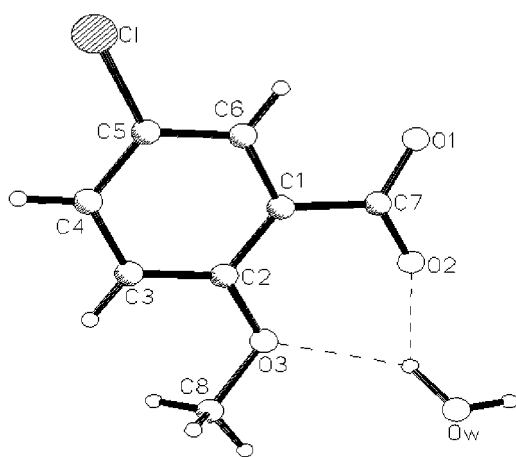
5-Chloro-2-methoxybenzoate ligands exist as aquaanions in the complexes with Mn(II), Co(II), Ni(II) and Zn(II). The scheme of aquaanion with atom numberings is shown in Figure 1.

As it is seen, the water molecule as proton donor interact with O2 and O3 oxygen atoms of the ligands as proton acceptors through three-centered intermolecular hydrogen bonds and forms  $\text{R}_1^2(6)$  motives.

The phenyl rings of all ligands are planar within the experimental error. The C7–O1 and C7–

O2 bond values in the carboxylate group lie in the range 1.255(5) - 1.269(2) Å in the Mn(II) and Co(II) complexes, and 1.248(4) - 1.287(4) Å in the Zn(II) complex, and are typical for the delocalized bonds. The COO<sup>-</sup> groups are approximately coplanar with the benzene ring plane. Torsion angles C2-C1-C7-O2 change from -0.4(6)° in Mn(H<sub>2</sub>O)<sub>4</sub>L<sub>2</sub> to -1.7(3)° (A ligand) and 8.7(3)° (B ligand) of the [Co(H<sub>2</sub>O)<sub>5</sub>L]L complexes. However, in the Zn(II) complex it rotates around C1-C7 bond, and the values of C2-C1-C7-O2 torsion angles are -43.4(3)° and -24.7(5)° in the A and B ligands, respectively.

The methoxy groups in all complexes are approximately coplanar with benzene ring planes.



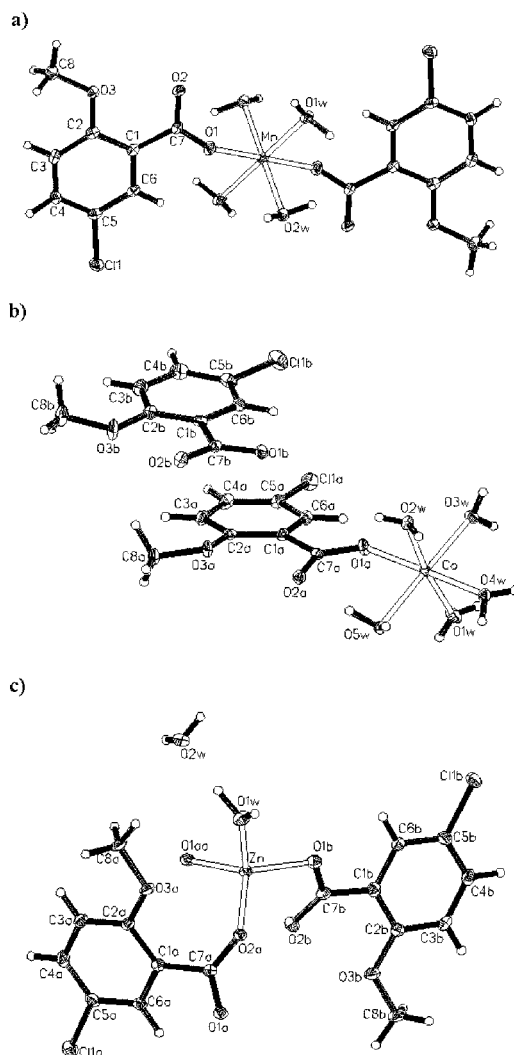
**Fig. 1.** View of the 5-chloro-2-methoxybenzoate anion showing the atom-numbering scheme. The dashed lines indicate hydrogen bonds.

#### Structure of Mn(H<sub>2</sub>O)<sub>4</sub>L<sub>2</sub>

The perspective view of the Mn(H<sub>2</sub>O)<sub>4</sub>L<sub>2</sub> complex is shown in Figure 2a.

The values of Mn-O bond lengths and O-Mn-O angles in the cation coordination spheres are given in Table 3.

The Mn(II) ion is positioned on the symmetry center and bonded to four oxygen atoms of water molecules and two of monodentate carboxylate groups (Figure 2a). Two independent Mn-O<sub>w</sub> (O<sub>w</sub> - oxygen atom of water molecule) bond lengths are almost equal (Table 3) and longer than Mn-O<sub>c</sub> (O<sub>c</sub> - oxygen atom of carboxylate group). The coordination geometry would be the best described by the distorted octahedral whose base



**Fig. 2.** Perspective view of the Mn(II), Co(II), Zn(II) coordination spheres in the: (a) Mn(H<sub>2</sub>O)<sub>4</sub>L<sub>2</sub>, (b) [Co(H<sub>2</sub>O)<sub>5</sub>L]L, (c) [Zn(H<sub>2</sub>O)<sub>5</sub>]·H<sub>2</sub>O complexes with atom numbering. Thermal ellipsoids at the 50% probability level.

contains water molecules and the vertices are occupied by symmetrically equivalent oxygen atoms of monodentate carboxylate groups. The MnO<sub>6</sub> spheres are linked through O1<sub>w</sub>-H1<sub>w</sub>1...O2<sub>w</sub><sup>i</sup> (-x, y - 0.5, -z + 0.5) intermolecular hydrogen bonds and build two-dimensional hydrophilic cation-layers parallel to (100) lattice plane. Also, there are three types of intermolecular hydrogen bonds within cation-layers in which water molecule acts as the proton donor and the uncoordinating O2 carboxyl oxygen atom and O3

*ortho*-methoxy oxygen atom are proton acceptors. Mn(II)⋯Mn(II) separations within cation-layers are 5.887 Å (Table 4).

**Table 4.** Geometry of hydrogen bonds and weak contacts (Å, °). \* means the hydrogen atoms in water molecules forming aqua-anions.

Mn(H <sub>2</sub> O) <sub>5</sub> L <sub>2</sub>					
D-H	A	d(D...A)	d(D-H)	d(H...A)	∠DHA
O1w-H1w1	O2w <sup>i</sup>	2.796(4)	0.75(5)	2.05(5)	174
O1w-H2w1	O2 <sup>ii</sup>	2.797(4)	0.95(5)	1.89(5)	161
O2w-H1w2	O2 <sup>iii</sup>	2.642(4)	0.98(5)	1.67(5)	172
O2w-H2w2 <sup>†</sup>	O2 <sup>iiii</sup>	2.838(4)	1.05(5)	1.94(5)	141
O2w-H2w2 <sup>†</sup>	O3 <sup>vii</sup>	3.009(4)	1.05(5)	2.14(5)	139
C8-H8A	Cl <sup>iv</sup>	3.365(5)	0.98	3.05	100
C8-H8B	Cl <sup>iv</sup>	3.365(5)	0.98	3.09	97

Symmetry codes: <sup>i</sup> -x, y-0.5, -z+0.5; <sup>ii</sup> -x, y+0.5, -z+0.5; <sup>iii</sup> x, -y-0.5, z+0.5; <sup>iiii</sup> x, y-1, z

[Co(H <sub>2</sub> O) <sub>5</sub> L]L					
O1w-H1w1 <sup>†</sup>	O2B <sup>f</sup>	3.070(2)	0.80(3)	2.36(3)	149
O1w-H1w1 <sup>†</sup>	O3B <sup>f</sup>	3.216(2)	0.80(3)	2.64(3)	130
O1w-H2w1	O1B <sup>ii</sup>	2.674(2)	0.85(3)	1.84(3)	168
O2w-H1w2	O5w <sup>iii</sup>	2.810(2)	0.79(3)	2.03(3)	170
O2w-H2w2	O2B <sup>iv</sup>	2.611(2)	0.87(3)	1.75(3)	172
O3w-H1w3 <sup>†</sup>	O2A <sup>v</sup>	2.759(2)	0.79(3)	2.00(3)	161
O3w-H1w3 <sup>†</sup>	O3A <sup>v</sup>	2.938(2)	0.79(3)	2.45(3)	121
O3w-H2w3 <sup>†</sup>	O2B <sup>vi</sup>	2.800(2)	0.86(3)	1.98(3)	160
O3w-H2w3 <sup>†</sup>	O3B <sup>vi</sup>	2.957(2)	0.86(3)	2.37(3)	126
O4w-H1w4	O2w <sup>vii</sup>	2.801(2)	0.87(3)	1.94(3)	171
O4w-H2w4 <sup>†</sup>	O2A <sup>viii</sup>	2.828(2)	0.80(3)	2.12(3)	147
O4w-H2w4 <sup>†</sup>	O3A <sup>viii</sup>	2.934(2)	0.80(3)	2.34(3)	132
O5w-H1w5	O2A	2.675(2)	0.93(3)	1.80(2)	155
O5w-H2w5	O1B <sup>ix</sup>	2.690(2)	0.82(3)	1.87(2)	177
C8A-H8A3	O3B	3.586(3)	0.96(2)	2.70	153
C8B-H8B1	O1A <sup>x</sup>	3.611(3)	0.96(3)	2.67	165
C8B-H8B2	Cl1B <sup>y</sup>	3.827(3)	0.99(3)	2.89	158
C4A-H4A	Cl1A <sup>z</sup>	3.667(2)	0.96(2)	2.84	145
O3A...C7B		3.098(2)			
C2A...C1B		3.376(3)			

Symmetry codes: <sup>i</sup> x-1, y-1, z; <sup>ii</sup> x, y-1, z; <sup>iii</sup> w-x+1, y+0.5, -z+0.5; <sup>iv</sup> -x+1, y-0.5, -z+0.5; <sup>v</sup> x-1, y, z; <sup>vi</sup> x-1, y-1, z; <sup>vii</sup> w-x, y-0.5, -z+0.5; <sup>viii</sup> -x+1, y-0.5, -z+0.5; <sup>ix</sup> 1-x, 1-y, z; <sup>x</sup> 1+x, y+1, z; <sup>y</sup> x, y+1, z; <sup>z</sup> x, y+1, z

[Zn(H <sub>2</sub> O) <sub>4</sub> ]·H <sub>2</sub> O					
O1w-H1w1	O2w	2.663(4)	1.01	1.66	172
O1w-H2w1 <sup>†</sup>	O2B <sup>f</sup>	2.656(3)	1.01	1.72	154
O1w-H2w1 <sup>†</sup>	O3B <sup>f</sup>	3.132(4)	1.01	2.44	125
O2w-H1w2 <sup>†</sup>	O2A <sup>g</sup>	3.185(4)	1.01	2.51	124
O2w-H1w2 <sup>†</sup>	O3A <sup>g</sup>	2.968(3)	1.01	2.01	158
O2w-H2w2	O2B <sup>h</sup>	2.794(3)	0.98	1.88	153
C8B-H8B1	O1B <sup>iv</sup>	3.417(4)	0.98	2.63	138
C8B-H8B1	O1w <sup>vi</sup>	3.556(4)	0.98	2.68	149
C8B-H8B3	O1B <sup>v</sup>	3.323(5)	0.98	2.55	136

Symmetry codes: <sup>i</sup> x, y-1, z; <sup>ii</sup> x-1, y, z; <sup>iii</sup> w-x-1, y-1, z; <sup>iv</sup> 1+x, y+1, z; <sup>v</sup> x, y+1, z; <sup>vi</sup> -x+1, y-0.5, -z+0.5

The methyl group of the monodentate ligands forms C8-H8⋯Cl<sup>iv</sup> (<sup>iv</sup> x, y-1, z) hydrogen bonds with neighbouring anions and build ribbons parallel to *a* axis. Moreover, p⋯p stacking was found to exist among the 5-chloro-2-methoxybenzoate aqua-anions, the distances between the centroid of the benzene ring planes are 3.34 Å.

**Table 3.** Selected bond lengths and angles for M(II) coordination spheres of 5-chloro-2-methoxybenzoates.

	Mn(II)*	Co(II)		Zn(II)	
		Bond lengths (Å)			
O1	2.095(3)	O1A	2.059 (1)	O1A <sup>ii</sup>	1.956(2)
O1w	2.240(3)	O1w	2.108(2)	O2A	1.978(2)
O2w	2.234(3)	O2w	2.134 (2)	O1B	1.951(2)
		O3w	2.075(2)	O1w	1.986(2)
		O4w	2.082 (2)		
		O5w	2.159(1)		
Bond angles (°)					
O1w-Mn-O1	92.6(1)	O1w-Co-O2w	172.52(7)	O2A-Zn-O1B	109.8(1)
O1w-Mn-O2w	87.9(1)	O3w-Co-O5w	177.39(6)	O1A <sup>i</sup> -Zn-O2A	111.2(1)
O1-Mn-O2w	89.2(1)	O1A-Co-O4w	176.76(6)	O2A-Zn-O1w	105.7(1)
		O1w-Co-O1A	93.01(6)	O1A <sup>i</sup> -Zn-O1w	103.8(1)
		O1w-Co-O3w	82.02(7)	O1B-Zn-O1A <sup>i</sup>	124.2(1)
		O1w-Co-O4w	89.22(6)	O1B-Zn-O1w	99.8(1)
		O1w-Co-O5w	97.78(6)		
		O2w-Co-O1A	92.83(6)		
		O2w-Co-O3w	93.08(6)		
		O2w-Co-O4w	85.14(6)		
		O2w-Co-O5w	86.85(5)		
		O1A-Co-O3w	92.27(6)		
		O1A-Co-O5w	90.34(6)		
		O4w-Co-O3w	90.36(6)		
		O4w-Co-O5w	87.03(6)		

\* Mn(II) occupy symmetry center; symmetry code: <sup>i</sup> x-1, y, z.

### Structure of [Co(H<sub>2</sub>O)<sub>5</sub>L]L

The Co(II) complex consists of two discrete units: [Co(H<sub>2</sub>O)<sub>5</sub>L]<sup>+</sup> cations and free ligands L<sup>-</sup> as anions (Figure 2b).

The Co(II) cation occurs in distorted octahedral coordination (Table 3). The coordination sphere of Co(II) ion contains one oxygen atom of monodentate carboxylate group of A ligand and five water molecules completing octahedral coordination. In this complex there are intramolecular O<sub>w</sub>-H...O<sub>c</sub> (i.e., O5w-H1w5...O2A) and C-H...O<sub>m</sub> (O<sub>m</sub> - oxygen atom of methoxy group; i.e., C8A-H8A3...O3B) hydrogen bonds, and moreover intramolecular C7B...O3A electrostatic interaction (Table IV). The benzene ring plane of the coordinating (A) and uncoordinating (B) ligands are not entirely parallel, the values of the bond angles are 7.4(1)°. The first coordination spheres of the cations are connected through O<sub>w</sub>-H...O<sub>w</sub> (i.e., O1w-H1w4...O2w<sup>vii</sup> and O2w-H1w2...O5w<sup>iii</sup>) hydrogen bonds and build cation-layer parallel to (001) lattice plane with Co...Co distances 5.92 and 5.94 Å. Free anions are connected *via* C8B-H8B...Cl1B<sup>xi</sup> weak hydrogen bonds along *a* axis.

### Structure of {[Zn(H<sub>2</sub>O)<sub>4</sub>]·H<sub>2</sub>O}<sub>n</sub>

The Zn(II) cations function in distorted tetrahedral ZnO<sub>4</sub> coordination (Figure 2c).

Their coordination spheres contain one oxygen atom of monodentate carboxylate group of B ligand, two oxygen atoms of bidentate-bridging carboxylate group of A ligand and one

water molecule. Coordination spheres are connected by bridging carboxylate groups forming the  $\{[\text{Zn}(\text{H}_2\text{O})\text{L}_2]\cdot\text{H}_2\text{O}\}_n$  polymeric chains along the [100] direction.

The magnetic susceptibility of 5-chloro-2-methoxybenzoates of Mn(II), Co(II) and Ni(II) was determined in 4.4–294 K. All complexes show paramagnetic properties and they obey the Curie-Weiss law. The effective magnetic moment values experimentally determined for 5-chloro-2-methoxybenzoates of Mn(II) and Ni(II) change from  $5.28 m_B$  (at 4.5 K) to  $6.13 m_B$  (at 291 K) and from  $2.80 m_B$  (at 4.3 K) to  $3.04 m_B$  (at 293 K) for those of two appropriate complexes, respectively. The experimental data reveal that the magnetic moments of  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  ions in the complexes are connected with spin-only moments. Their theoretical values at room temperature are equal to  $5.92 m_B$  for the  $\text{Mn}^{2+}$  and  $2.83 m_B$  for the  $\text{Ni}^{2+}$ , respectively. These spin – only values of magnetic moments of Mn(II) and Ni(II) indicate that they are high-spin  $d^5$  and  $d^8$  ions, respectively. In the case of 5-chloro-2-methoxybenzoate of Co(II) the effective magnetic moments of cobalt ion determined in 4.6–294 K are in the range of  $4.08 - 4.64 m_B$ . The magnetic moment measured at room temperature for the  $\text{Co}^{2+}$  ion is equal to  $4.64 m_B$ . This value differs from that of the spin-only moment which amounts to  $3.88 m_B$ . The relatively large difference between measured and calculated values results from a spin-orbital coupling. The obtained values indicate that the studied compounds are high-spin complexes with octahedral coordination and the ligands form the weak electrostatic field in the coordination sphere of the central ions. The Zn(II) complex is diamagnetic as may be expected from its closed shell electronic configuration and the absence of unpaired electrons [2, 4, 8-14].

#### Supplementary data

The lists of the atomic coordinates, displacement parameters and complete geometry have been deposited with the Cambridge Crystallographic Data Centre as supplementary material No. CCDC 610630–610632. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0) 1223-336033; or e-mail: deposit@chemcryst.cam.ac.uk). The list of  $F_o/F_c$ -data is available from the author.

#### Conclusions

The complexes of Mn(II), Co(II), Ni(II), and Zn(II) with 5-chloro-2-methoxybenzoic acid anion were synthesized as hydrated salts. They form tetra-, penta-, and dihydrates, respectively. Their crystal structures were determined. The crystals of Zn(II) complex are monoclinic. Mn(II) and Co(II) ions adopt the distorted octahedral coordination but Zn(II) the tetrahedral one. Complexes of Co(II) and Ni(II) are isostructural. The carboxylate anion in the analysed complexes function as monodentate, bidentate and/or free  $\text{COO}^-$  groups. The Mn(II), Co(II), and Ni(II) compounds are high-spin complexes with octahedral coordination and the ligands form the weak electrostatic field in the coordination sphere of the central ions.

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#### References

- [1] *Beilsteins Handbuch der Organischen Chemie*, Bd. X, Springer-Verlag, Berlin 1949, 62.
- [2] W. Ferenc, B. Bocian; B. Czajka, *Acta Chim. Hung.* 137 (2000) 659-670.
- [3] B. Bocian, B. Czajka, W. Ferenc, *J. Therm. Anal. Cal.* 66 (2001) 729-741.
- [4] B. Bocian, W. Ferenc, *J. Serb. Chem. Soc.* 67 (2002) 605-615.
- [5] W. Ferenc, B. Bocian, *J. Therm. Anal. Cal.* 74 (2003) 521-527.
- [6] G. M. Sheldrick SHELXS97, University of Göttingen, Germany, (1997).
- [7] G. M. Sheldrick SHELXL97, University of Göttingen, Germany, (1997).
- [8] E. König, *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Berlin 1966, 24-29.
- [9] A. Ernschaw, *Introduction to Magnetochemistry*, Academic Press, London 1968, 1-112.
- [10] J. Mroziński, *Material Science* 14 (1988) 23-30.
- [11] J. Mroziński, L. Natkaniec, *Materials Science* 14 (1988) 69-80.
- [12] M. Hvastijova, J. Kohout, J. Mroziński, L. Jäger, *Polish J. Chem.* 69 (1995) 852-857.
- [13] B. Korybut-Daszkiewicz, D. Mrozińska, J. Mroziński: *J. Coord. Chem.* 15 (1987) 357-365.
- [14] B. Korybut-Daszkiewicz, J. Mroziński, *Bull. Pol. Acad. Sc. Chem.* 33 (1985) 412-419.