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Structure, thermal stability and magnetic behavior of Mn(II) complexes with phenoxyacetic acid herbicides

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ABSTRACT

The reaction of manganese(II) chloride with ammonium salt of 4-chloro-2-methylphenoxyacetic acid (MCPA), 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-bromophenoxyacetic acid (4-Br) gave rise to the formation of hydrated complexes with formulas: $Mn(MCPA)_2{\cdot}2H_2O$, $Mn(2,4\text{-}D)_2{\cdot}2H_2O$ and $Mn(4\text{-}Br)_2{\cdot}3H_2O$. The compounds were characterized by elemental and thermal analyses, spectroscopic methods, as well as, by magnetic measurements. The complexes crystallize in monoclinic system. The Mn(II) ion is surrounded by oxygen atoms (from carboxylate groups and water molecules) in the octahedral arrangement. Variable-temperature (1.8–300 K) magnetic susceptibility measurements showed that compounds obey the Curie-Weiss law and have the paramagnetic properties. Being heated up to 1173 K the complexes decompose in three steps - first to anhydrous compounds: $Mn(MCPA)_2$/$Mn(2,4\text{-}D)_2$/$Mn(4\text{-}Br)_2$ through intermediate products: MnO/Mn_2OCl_2/Mn_2OBr_2 to the following oxides: Mn_2O_3/Mn_3O_4/Mn_3O_4. The X-ray single crystal structure analysis was performed for Mn(II) complex with 4-bromophenoxyacetic acid after its recrystallization from *N,N*-dimethylformamide. The formation of hexanuclear cluster of manganese(II) carboxylate with a hydrophobic exterior was observed.

1. Introduction

Manganese (Mn) is considered an essential element in most organisms. In the human, it is absorbed through the gastrointestinal tract (from food and water) and transported to organs such as liver, pancreas or pituitary where it is rapidly accumulated. This biometal is involved in (*i*) the synthesis and activation of enzymes including oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases etc., (*ii*) regulation of the metabolism of glucose and lipids, (*iii*) the acceleration of the synthesis of proteins and vitamins (B, C, E), (*iv*) catalysis of hematopoiesis, (*v*) endocrine regulation and (*vi*) improving immune function [1]. Moreover, it is present in the active centers of several important enzymes like arginase, phosphoenolpyruvate decarboxylase, glutamine synthetase and superoxide dismutase (MnSOD) that is involved in mitochondrial oxidative stress to clear reactive oxygen species (ROS) [1]. In plants, manganese is taken up from the soil by the active transport system of epidermal root cells and translocated to the shoot [2]. It is an important micronutrient for growth and reproduction of photosynthetic organisms as it is involved in diverse processes such as (*i*) photosynthesis, (*ii*) respiration, (*iii*) scavenging of reactive oxygen species, (*iv*) pathogen defense and (*v*) hormone signaling [2].

In soils, manganese can exist in eleven oxidation states: from −3 to +7. The most common ones are +2, +3 and +4. The Mn(III) and Mn(IV) species form insoluble oxides that quickly sediment. Mn(II) is the most soluble species and the only plant available form. Divalent manganese, present in soil and plant tissues, can interact with anions as phenoxyacetate herbicide [3]. The phenoxy herbicides can be introduced to the environment as free acids, alkali and amine salts or esters. All these forms are highly soluble in water, in which they dissociate into acid anions. They persist around 1 month in soil [4] and are degraded by microorganisms. However, before they are degraded by microbes, they can react with metals present in soil and plants tissues, forming metal-organic complexes.

The aim of the research was to obtain, in laboratory conditions, analogous systems with manganese cations only in +2 oxidation state and then to study their structure, thermal stability and magnetic properties. Therefore, we synthesized Mn(II) complexes with 4-chloro-2-

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Table 1
The unit cell parameters for polycrystalline complexes.

Complex	Crystal system	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*V* (Å^3)
Mn(MCPA)$_2$·2H$_2$O	Monoclinic	6.7839 ± 0.0077	17.3769 ± 0.0066	20.547 ± 0.030	90	95.213 ± 0.035	90	2412.12 ± 0.05
Mn(2,4-D)$_2$·2H$_2$O	Monoclinic	8.0300 ± 0.0072	7.3310 ± 0.0063	17.679 ± 0.0083	90	94.233 ± 0.064	90	1037.86 ± 0.02
Mn(4-Br)$_2$·3H$_2$O	Monoclinic	20.3700 ± 0.0056	3.8300 ± 0.0013	5.1200 ± 0.0029	90	115.170 ± 0.075	90	399.44 ± 0.02

methylphenoxyacetic (MCPA), 2,4-dichlorophenoxyacetic (2,4-D) and 4-bromophenoxyacetic (4-Br) acids. The compounds were characterized by elemental analysis, X-ray fluorescence spectroscopy (XRF), X-ray powder diffraction (XRD), thermogravimetry method, attenuated total reflection infrared spectroscopy (ATR-IR) and magnetic susceptibility measurements. For the complex with bromo derivative, after its recrystallization from *N,N*-dimethylformamide (DMF) solution, we were able to receive crystals for X-ray single crystal structure analysis.

2. Experimental part

2.1. Synthesis of complexes

The solvents and all chemicals used for the synthesis were of commercially available reagent grade and were applied without further purification. 4-Chloro-2-methyl-; 2,4-dichloro-, and 4-bromo-phenoxyacetates of ammonium (pH ~ 5) of 0.1 mol/L concentration were prepared by the addition of NH$_3$ (aq) solution (25% pure) to respective phenoxyacetic acids in water solution (99% pure).

The complexes were synthesized by the addition of equivalent quantities of 0.1 mol/L ammonium salt of respective acid (pH ~ 5) to a warm solutions of MnCl$_2$·4H$_2$O and by crystallizing at 293 K. To reach of equilibrium state the solids were constantly stirred for 1 h. Next they were filtered off, washed with warm water to remove ammonium and chloride ions and dried at 303 K to a constant mass.

Mn(MCPA)$_2$·2H$_2$O

Yield: 53.84%, pinkish solid

ATR-IR: 3471, 3264 (νOH$_{water}$), 1631 (ν_{as}COO$^-$), 1593 (ν_{as}COO$^-$), 1557 (ν_{as}COO$^-$), 1334 (ν_sCOO$^-$),1223 (νC$_{ar}$–O$_{ether}$), 1054 (νC$_{ar}$–Cl) cm^{-1}

Anal. Calc. for Mn(C$_9$H$_5$O$_3$Cl)$_2$·2H$_2$O: C, 44.49; H, 4.08; Cl, 14.49; Mn, 11.21% Found: C, 44.08; H, 4.07; Cl, 14.40; Mn, 11.00%

Mn(2,4-D)$_2$·2H$_2$O

Yield: 63.42%, white solid

ATR-IR: 3554, 3292 (νOH$_{water}$), 1606 (ν_{as}COO$^-$), 1579 (ν_{as}COO$^-$), 1560 (ν_{as}COO$^-$), 1341 (ν_sCOO$^-$), 1230 (νC$_{ar}$–O$_{ether}$), 1049 (νC$_{ar}$–Cl) cm^{-1}

Anal. Calc. for Mn(C$_8$H$_5$O$_3$Cl$_2$)$_2$·2H$_2$O: C, 36.16; H, 2.64; Cl, 26.74; Mn, 10.36% Found: C, 36.18; H, 2.64; Cl, 26.68; Mn, 9.82%

Mn(4-Br)$_2$·3H$_2$O

Yield: 69.80%, pinkish solid

ATR-IR: 3507, 3348 (νOH$_{water}$), 1646 (ν_{as}COO$^-$), 1589 (ν_{as}COO$^-$), 1580 (ν_{as}COO$^-$), 1341 (ν_sCOO$^-$), 1231 (νC$_{ar}$–O$_{ether}$), 1054 (νC$_{ar}$–Br) cm^{-1}

Anal. Calc. for Mn(C$_8$H$_6$O$_3$Br)$_2$·3H$_2$O: C, 33.62; H, 3.50; Br, 28.02; Mn, 9.63% Found: C, 33.62; H, 3.25; Br, 28.00; Mn, 9.62%

The colourless crystals of Mn(II) complex with 4-bromophenoxyacetic acid (recrystallized from DMF) suitable for an X-ray single crystal structure analysis, were obtained by a slow evaporation of the solvent from DMF solution at room temperature.

2.2. Structural characterization of complexes

The contents of carbon and hydrogen in complexes were determined by elemental analysis using CHN 2400 Perkin – Elmer analyser. The amounts of metal and halogen atoms were established by X-ray fluorescence (XRF) method using spectrophotometer with energy dispersion ED XRF-1510 (Canberra – Packard). The ATR-IR spectra of complexes and their parent ligands were recorded over the range of 4000 – 400 cm^{-1} using Thermo Scientific Nicolet iS5 spectrometer. The X-ray diffraction patterns of all complexes and the products of their decomposition process were registered on a HZG-4 (Carl-Zeiss, Jena) diffractometer using Ni filtered CuK$_\alpha$ radiation. The measurements were made within the range of 2θ = 4-80° by means of Bragg-Brentano method. For the interpretation of diffractograms (Figs. 1S-3S in the Supplementary material) the Dicvol 06 programme was used.

2.3. Thermal characterization of complexes

The thermal stability and decomposition process of complexes were studied in air using a Setsys 16/18 (Setaram) TG, DTG and DSC instrument. The experiments were carried out under air flow in the temperature range of 293 – 1173 K at a heating rate of 5 K·min^{-1}. The initial masses of samples changed from 5.42 to 5.01 mg. The compounds were heated in Al$_2$O$_3$ crucibles.

2.4. Magnetic characterization of complexes

Magnetic susceptibilities of samples were investigated at 1.8 – 300 K with the use of Quantum Design SQUID-VSM magnetometer. The superconducting magnet was operated at a field strength ranging from 0 to 7 T. Measurements of samples were made at magnetic field of 0.1 T. The SQUID magnetometer was calibrated with the palladium rod sample. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants. The effective magnetic moment values were calculated from the equation: $\mu_{eff} = 2.83\ (\chi_m \cdot T)^{1/2}$, where: μ_{eff} - effective magnetic moment, χ_m – magnetic susceptibility per molecule and T - absolute temperature.

2.5. Single crystal X-ray diffraction of the recrystallized complex

The X-ray diffraction intensities for the single crystal of the Mn(II) complex with 4-bromophenoxyacetic acid (recrystallized from DMF) were collected at 120 K on SuperNova X-ray diffractometer equipped with Atlas S2 CCD detector using the mirror-monochromatized CuK$_\alpha$ radiation (λ = 1.54184 Å). Data were collected using the ω scan technique, with an angular scan width of 1.0°. The programs CrysAlis CCD, CrysAlis Red and CrysAlisPro [5,6] were used for data collection, cell refinement and data reduction. The analytical numeric absorption correction based on indexing of crystal faces was applied [7]. The structure was solved by direct methods using SHELXS-97 and refined by the full-matrix least-squares on F^2 using the SHELXL-97 [8]. The H-atoms were positioned geometrically and allowed to ride on their parent atoms, with U_{iso}(H) = 1.5 U_{eq}(C) for methyl groups and 1.2 U_{eq}(C) for the rest groups. The DMF molecule has high thermal ellipsoids due to weak intermolecular interactions. Crystallographic data are given in Tables 1S in the Supplementary Material.

Crystal Data for C$_{114}$H$_{114}$Br$_{12}$Mn$_6$N$_6$O$_{42}$ (M = 3528.66 g/mol): trigonal, space group *P*-3 (no. 147), *a* = 16.9142(6) Å, *c* = 13.4364(6) Å, *V* = 3329.0(2) Å^3, *Z* = 1, *T* = 120.01(10) K, *μ*(Cu Kα) = 9.411 mm-1, D_{calc} = 1.76 g/cm^3, 56,180 reflections measured (8.94° ≤ 2Θ ≤ 154.92°), 4662 unique (R_{int} = 0.0710, R_{sigma} = 0.0244) which were used in all calculations. The final R_1 was 0.0432 (I>=2μ(I)) and wR_2 was 0.1174 (all data).

CCDC 2,089,845 contains the supplementary crystallographic data, which can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)

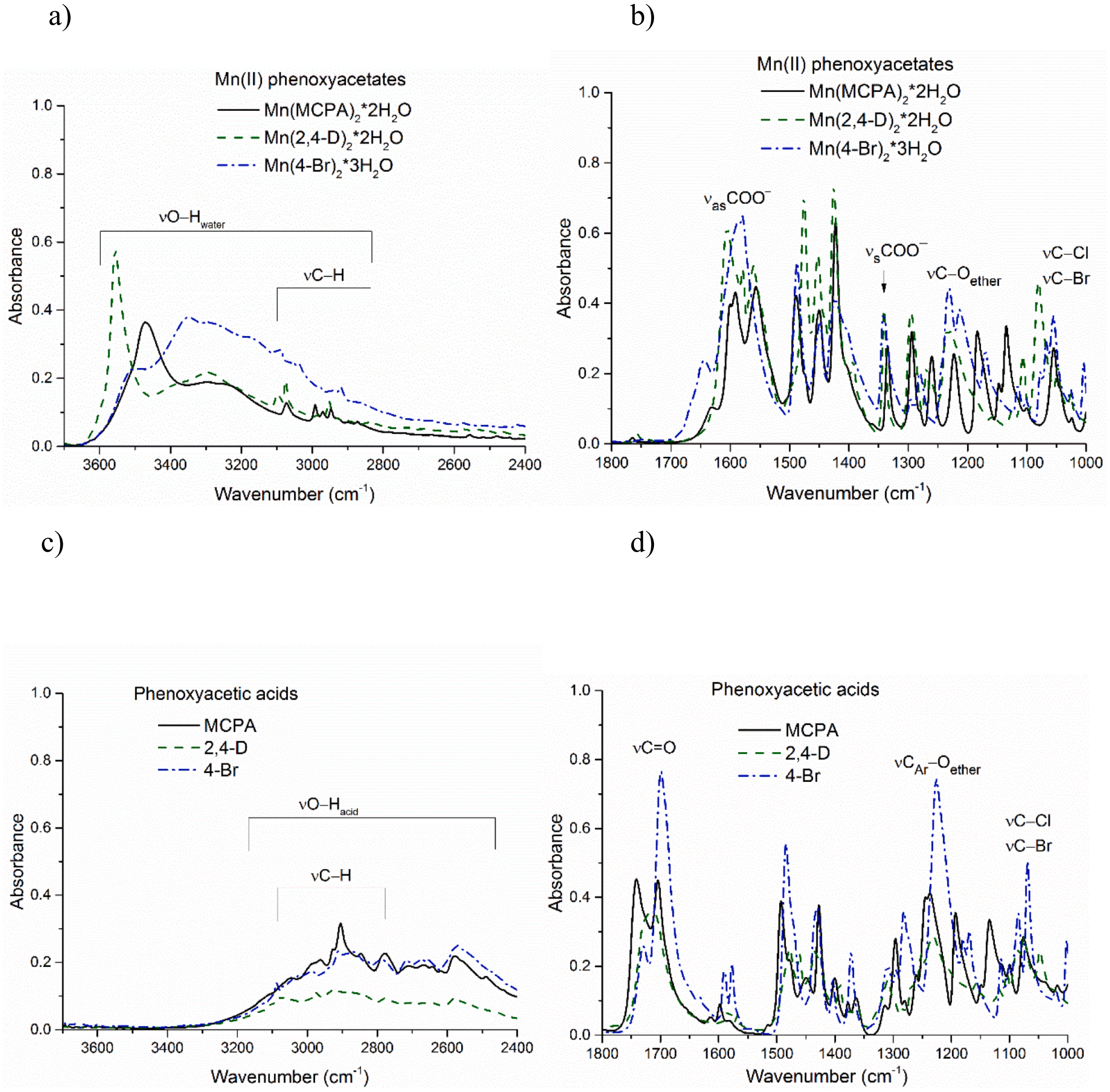

Fig. 1. The comparison of ATR-IR spectra of Mn(II) complexes (a,b) with initial acids (c,d) in two spectral ranges: 3700–2400 cm^{-1} (left) and 1800–1000 cm^{-1} (right).

1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk.

3. Results and discussion

The complexes were synthesized by the reaction of manganese(II) chloride with ammonium salt of 4-chloro-2-methylphenoxyacetic acid (MCPA); 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-bromophenoxyacetic acid (4-Br) according to the procedure described in the experimental section. The compounds were obtained in the form of microcrystalline powders and were initially characterized by X-ray powder diffraction technique and infrared spectroscopy. The formulas of the complexes were determined based on the results of elemental and X-ray fluorescence analyses. The structural changes of substances during thermal treatment were studied in the range of 293–1173 K. In order to estimate the nature of metal–ligand bonding and to study the surroundings of metal ions the magnetic susceptibility of complexes was measured in temperature range of 1.8–300 K.

The toxicity of Mn(II) complexes with herbicides was tested using Chinese hamster lung fibroblast (V79) and the human immortalized keratinocyte cells (HaCaT) with the procedure presented in our previous article describing the Co(II), Ni(II) and Cu(II) coordination compounds with MCPA and 2,4-D [9]. As for these three cations, connections with Mn(II) showed low cytotoxicity against studied cells, therefore the biological research will not be discussed further.

For manganese(II) complex with 4-bromophenoxyacetic acid, dissolved in the DMF solution, it was possible to obtain single crystals suitable for X-ray crystallography. The X-ray crystal structure analysis showed the formation of new hexanuclear compound with solvent molecules included in the metal coordination sphere.

3.1. *Structural characterization*

The synthesis gave rise to the formation of hydrated complexes: $Mn(MCPA)_2{\cdot}2H_2O$, $Mn(2,4\text{-}D)_2{\cdot}2H_2O$ and $Mn(4\text{-}Br)_2{\cdot}3H_2O$. All compounds were obtained as microcrystalline powders. The Mn(II) complexes crystallized in monoclinic crystal system with different volumes of the unit cell with the smallest value observed for the bromine derivative (Table 1).

Despite of the differences in the unit cell parameters, phenoxyacetates of Mn(II) had analogous infrared spectra (Fig. 1a and 1b). In

Table 2
Temperature ranges of thermal stability in air at 293 – 1173 K and the enthalpy values of dehydration process for analysed complexes.

Complex	ΔT_1 (K)	Mass loss (%)		n H_2O	ΔT_2 (K)	Mass losses (%)		ΔH_{1H2O}
		calcd.	Found			calcd.	Found	(kJ/mol)
$Mn(MCPA)_2{\cdot}2H_2O$	350–386	7.45	8.13	2	400–522	85.31	85.77	38.38
$Mn(2,4\text{-}D)_2{\cdot}2H_2O$	378–408	6.78	7.23	2	423–893	85.62	87.60	44.64
$Mn(4\text{-}Br)_2{\cdot}3H_2O$	298–403	10.77	9.72	3	497–640	85.04	85.04	26.04

ΔT_1 - temperature range of dehydration process, ΔT_2 - temperature range of anhydrous complex degradation, n – number of water molecules lost in one stage, ΔH_{1H2O} - enthalpy value for 1 molecule of dehydration process.

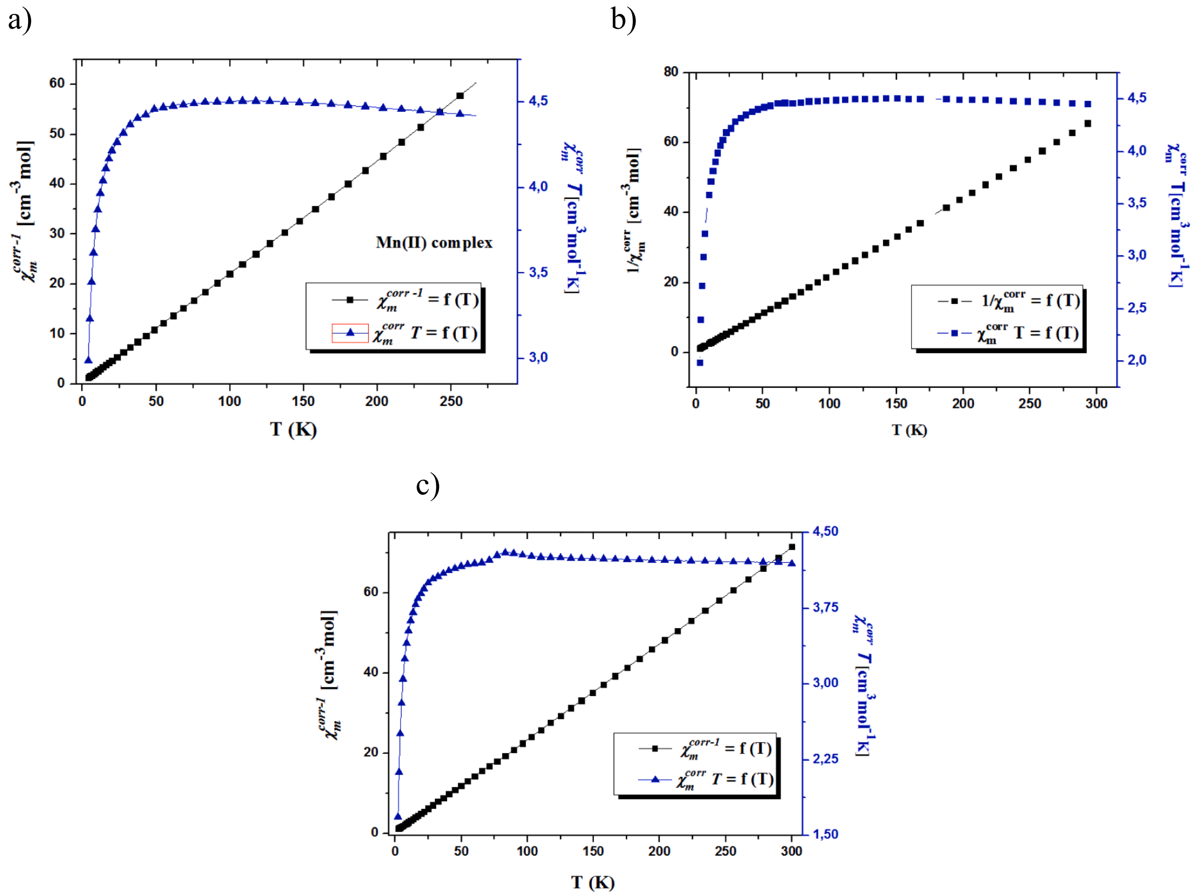

Fig. 2. Relationships of χ_m^{corr} and χ_m^{corr-1} *vs. T* in the range of 1.8–300 K for Mn(II) complexes with a) 4-chloro-2-methylphenoxyacetic acid (MCPA), b) 2,4-dichlorophenoxyacetic acid (2,4-D) and c) 4-bromophenoxyacetic acid (4-Br).

their ATR-IR spectra there was a broad band between 3600 and 2800 cm^{-1} indicating the presence of water molecules (confirmed by elemental and thermal analyses, Fig. 1a). Additionally, several maxima between 3100 and 2800 cm^{-1} correspond to the C–H stretching vibrations. The infrared spectra of free ligands had also a broad band but in different region, viz. 3200–2500 cm^{-1} assigned to the –OH (from carboxyl group) stretching vibration (Fig. 1c). Several bands corresponding to the C–H stretching modes were observed at the same position (within the experimental error) for each pair of free organic ligand and its Mn(II) complex.

Moreover, the carboxylic groups in free acids yielded absorption double bands around 1700 cm^{-1} (Fig. 1d). After the deprotonation, the bands corresponding to the asymmetric and symmetric carboxylate stretching vibrations, $v_{as}COO^-$ and $v_{sym}COO^-$, were observed in the spectra of Mn(II) complexes with acid anions (Fig. 1b). In the IR spectra, the position and the shape of bands corresponding to the carboxylate stretching modes were similar to those reported in our previous papers [9–11] for complexes of MCPA, 2,4-D and 4-Br with Co(II) and Ni(II) - compounds with octahedral molecular geometry.

The positions of bands, assigned to the C–O$_{ether}$ and C–Cl/Br stretching vibrations were very similar in the IR spectra of parent ligands and their Mn(II) complexes (Fig. 1b and 1d), which suggests that neither O ether nor Cl/Br atoms had coordinated to the Mn(II).

3.2. Thermal characterization of complexes

Thermogravimetric measurements of analysed complexes were carried out in air in the range of 293–1173 K (Table 2). TG, DTG and DSC curves were recorded using the DSC/TG technique (Figs. 4S-6S in the Supplementary material). Being heated up to 1173 K the Mn(II) complexes decomposed in three steps. They were stable up to 298–378 K. Next, in the range of 298 – 408 K, all complexes underwent a one-step dehydration with endothermic peaks (DSC curves) loosing 2–3 molecules of water and formed anhydrous compounds. For dihydrate Mn(II) complexes with MCPA and 2,4-D the energetic effects accompanying the dehydration process were similar, whereas the enthalpy for the

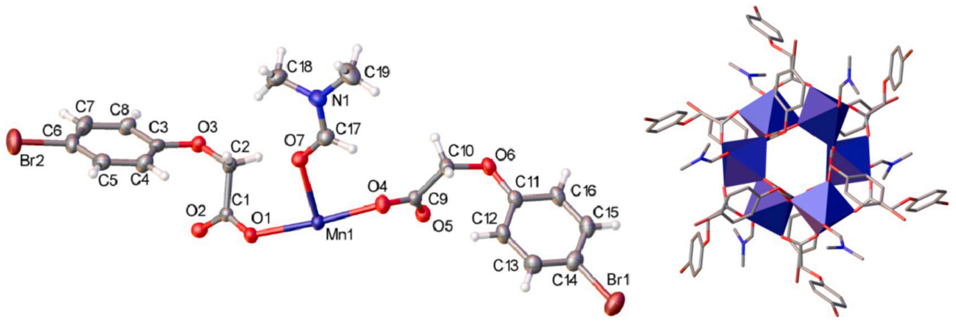

Fig. 3. Molecular structure and atom labelling scheme of the asymmetric unit (left, displacement ellipsoids were drawn at 50 % probability level). The structure of the coordination units composed of six manganese cores linked through oxygen bridges (right).

Table 3
Selected bond lengths and angles for Mn(II) complex with 4-bromophenoxyacetic acid recrystallized from DMF.

Bond	Length /Å	Bond	Length /Å
Mn1-O1	2.220(2)	Mn1-O5^{iii}	2.158(2)
Mn1-O1^{ii}	2.223(2)	Mn1-O4	2.141(2)
Mn1-O2^{i}	2.190(2)	Mn1-O7	2.212(2)
Angle	**Value/°**	**Angle**	**Value/°**
O2^{i}–Mn1–O1^{ii}	89.15(8)	O5 ^{iii}–Mn1–O2^{i}	174.68(8)
O2^{i}–Mn1–O1	85.16(8)	O4–Mn1–O1	173.09(9)
O5^{iii}–Mn1–O1^{ii}	95.87(8)	O7–Mn1–O1^{ii}	171.10(8)
O5 ^{iii}–Mn1–O1	96.04(8)	O7–Mn1–O1	91.75(8)
O4–Mn1–O1^{ii}	85.38(8)	O7–Mn1–O2^{i}	87.69(8)
O4–Mn1–O2^{i}	88.17(8)	O7–Mn1–O5^{iii}	87.09(9)
O4–Mn1–O5^{iii}	90.45(8)	O7–Mn1–O4	86.21(9)

Symmetry codes: ^{i} *y–x, –x, z*; ^{ii} *y, –x +y, 2–z*; ^{iii} *–y +x, x, 2–z.*

trihydrate bromine compound was lower, which suggests weaker bonding of water molecules (Table 2).

Further heating of anhydrous compounds led to the formation of MnO in the case of Mn(MCPA)$_2$·2H$_2$O, while Mn$_2$OCl$_2$ and Mn$_2$OBr$_2$ were formed for Mn(2,4-D)$_2$·2H$_2$O and Mn(4-Br)$_2$·3H$_2$O, respectively. The final product of decomposition of Mn(II) compound with MCPA herbicide was Mn$_2$O$_3$ whereas Mn$_3$O$_4$ was formed for complexes with 2,4-D and 4-Br anions, respectively.

3.3. Magnetic characterization of complexes

In order to investigate the coordination spheres of Mn(II) ion the magnetic susceptibilities of complexes were measured. The relationships of χ_m^{corr} and χ_m^{corr-1} *vs. T* in the range of 1.8 – 300 K are presented in Fig. 2. The experimentally determined values of magnetic moments were in the ranges 4.89 – 5.94 μ_B for Mn(MCPA)$_2$·2H$_2$O; 3.99 – 5.97 μ_B for Mn(2,4-D)$_2$·2H$_2$O and 5.37 – 5.78 μ_B for Mn(4-Br)$_2$·3H$_2$O. Those values are close to spin only values for the Mn(II) ion calculated from the equation $\mu_{eff} = [4\ s(s+1)]^{1/2}$ in the absence of the magnetic interactions for present spin-system. Its theoretical value calculated at room temperature is equal to 5.9 μ_B. For Mn(II) ion complexes the magnetic moments were 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 a heavy atom in opposite directions and this diminishes the resultant magnetic moment.

The experimental data showed that the studied Mn(II) compounds are high – spin complexes with octahedral symmetry around the central ion and weak ligand field. They obey the Curie-Weiss law showing the paramagnetic properties. A very weak antiferromagnetic interaction between Mn(II) cations within complex molecule or a weak intermolecular hydrogen bonds in the crystal lattice may appear [12–14].

3.4. Single crystal X-ray diffraction of the recrystallized complex

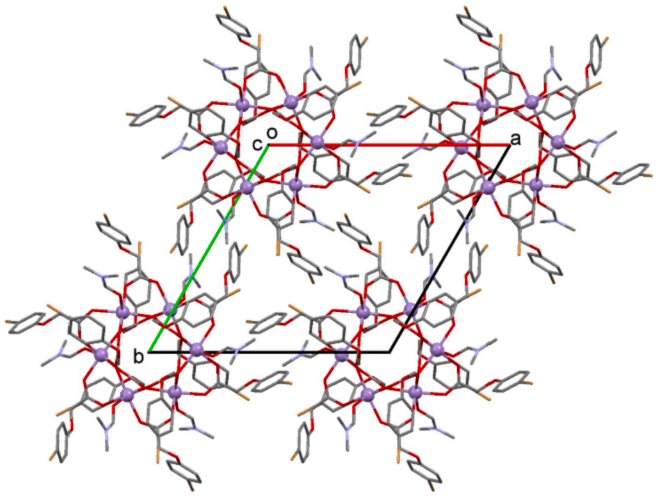

Fig. 4. Crystal packing of Mn$_6$(4-Br)$_{12}$·6DMF with the hexanuclear coordination units stacked in columns along the *c* crystallographic axis.

The colourless crystals of Mn(II) complex with 4-bromophenoxyacetic acid (recrystallized from DMF) suitable for an X-ray single crystal structure analysis, were obtained. The asymmetric unit of the new compound was composed of one metal cation, one DMF molecule and two deprotonated 4-bromophenoxyacetate anions (Fig. 3).

The coordination unit occupied a special position of an inversion three-fold axis. It was multiplied by this symmetry element and formed a closed cyclic hexameric unit with Mn…Mn distances of 3.6772(6) Å (Fig. 3).

The carboxylic acid anions differ in the coordination mode. The ligands occupying the horizontal part of the complex coordinated to three Mn(II) ions through one bifurcated O atom and one simple bridge. The vertically located carboxylic acid anions served as bidentate ligands, each bridging two metal cations. Around each Mn(II) the octahedron was formed and the Mn–O bond distances ranged from 2.141(2) to 2.223 (2) Å (Fig. 3, Table 3).

The search in the Cambridge Structural Database showed that such Mn(II) complex with hexameric structure is unusual, since the analogous polynuclear manganese carboxylate clusters contain usually manganese cations in two oxidation states simultaneously: +2 and +3 [15].

In the crystal net the hexanuclear coordination units were arranged

Table 4
Intermolecular interactions (Å, °).

D–H···A	D–H	H···A	D···A	<DHA
*C*2–H2A…O2^{i}	0.97	2.342	3.116(4)	136
*C*2–H2A…O3^{i}	0.97	2.559	3.435(3)	150
C7–H7…Br^{ii}	0.93	2.989	3.840(5)	153

Symmetry codes: ^{i} –x + y, –x, z; ^{ii} ×, 1 + y, –1 + z.

in columns along the *c* crystallographic axis (Fig. 4). Between the molecules there were only weak intermolecular interactions (Table 4) because of a hydrophobic exterior layer structure of complex. The most pronounced intermolecular interaction was C7–H7…Br1^{i} (symmetry code: $^{i} \times , 1 + y, -1 + z$). Additionally the halogen atoms formed short Br…Br contacts at 3.665(1) Å distance.

4. Conclusion

Three Mn(II) complexes with 4-chloro-2-methylphenoxyacetic acid (MCPA), 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-bromophenoxyacetic acid (4-Br) were synthesized and characterized. The thermal decompositions of obtained compounds proceeded in three steps as follows:

$$\mathbf{Mn(MCPA)_2{\cdot}2H_2O} \rightarrow \mathrm{Mn(MCPA)_2} \rightarrow \mathrm{MnO} \rightarrow \mathrm{Mn_2O_3}$$
$$\mathbf{Mn(2{,}4\text{-}D)_2{\cdot}2H_2O} \rightarrow \mathrm{Mn(2{,}4\text{-}D)_2} \rightarrow \mathrm{Mn_2OCl_2} \rightarrow \mathrm{Mn_3O_4}$$
$$\mathbf{Mn(4\text{-}Br)_2{\cdot}3H_2O} \rightarrow \mathrm{Mn(4\text{-}Br)_2} \rightarrow \mathrm{Mn_2OBr_2} \rightarrow \mathrm{Mn_3O_4}$$

The hydrated Mn(II) compounds are high – spin complexes with octahedral symmetry around the central ion and weak ligand field. They obey the Curie-Weiss law and are paramagnetic. The analysis of infrared spectra indicated the similar bonding of phenoxyacetates anions to the metal cation. The Mn(II) cations are surrounded by carboxylate oxygen atoms and water molecules. The coordination sphere of metal center can be rearranged, as was observed in the case of complex with 4-bromophenoxyacetic acid with the weakest bonding of water molecules. After its recrystallization from dimethylformamide (DMF), the detachment of water molecules and attachment of the DMF molecules were observed. Due to the exchange of solvent molecules, the formation of a hexanuclear manganese(II) carboxylate coordination clusters with a hydrophobic exterior was observed in crystal.

CRediT authorship contribution statement

Aleksandra Drzewiecka-Antonik: Conceptualization, Validation, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Wiesława Ferenc:** Resources. **Barbara Mirosław:** Investigation. **Dariusz Osypiuk:** Investigation. **Jan Sarzyński:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115370.

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