COMMUNICATION

The Synthesis of Zinc(II) and Cadmium(II) 2, 4-Dichlorophenoxyacetates in Water–Methanol Environment. Structure and Properties of Polymeric [Zn(2,4-D)$_2$(MeOH)$_2$]$_n$ and [Cd(2,4-D)$_2$(H$_2$O)$_2$]$_n$

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Abstract The zinc(II) and cadmium(II) 2,4-dichlorophenoxyacetate salts were synthesized in mixed water–methanol environment and characterized by elemental analysis, IR spectrometry and thermal analysis coupled with mass spectrometry. The crystal structures were determined by X-ray crystallography (compound **1**, [C$_{18}$H$_{18}$Cl$_4$O$_8$Zn]$_n$: monoclinic, $P2_1/c$, $a = 19.094$, $b = 7.378$, $c = 8.008$, $\alpha = 90.00$, $\beta = 101.134$, $\gamma = 90.00$, $V = 1106.95$; compound **2**, [C$_{16}$H$_{14}$Cl$_4$O$_8$Cd]$_n$: monoclinic, $P2_1/c$, $a = 17.730$, $b = 7.293$, $c = 8.060$, $\alpha = 90.00$, $\beta = 95.18$, $\gamma = 90.00$, $V = 1037.9$). The structural and some thermal data about the presented cadmium salt were previously reported (Song et al. Acta Crystallogr E 62:m2397, 2006; Kobylecka et al. Thermochim Acta 482:49, 2009).

Keywords Zinc · Cadmium · 2,4-Dichlorophenoxyacetic acid · Crystal structure · IR spectroscopy · Thermal decomposition

Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D-H) is a member of arylcarboxylic acids family, and compounds belonging to it are commonly used as herbicides [1–4]. They herbicidal activities originate from their structural similarity with auxins and, in consequence of auxins replacement in biological processes, changes in the plant protein synthesis accompanied by decrease or disfunctionalisation of plants cell division [5] as well as by increase of oxygen reactive

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species synthesis causing the oxidative stress in the plants [6, 7]. Particular compounds of this group have special applications, for example, in high concentration they are the potent weed killers e.g. against broad-leaf weed [8], sugarcane [2], pastures [8], turf [2], woody plants [9, 10] in cereal grains growing such as wheat, rice, oats, corn [11], in little amounts as auxins analogues increasing the selected plants growth [12], as a plant hormones [13]. They are also commonly used in aquatic areas (lakes, ponds, etc.) to prevent the growth of selected aquatic plants (including helophytes) and in non-crop areas (parks, roadsides, railroads, etc.) [14]. The 2,4-D is a peroxisome proliferator [15] and in plant cells it causes the abnormality of mitosis and meiosis [16]. Due to it relatively high solubility [17] it can be easily applied to the soil as we as the aquatic areas.

In recent years there is observed an increasing interest on 2,4-D-H salts and coordination compounds, including salts of transition metals such as Cd(II) [12, 18, 19], Mn(II) [20–22], Zn(II) [23, 24], Mg(II) [21], Ni(II) [25], Ag(I) [26], Fe(II) [27], Cu(II) [28], alkaline metals and p block elements such as Ba(II) [29], Ca(II) [30], Pb(II) [12] and lanthanides like Gd [31], Nd [32] and Eu [33]. Several mixed-ligand coordination compounds with 2, 4-dichlorophenoxyacetate (2,4-D) and other ligands (e.g. α-aminoacids [34], N-bases such as phenanthroline [33, 35], pyrazole [36], pyridine [37], pyrazine [38], imidazole [39] and bipyridine [28, 40]) are also known. As it was mentioned, the formation of zinc and cadmium salts in water environment was previously reported. Because the hydroxyl group is one of the most common oxygen type donors in biological system, the examination of compound formed in such group presence (competing with water molecules) was undertaken. As a model for –OH group the MeOH was chosen as the simplest molecule with size comparable to water molecules.

## Experimental

Materials and Synthesis

The technical grade 2,4-D-H from "Rokita S.A." in Brzeg Dolny was purified by double crystallization from toluene. The purity of the recrystallised compound was investigated by DSC determination. The measured melting point (140.4 °C) is adequate to the literature data (140.5 °C [41]). The identity of purified compound was confirmed by ^{1}H NMR. Other chemicals were analytical grade form POCh Gliwice.

The $ZnCl_2$ (1.364 g, 10.0 mmol) and $CdCl_2$ (2.281 g, 10.0 mmol) were dissolved in 20 cm^3 of water each. The both solutions were prepared in septuplicate. The 20.0 mmol of purified 2,4-D-H was dissolved in 20 cm^3 of water:methanol mixtures (the solution with following molar proportions were prepared in duplicate 0:20, 2:18, 5:15, 8:12, 10:10, 15:5 and 18:2) and heated. To the boiling solutions equimolar amounts of solid NaOH (20.00 mmol) were added to transfer the acid into well dissociated sodium salt (2,4-D-Na) [41]. The prepared solutions of $ZnCl_2$ and $CdCl_2$ were added very slowly to the stirring solutions of 2,4-D-Na (above described). Immediately, after two solutions mixing the white crystals were formed.

The obtained products were filtered, washed three times with distilled water and dried in air. The usage of different amounts of water and methanol in the syntheses did not affect obtained product formula, i.e. all zinc salts have the same composition as well as the cadmium salts. The identity of fractions was confirmed by X-ray powder diffraction (XRPD), IR spectroscopy and elemental analyses.

Physical Measurements

IR spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4,000–400 cm^{-1} with the samples in the form of KBr pellets. The thermal analysis was carried out in a TG/DTA-SETSYS-16/18 thermoanalyser coupled with ThermoStar (Balzers) mass spectrometer. The sample was heated in corundum crucibles up to 1,000 °C at a heating rate 5 °C/min in air atmosphere. The processes temperature ranges were determined by means of thermoanalyser Data Processing Module [42]. The solid transition products of thermal decomposition were determined from derivatographic curves and on the basis of IR spectra and elemental analyses of the sinters. The final and some transition products of decomposition were confirmed by XRPD using the Powder Diffraction File [43]. Elemental analyses were
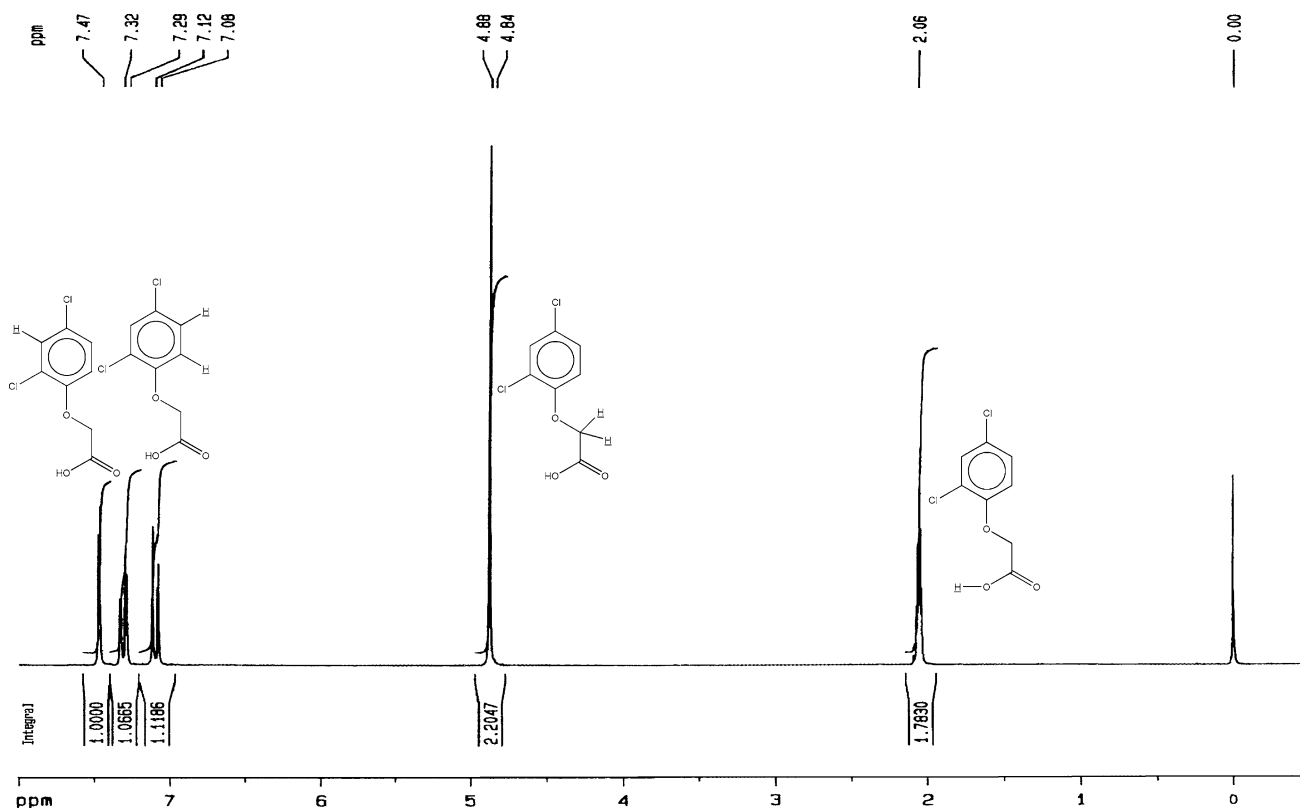
Fig. 1 The ^{1}H NMR spectrum of 2,4-D-H in deuterated chloroform

carried out using Vario EL III CHNOS Elemental Analyzer (C, H, N, O). The chlorine contents were determined in mineralised samples by nephelometric titration with the 0.01 mol/dm^3 water solution of $AgNO_3$ serving as a precipitation agent. The zinc and cadmium contents were determined in mineralised samples by complexometric titration with the 0.01 mol/dm^3 water solution of EDTA serving as complexing agent and eriochrome black T serving as indicator. Analysis for complexes [Calculated/ Found (%)]: compound **1**: C 37.96%/37.86%, H 3.19%/ 3.22%, O 22.47%/22.61%, Cl 24.90%/24.96%, Zn 11.48%/ 11.38%; compound **2**: C 32.65%/32.44%, H 2.40%/2.28%, O 21.75%/21.66%, Cl 24.10%/23.99%, Cd 19.10%/ 19.17%.

NMR Spectroscopy

^{1}H NMR spectrum was recorded on Bruker Avance DPX 250 MHz spectrometer with the deuterated chloroform used as a solvent of 2,4-D-H. Chemical shifts were reported in ppm in references to TMS for ^{1}H NMR spectrum.

In the ^{1}H NMR spectrum typical bands of pure 2,4-D-H are observed (Fig. 1). The methylene group protons signals are observed as two singlets at 4.84 and 4.88 ppm. Proton in the aromatic ring existing between two chlorine atoms gives the singlet signals at 7.47 ppm and it is shifted to a lower field in comparison to other aromatic ones because of the influence of the environment. Two other protons of aromatic ring form a doublet signals at 7.10 and 7.32 ppm. Proton of carboxylic group exhibits in NMR spectra as a broadened singlet signal at 2.06 ppm.

X-Ray Crystallography

Colourless rectangular prism shape crystals were mounted on a KM-4-CCD automatic diffractometer equipped with CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at temperature 291.0 (3) K, with

Table 1 Crystal data and structure refinement details for studied compounds

Compound	1 (Zn)	2 (Cd)
Empirical formula	$C_{18}H_{18}Cl_4O_8Zn$	$C_{16}H_{14}CdCl_4O_8$
Formula weight	569.49	588.47
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature	291.0 (3)	291.0 (3)
Wavelength	$\lambda(\mathrm{Mo}K\alpha) = 0.71073$	$\lambda(\mathrm{Mo}K\alpha) = 0.71073$
Unit cell dimensions (Å, °)	$a = 19.0940(9)$	$a = 17.730(4)$
	$b = 7.3781(4)$	$b = 7.2930(10)$
	$c = 8.0083(4)$	$c = 8.060(2)$
	$\alpha = 90.00$	$\alpha = 90.00$
	$\beta = 101.134(4)$	$\beta = 95.18(3)$
	$\gamma = 90.00$	$\gamma = 90.00$
Volume (Å^3)	1106.95(10)	1037.9(4)
Z, calculated density (mg/m^3)	2, 1.709	2, 1.883
Absorption coefficient (mm^{-1})	1.635	1.608
$F(000)$	576	580
Crystal size (mm)	$0.276 \times 0.208 \times 0.103$	$0.359 \times 0.180 \times 0.024$
θ range for data collection (°)	3.52–25.11	3.62–25.10
Index ranges	$-22 \leq h \leq 22, -8 \leq k \leq 8, -9 \leq l \leq 9$	$-21 \leq h \leq 21, -8 \leq k \leq 8, -9 \leq l \leq 9$
Reflections collected/unique	11889/1878 [$R_{(int)} = 0.0368$]	27043/1843 [$R_{(int)} = 0.0101$]
Completeness to $\theta = 25°$	99.9%	99.7%
Min. and max. transmission	0.660 and 0.852	0.593 and 0.971
Data/restraints/parameters	1878/0/143	1843/0/133
Goodness-of-fit on F^2	1.197	1.092
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0448$, $wR_2 = 0.1144$	$R_1 = 0.0280$, $wR_2 = 0.0694$
R indices (all data)	$R_1 = 0.0451$, $wR_2 = 0.1145$	$R_1 = 0.0351$, $wR_2 = 0.0740$
Largest diff. peak and hole (e Å^{-3})	0.450 and -0.543	0.576 and -0.403
CCDC deposition no.	832494	832495

ω scan mode. The 15 s exposure time was used in both measurements, and reflections inside Ewald sphere were collected up to $2\theta = 50°$. The unit cells parameters were determined from least-squares refinement of 3,009 and 4,821 strongest reflections, respectively for **1** and **2**. Details concerning crystal data and refinement are given in Table 1. Examination of reflections on two reference frames monitored after each 20 frames measured showed no loss of the intensity during measurements. Lorentz, polarization, and numerical absorption [44] corrections were applied. The structures were solved by direct methods. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F^2. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent atom with individual isotropic displacement factor equal 1.2 times the value of equivalent displacement factor of the patent non-methyl carbon atoms and 1.5 times for patent oxygen atoms and methyl group carbon atoms. The carbon bonded hydrogen atom positions were idealised after each cycle of refinement. The SHELXS97, SHELXL97 and SHELXTL [45] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs. Selected interatomic bond distances and angles are listed in Table 2, and geometrical parameters of intermolecular interactions are listed in Table 3. The determined structural parameters of **2** were consistent with previously reported ones [18].

Table 2 Selected structural data for studied compounds (Å, °)

1		**2**	
Zn1–O2	2.142(3)	Cd1–O2	2.269(2)
Zn1–O3	2.060(3)	Cd1–O3	2.281(2)
Zn1–O4	2.093(3)	Cd1–O4	2.332(3)
C1–Cl2	1.731(5)	C2–Cl2	1.722(4)
C3–Cl1	1.738(5)	C4–Cl1	1.737(4)
O3^{iii}–Zn1–O3^{ii}	180.0	O2^{iv}–Cd1–O2	180.0
O3^{iii}–Zn1–O4^{i}	91.08(12)	O2–Cd1–O3^{v}	77.32(7)
O3^{iii}–Zn1–O4	88.92(12)	O2–Cd1–O3^{iii}	102.68(7)
O4^{i}–Zn1–O4	180.0	O3^{iii}–Cd1–O3^{v}	180.0
O3^{iii}–Zn1–O2^{i}	87.43(13)	O2–Cd1–O4^{iv}	96.01(8)
O3^{iii}–Zn1–O2	92.57(13)	O2–Cd1–O4	83.99(8)
O4–Zn1–O2^{i}	90.12(14)	O3^{v}–Cd1–O4	90.15(8)
O4–Zn1–O2	89.88(14)	O3^{iii}–Cd1–O4	89.85(8)
O2–Zn1–O2^{i}	180.0	O4^{iv}–Cd1–O4	180.0

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, y + 0.5, -z + 1.5$; (iii) $x, -y + 0.5, z - 0.5$; (iv) $-x + 1, -y + 1, -z$; (v) $-x + 1, -y + 0.5, -z + 0.5$

Table 3 Hydrogen bonds in studied compounds (Å, °)

	D–H	H⋯A	D⋯A	D–H⋯A
1				
O4–H4O⋯O2^{v}	0.85	1.86	2.681 (5)	159.9
C8–H8B⋯O3^{iii}	0.97	2.40	3.239 (6)	144.1
2				
O4–H4O⋯O3^{i}	0.80	2.19	2.847(3)	139.1
O4–H4O⋯O2^{vi}	0.80	2.44	3.109(3)	140.8
O4–H4P⋯O1^{vi}	0.74	2.43	3.047(3)	142.6

Symmetry codes: (i) $-x + 1, +0.5 + y, +0.5 - z$; (iii) $x, 0.5 - y, -0.5 + z$; (v) $-x + 1, 0.5 + y, 1.5 - z$; (vi) $x, 1.5 - y, -0.5 + z$

Results and Discussion

The structural investigations show that the Zn and Cd atoms occupies, respectively, special positions *b* and *d* of $P2_1/c$ space group (cell choice 1) with site symmetry $\bar{1}$ and multiplicity 2 [46], thus asymmetric units contain a half of the $ZnC_{18}H_{18}Cl_4O_8$ and $CdC_{16}H_{14}Cl_4O_8$ moieties (Figs. 2, 3). These moieties are expanded to the two dimensional polymers (Figs. 4, 5) via symmetry centres located at 1/2, 1/2, 0; 1/2, 0, 1/2 in compound **1**, at 1/2, 1/2, 1/2; 1/2, 0, 0 in compound **2** and *c* glide planes. These polymers create layers along crystallographic (100) plane (Figs. 4, 5). The both metal centres of title compounds create the 4-c uninodal sql/Shubnikov tetragonal plane net, described by $\{4^4.6^2\}$ Schläfli symbol and [4.4.4.4.6(2)0.6(2)] extended point symbol. The central atoms are six coordinated, and the coordination sphere contains four carboxylate oxygen atoms form four bridging groups and two oxygen atoms from two methanol or water molecules (respectively for compound **1** and **2**), thus each anion acts as bridging ligand toward two cations. The coordination polyhedra of central atoms can be described as slightly distorted tetragonal bipyramids (Fig. 6) [47] (all three polyhedron internal tetragons are planar and cross the central atom by symmetry). The polyhedron internal planes of **1** are inclined at 88.48(8), 77.23(8), and 83.80(7)°, respectively for pairs containing O2/O3–O2/O4, O2/O4–O3/O4 and O2/O3–O3/O4 atoms and their respect symmetry equivalents. These angles for **2** are 88.91 (11), 87.43 (11), and 89.83 (11)°, respectively as above. Thus it can be stated that the distortion from the ideal polygon is distinctly smaller in **2** than in **1**. In both compounds the organic anion stiff parts (dichlorophenoxy and acetate moieties) are inclined (in terms of the dihedral angle calculated between respect weighted least-squares planes), but the inclination is distinctly smaller in **1** (26.64 (19)°) than in **2** (85.15 (10)°), than in pure 2,4-D-H acid (81.30° [48]) and than in the solvent-free zinc 2,4-D salt (77.61 and 82.26° [24]).

Fig. 2 The solid state structure of compound **1** with atom numbering scheme, plotted with 50% probability of displacement ellipsoids of non-hydrogen atoms. The hydrogen atoms are plotted as the spheres of arbitrary radii. The symmetry generated atoms indicated by A, B, C, and D letters were obtained via $-x + 1$, $-y + 1$, $-z + 1$; $-x + 1$, $y - 1/2$, $-z + 3/2$; $-x + 1$, $y + 1/2$, $-z + 3/2$ and x, $-y + 1/2$, $z - 1/2$ symmetry transformations, respectively
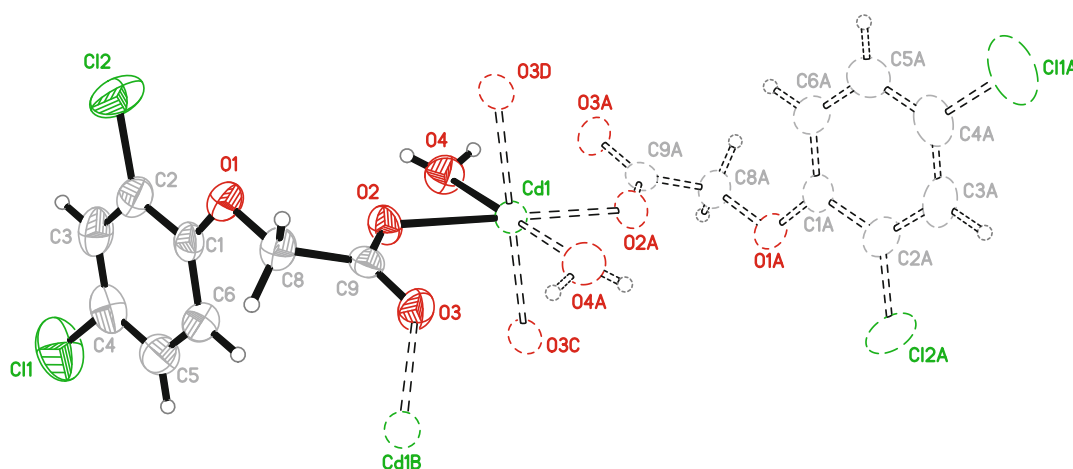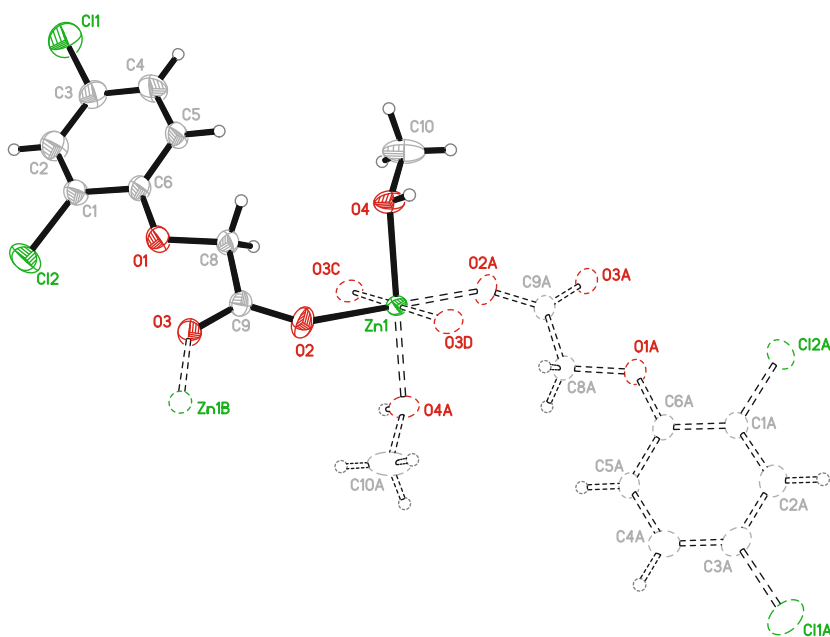
Fig. 3 The solid state structure of compound **2** with atom numbering scheme, plotted with 50% probability of displacement ellipsoids of non-hydrogen atoms. The hydrogen atoms are plotted as the spheres of arbitrary radii. The symmetry generated atoms indicated by A, B, C, and D letters were obtained via $-x + 1$, $-y + 1$, $-z$; $-x + 1$, $y - 1/2$, $-z + 1/2$ and $-x + 1$, $y + 1/2$, $-z + 1/2$ and x, $-y + 1/2$, $z - 1/2$ symmetry transformations, respectively

The bridging carboxylate groups are bonded unsymmetrically to the central atoms (in terms of metal–oxygen bond distances and bond strengths based on the bond valences, as described below), however the unsymmetricity is distinctly smaller in compound **2**. In both compounds the delocalised COO bond lengths are equal in the range of the experimental error, thus it can be stated that carboxylate groups exhibit almost perfect delocalisation and that the π electrons are divided equally to the C–O bonds.

The bond valences were computed as $v_{ij} = \exp[(R_{ij} - d_{ij})/b]$ [49, 50], where R_{ij} is the bond-valence parameter (in the

formal sense R_{ij} can be considered as a parameter equal to the idealised single-bond length between i and j atoms for given b) and b was taken as 0.37 Å [51, 52]. The R_{Zn-O}, R_{Cd-O}, were calculated by previously described method [53–55] and calculated values were 1.6950, 1.8818, Å respectively. The computed bond valences are $v_{Zn1-O2} = 0.299$, $v_{Zn1-O3} = 0.373$, $v_{Zn1-O4} = 0.341$, $v_{Cd1-O2} = 0.351$, $v_{Cd1-O3} = 0.340$ and $v_{Cd1-O4} = 0.296$. The computed total valences of the central atoms are very close to the expected value $+2$ (2.025 and 1.975 respectively for **1** and **2**) and observed small deviations may originate from restrains imposed by bridging ligands creating polymeric
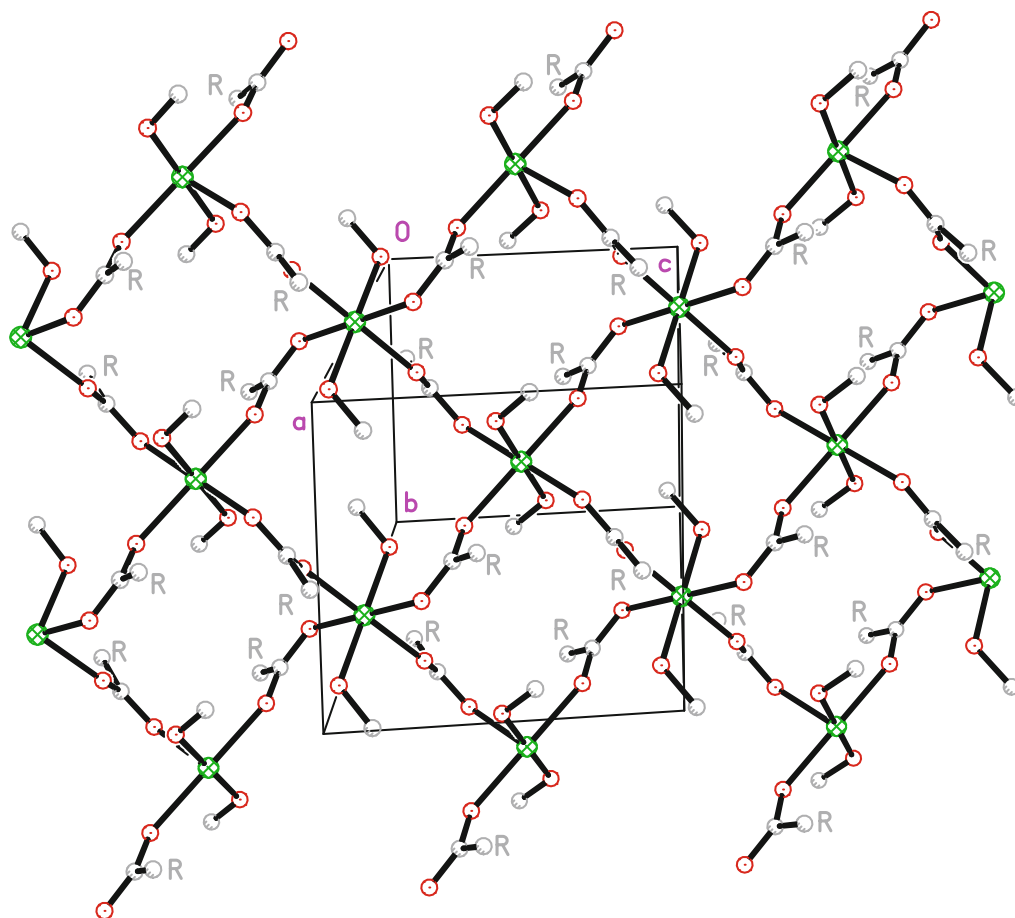
Fig. 4 The part of molecular packing of compound **1** showing polymeric net. The R letter indicates the 2,4-dichlorophenoxy moiety and the hydrogen atoms are omitted for clarity

net, what prevents the coordination environment from attaining most favourable geometry. In compound **1** the solvent molecule is bound with strength comparable to the carboxylate bonds strength and in compound **2** these last bonds are the strongest ones (see Table 2 and above bond-valence values).

The polymer chains of the both compounds are internally linked by the O–H⋯O hydrogen bonds, an in case of **1** also by C–H⋯O weak intramolecular interactions (Table 3). In both cases the neighbouring chains are well separated and do not interact even by weak intramolecular bonds.

Ionisation and complexation of the carboxylic group leads to the absence of vibrations of non dissociated moiety about 1,770 cm^{-1} [56, 57] (Table 4) and appearance of the two bands characteristic for carboxylate ions (at about 1,400 and 1,600 cm^{-1}). The separation factor $\Delta v = v_{as}$ (COO) $- v_s$(COO) in **1** and **2** is close to the 190 cm^{-1}, what confirms presence of bridging bidentate carboxylate groups [58–60]. Strong bands at 1,481 and 1,483 cm^{-1} attributed to symmetric stretching C$_{aromatic}$–O vibrations

are shifted to a lower frequencies in comparison to pure organic acid, and it could be explained by redistribution of electron density in the oxyacetate moiety after complexation [61]. The oscillators containing the metal atoms as one of they elements lead to creation of bands at about 1,070 and 415 cm^{-1} (Table 4) obviously absent in pure acid. The close packing of aromatic ring caused by formation of polymeric structure leads to changes in regions of spectra at 1460–1440, 1340–1300 and 960–900 cm^{-1}, originating from differed aromatic atoms system vibrations (v_s(C$_{aromatic}$–O), δ(CH$_2$), δ(CH), v(CC), aromatic breathing mode etc. [62–64]). In general complexation leads to shift of these oscillators to higher frequencies.

The thermal decomposition of investigated complex compounds is a gradual process (Fig. 7). According to TG and DTG curves, analyzed compounds decomposes in four steps (Scheme 1). The three steps decompositions were previously reported for Zn(2,4-D)$_2$·3H$_2$O and **2** heated at faster rate (10 °C/min) in static air atmosphere [57] and for these processes the individual steps as well as the transition products differs form currently reported ones.
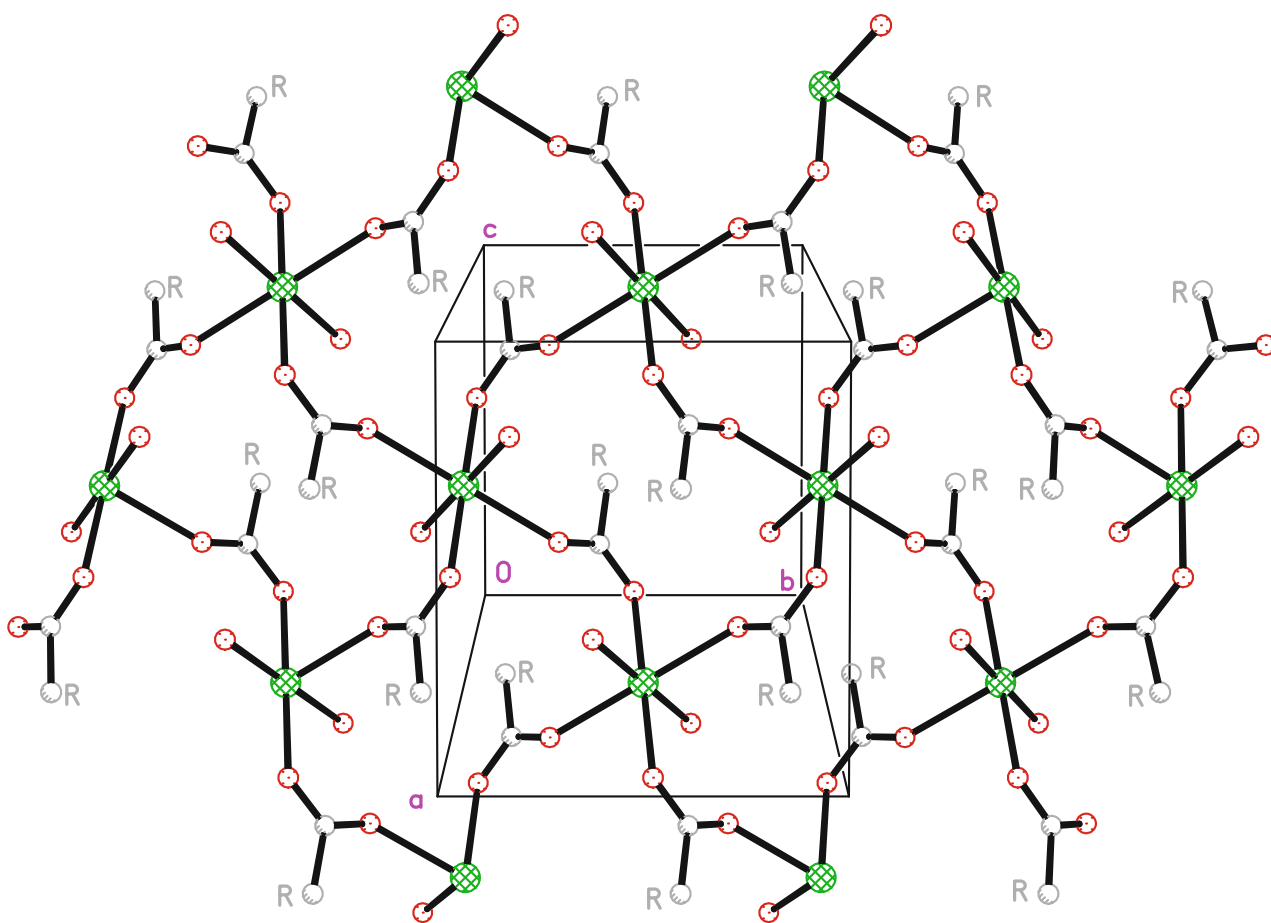
Fig. 5 The part of molecular packing of compound **2** showing polymeric net. The R letter indicates the 2,4-dichlorophenoxy moiety and the hydrogen atoms are omitted for clarity
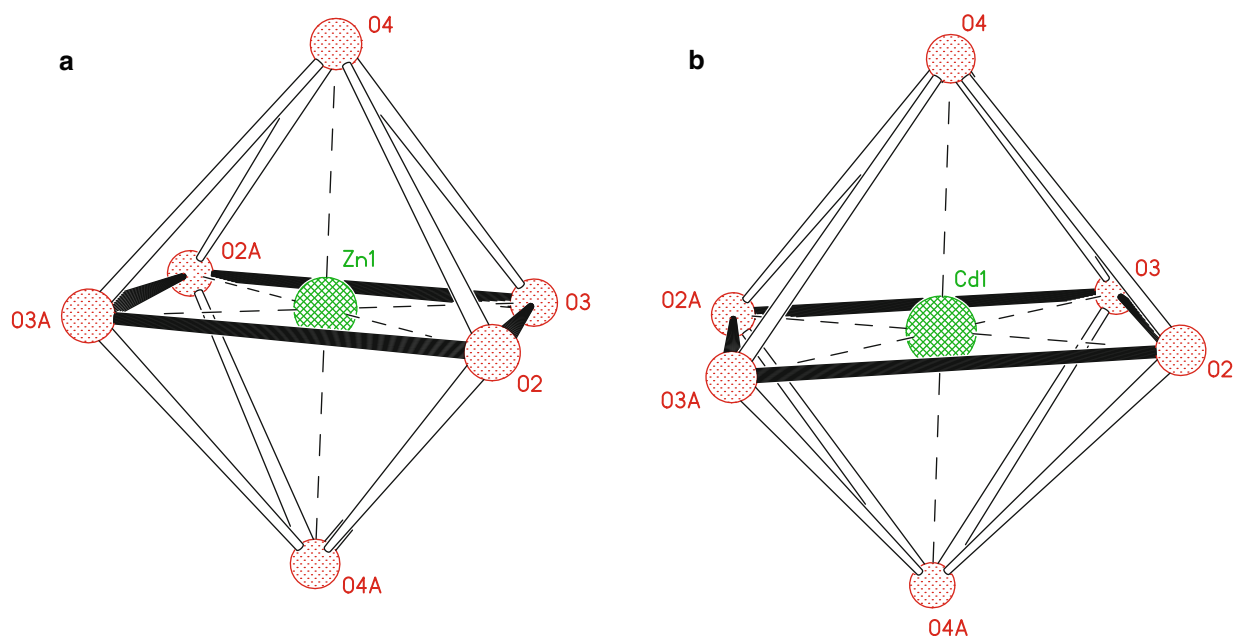
Fig. 6 The coordination polyhedra in compound **1** (**a**) and **2** (**b**)

Table 4 Vibrational frequencies (cm^{-1}) with assignment

Compound 1	Compound 2	2,4-D [56]	Assignment
3445bb	3446bb	3445bb	υ(O–H)
3250vw	3253w	3075m	υ_{as}(O–H)
–	–	1773vs	υ(C=O)
1620vs	1618vs	–	υ_{as}(OCO)
1556w	1554w	1580w	σ(C–H)
1483vs	1481vs	1486vs	υ_s(C$_{aromatic}$–O)
1465vw	1460vw	1449m	δ(CH$_2$)
1443vw	1440w	1434w	δ(CH$_2$), δ(CH), υ(CC)
1430s	1429m	–	υ_s(OCO)
1386w	1392m	1311w	δ(CH$_2$), δ(O–H)
1338s	1338s	1298s	δ(CH$_2$), δ(CH), υ(CC)
1284s	1286vs	1298s	δ(CH$_2$), δ(CH), υ(CC)
1261w	1269w	1262w	β(C–H), δ(C–H) (ring)
1248m	1247m	1235vs	υ-β-rd(CC)
1106m	1107m	1105vs	δ-β(CH)
1070s	1064s	–	υ_s COZn, υ_s COCd
958m	945m	895m	Aromatic breathing mode
802s	796s	842s	δ COO,
765s	767s	796vs	τ(C–H$_{aromatic}$)
716m	713w	721m	τ(C–H$_{aromatic}$), υ(C–Cl)
615w	617m	647m	ρ aromatic
547w	520w	570m	Ring deformation
445w	474m	480vw	Torsion (O–H), δ(CH$_2$),
422w	411w	–	υ Zn–O, υ Cd–O,

Used symbols: *vw* very weak, *w* weak, *m* medium strength, *s* strong, *vs* very strong, υ stretching, δ bending, ρ rocking, σ scissoring, τ waging, ω twisting, β in plane, *s* symmetric, *as* asymmetric, *bb* broad band, *rd* resonance depending mode

The zinc complex compound releases two methanol molecules in two steps (Scheme 1), whereas in hydrated salt Zn(2,4-D)$_2$·3H$_2$O (**1a**) all water molecules are lost in one step [57]. The **1** is stable to about 30 °C higher temperature than **1a** and thermal releasing of methanol molecules it slower process than evolution of water molecules. The decomposition of solvent-free compound starts at distinctly lower temperature for **1** (Scheme 1) than it was previously observed for **1a** (260 °C) and it leads to degradation of whole organic anion in one step with formation of zinc chloride and carbon deposit in the vessel. This is similar to previously observed degradation of chlorinated aromatic compounds [65] and opposite to **1a** where the dichlorophenoxy moieties splits as first with retaining of the oxidised acetate moieties in the sinter. During this stage of the thermal decomposition the following principal volatile products are created: dichlorophenol, benzene, hydrogen chloride, carbon oxide and carbon dioxide. Only the traces of water are observed during this stage of

decomposition. Next, the carbon is removed by oxidation and in following step the zinc chloride slowly evaporates. After ending of the temperature increasing (1,000 °C) the about 0.75 of initial amount of ZnCl$_2$ remains. The further keeping of the sinter at (1,000 °C) leads to its total evaporation after about 3 h. This final product is different from this one observed during the decomposition of **1a** (the ZnO) [57].

The **2** loses the water molecules in one step, as it was previously reported [57], but slower heating leads to extension of this step and it finishes at temperature about 25 °C higher than this one observed in process with faster heating. In general the temperature extension of the dehydratation process as result of slower heating is the less common case, because such slowing generally leads to finishing of dehydratation at lower temperatures due to longer period of heating time. The second stage differs considerably for both speeds of heating. For slower heating, similarly to the **1**, the whole 2,4-D moiety degrades in one step forming the transition and volatile product analogous to these found in thermal decomposition of **1** (Scheme 1), while faster hating leads to splits of the dichlorophenoxy moieties as first, with retaining of the oxidised acetate moieties in the sinter [57]. In the next, third, step the oxidation of deposited carbon is simultaneously accompanied by evaporation of CdCl$_2$ (for **1** these processes were separated). After the complete removing of carbon the about 0.2 of the initial amount of CdCl$_2$ remains and it evaporates completely at about 840 °C (in case of faster heating the process ends also with 100% loss of mass but at distinctly lower temperature: the 770 °C [57]).

Conclusion

The synthesis of zinc and cadmium 2,4-D in mixed water–ethanol environment always lead to incorporate of methanol molecule into zinc salt and never to including of used alcohol to the cadmium salt. The synthesis of zinc salt in alcohol-free water environment leads to formation of [Zn(H$_2$O)$_4$(2,4-D)$_2$]·[Zn(H$_2$O)$_2$(2,4-D)$_2$] and [Zn(2,4-D)$_2$]$_n$ respectively for normal [23] and hydrothermal [24] conditions. Thus it can be postulated that zinc salt can be bound to the hydroxylic groups existing in living cell membranes, enzymes etc. while the cadmium salt will be exists as separate complex molecules dissolved in living organism fluids. The zinc salt after entering the plants systems can be immobilised whereas the cadmium salt content in the plant will be governed mainly by the diffusion equilibrium. Noteworthy is the fact that in the solid state both compounds create the same uninodal polymeric nets. During the thermal decomposition, the formation of
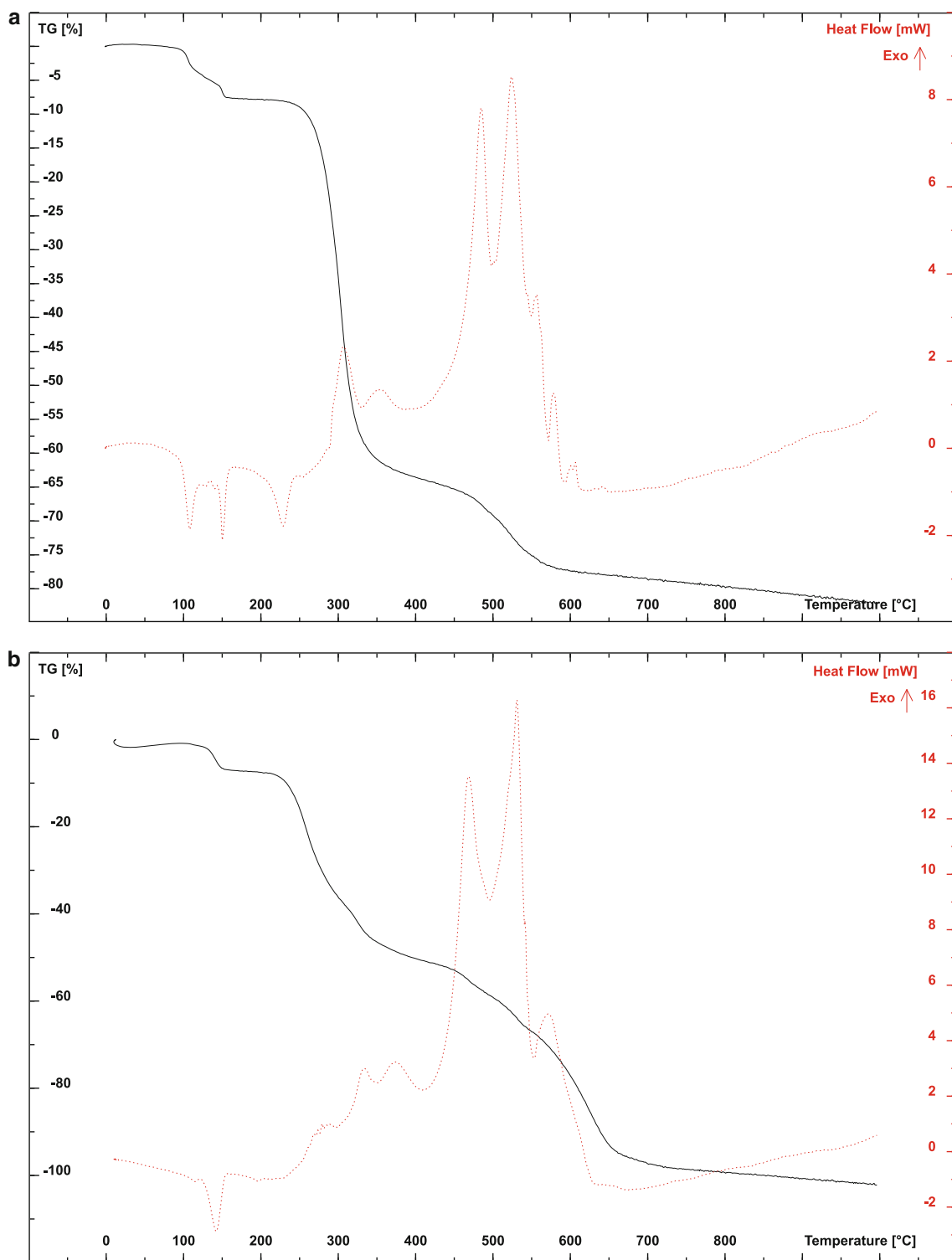
Fig. 7 TG and DTA curves of compound **1** (**a**) and **2** (**b**)

$Zn[(C_8H_5Cl_2O_3)_2(CH_3OH)_2]$
| stage I, m.l. 5.59%/5.62%
↓ - CH_3OH (91 - 110°C), 96°C endo
$Zn[(C_8H_5Cl_2O_3)_2(CH_3OH)]$
| stage II, m.l. 5.63%/5.62%
↓ - CH_3OH (110 - 148°C), 135°C endo
$Zn[(C_8H_5Cl_2O_3)_2]$
| stage III, m.l. 50.78%/50.73%
↓ - $HOC_6H_3Cl_2$, - CO, - CO_2, -C_6H_6, -HCl (226 - 392°C), 320°C exo
$ZnCl_2^* + 5C^*$
| stage IV, m.l. 14.16%/14.08 %
↓ -C, -CO, -CO_2 (405 - 591°C), 532°C exo
$ZnCl_2^*$
| stage V, m.l. 6.00%/ 5.98%
↓ -$ZnCl_2$ (591 - 1000°C), 689°C endo
$0.75\ ZnCl_2^*$

$Cd[(C_8H_5Cl_2O_3)_2(H_2O)_2]$
| stage I, m.l. 6.14%/6.12%
↓ - $2H_2O$ (95 - 154°C), 120°C endo
$Cd[(C_8H_5Cl_2O_3)_2]$
| stage II, m.l. 41.89%/40.92%
↓ - $HOC_6H_3Cl_2$, - CO, -CO_2, -C_6H_6, -HCl (207 - 397°C), 295°C exo
$CdCl_2^* + 8C^*$
| stage III, m.l. 47.06%/46.72%
↓ -C, -CO, -CO_2, -$CdCl_2$ (407 - 672°C), 582°C exo
$0.2\ CdCl_2^*$
↓ -$CdCl_2$ (672 - 842°C), 691°C endo
Total decomposition

Scheme 1 Thermal decomposition of studied compounds together with principal violate products evolving during processes (*m.l.* experimental mass loss/theoretical mass loss). The products marked by (*) were confirmed by XRPD

elemental carbon and metal chlorides was confirmed, what it is in opposition to previous studies of similar compounds.

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