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LEAD(II) AND CADMIUM(II) COMPOUNDS WITH 2,4-DICHLOROPHENOXYACETIC ACID (2,4D) AND 2-(2,4-DICHLOROPHENOXY)-PROPIONIC ACID (2,4DP)

Synthesis and properties

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Abstract

The paper presents the conditions under which compounds of the commercial herbicides, 2,4-dichlorophenoxyacetic acid (2,4D; $C_8H_6O_3Cl_2$) and 2-(2,4-dichlorophenoxy)-propionic acid (2,4DP; $C_9H_8O_3Cl_2$), with lead(II) and cadmium(II) are formed and the results of the examination of their properties.

On the basis of the elemental analysis and Pb and Cd determination, the following molecular formulae for the obtained compounds were proposed: $Pb(C_8H_5O_3Cl_2)_2{\cdot}H_2O$, $Cd(C_8H_5O_3Cl_2)_2{\cdot}2H_2O$, $Pb(C_9H_7O_3Cl_2)_2{\cdot}H_2O$ and $Cd(C_9H_7O_3Cl_2)_2{\cdot}H_2O$. Water solubility of the synthesized complexes at room temperature was examined. X-ray powder analysis was carried out. The discussion of IR spectra and conductivity data is presented. Thermal decomposition of these compounds in air was studied by TG/MS methods.

Keywords: complexes, 2,4-dichlorophenoxyacetic acid, 2-(2,4-dichlorophenoxy)-propionic acid, IR spectra, mass spectrometry, solubility, thermal decomposition, X-ray powder diffraction

Introduction

2,4-dichlorophenoxyacetic acid (2,4D; $C_8H_6O_3Cl_2$) and 2-(2,4-dichlorophenoxy)-propionic acid (2,4DP; $C_9H_8O_3Cl_2$) are commonly used herbicides. They belong to the group of arylcarboxyl agents. They are applied in agriculture as substances of growth (in little amounts) or weedkillers (in high concentrations).

2,4D (Scheme 1) and 2,4DP (Scheme 2) may, due to the presence of the carboxyl group in their molecules, coordinate with metal cations. It is supposed that 2,4D and 2,4DP react and form complexes with metals present in the soil. Therefore the studies of the structure, conditions of formation and physico-chemical properties

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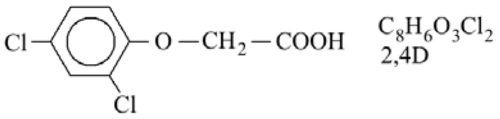
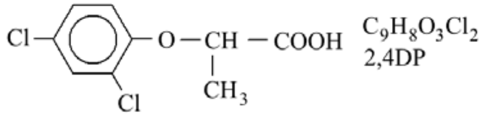


Scheme 1



Scheme 2

of 2,4D and 2,4DP complexes with metals present in the soil are interesting and can be practically useful.

The review of the available literature demonstrates that there have been no studies on simple complexes of 2-(2,4-dichlorophenoxy)-propionic acid with metals. Two publications have been found on mixed complexes of 2,4DP with copper(II) and 2.2'-bipyridine [1, 2].

Metal(II) compounds of 2,4-dichlorophenoxyacetic acid and its mixed complexes with N-bases [2–9], α-aminoacids [6] and bovine serum albumin [10, 11] are described in literature. Few papers concern investigation of simple complexes of 2,4D with metals(II) [12–18]. The crystal structures of Ag(I) [12], Zn(II) [13] and Cu(II) [14] complexes were determined by Kennard *et al.*, Konnik *et al.* investigated 2,4-dichlorophenoxyacetates of Co(II) [15], Mn(II) and Zn(II) [16] using spectrophotometric (IR, VIS), X-ray, thermal (TG/DTA) and conductometric methods. Ristici [17] synthesized and carried out thermogravimetric investigations of Cu, Zn, Cd, Co, Ni, Mn and Fe with 2,4D. Only one paper concerns studies of 2,4D complexes with metals in solution [18].

This paper is continuation our investigations of 2,4D and 2,4DP compounds with metals present in the soil [19]. Cd and Pb are highly toxic to the environment even in low amounts. The preparation, water solubility at room temperature, IR spectra, X-ray powder studies, molar conductivity investigation and thermal decomposition of $Pb(C_8H_5O_3Cl_2)_2\cdot H_2O$ (**Pb-2,4D**), $Cd(C_8H_5O_3Cl_2)_2\cdot 2H_2O$ (**Cd-2,4D**), $Pb(C_9H_7O_3Cl_2)_2\cdot H_2O$ (**Pb-2,4DP**) and $Cd(C_9H_7O_3Cl_2)_2\cdot H_2O$ (**Cd-2,4DP**) are described.

First researches of mass spectrometry coupled with thermal techniques (TG, DTA) have appeared in the sixties [20–23] and they are applied nowadays [19, 24–31]. In this study a coupled TG/MS system was used to analyse the main gaseous products evolved during pyrolysis of the obtained compounds. The solid intermediate and final products of decomposition were identified by X-ray diffraction (using Powder Diffraction File) [32].

Experimental

Chemicals

2,4-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy)-propionic acid, delivered to the authors by the Chemical Industrial Establishment 'Rokita S.A.' in Brzeg Dolny, were purified by double crystallisation from water–ethanol (1:1) solutions. 2,4D and 2,4DP purity was tested by measuring their melting point (*m.p.* of 2,4D=140.5°C; *m.p.* of 2,4DP=117.5–118.1°C) and confirmed by ^1H NMR studies.

Cadmium(II) nitrate(V) ($Cd(NO_3)_2 \cdot 4H_2O$) p.a. (POCh-Gliwice), lead(II) nitrate(V) ($Pb(NO_3)_2$) p.a. (Merck), methanol (anhydroscan – Lab-Scan) were used. Other chemicals were analytically pure products of POCh-Gliwice.

Physical measurements: techniques and apparatus

X-ray powder diffraction patterns were recorded on Siemens D 5000 diffractometer, using CuK_α radiation monochromatized by means of a secondary graphite monochromator. The curves were recorded over the 2θ range 2–90° with a scan step of 0.04° and time of scan step 1 s.

IR spectra were recorded on FTIR-8501 Shimadzu spectrophotometer over the range 4400–400 cm^{-1} using KBr discs technique.

Conductivity measurements were performed at 25±0.05°C on an OK.-102/1 conductometer with an OK.902 electrode. The cell constant was determined by the use of KCl standard aqueous solution. The molar conductivity (Λ_M) of the complexes were measured using $1.0 \cdot 10^{-3}$ mol dm^{-3} solution in methanol and DMF.

The thermal decomposition processes of the prepared complexes were studied by thermogravimetry (TG, DTG), differential thermal analysis (DTA) and TG/MS technique. Thermal curves were obtained on derivatograph OD-102/1500 in air over the temperatures range 25–1000°C with a heating rate 10°C min^{-1}. The mass of the samples was 100 mg. α-Al_2O_3 was used as a reference material.

The TG/MS system (thermoanalyser TG/DTA-SET SYS-16/18, mass spectrometer ThermoStar from Balzers, Pt crucible 100 μL) was used for the characterization of gaseous products of thermal decomposition of the Pb and Cd complexes (mass of the samples of Pb-2,4D, Pb-2,4DP, Cd-2,4D and Cd-2,4DP were 3.81, 2.73, 4.48 and 6.40 mg, respectively). The solid intermediate products of decomposition obtained in a furnace under conditions similar to those used in derivatograph were identified by X-ray diffraction method using Powder Diffraction File [32].

Elemental analysis was carried out by means of CHN analyser, Carlo Erba 1108. WL-1 shaker was used in the determination of solubility. Specol 11 spectrophotometer (Zeiss) was used to carry out analyses in the visible region.

Synthesis of the complexes

The reactions of 2,4-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy)-propionic acid with Pb(II) and Cd(II) nitrates were performed using amounts of substrates corresponding with molar ratio M:2,4D and M:2,4DP=1:2 (where *M*=Pb(II), Cd(II)) at pH=7. Pb-2,4D, Pb-2,4DP, Cd-2,4D and Cd-2,4DP are formed with yield: 98.5, 95.5, 83.7 and 78.5%, respectively.

As 2,4D and 2,4DP are sparingly soluble in water, whereas their sodium salt are readily soluble, the water solution of these compounds (30 mmol in 150 cm^3 of the water) were obtained by dissolving their weighed samples with the addition of solid NaOH in water heated to about 60°C (equimolar amounts of NaOH and acids). Next, pH of the acid solution was brought to 7 by adding 1 mol dm^{-3} NaOH. The solution was filtered and slowly added to a solution containing the ions of a metal (15 mmol in 60 cm^3 of the water), while stirring vigorously. The precipitates formed immediately. All compounds are white. Pb-2,4D, Cd-2,4D and Pb-2,4DP formed fine granules. Cd-2,4DP stuck to the beaker and the glass rod and in the course of stirring formed porous lumps. The precipitated complexes were filtered off after 24 h and dried in air at room temperature. They were crushed in a mortar for further analyses.

Analyses of the complexes

The composition of the synthesized compounds was established on the basis of determination of metals, carbon and hydrogen (Table 1). Lead(II) and cadmium(II) in mineralized samples were determined by complexometric titration using EDTA [33] *vs.* eriochrome black T, whereas carbon and hydrogen were determined by elemental analysis.

Table 1 Analytical data, solubility S [mol dm^{-1}] in water at room temperature and molar conductivity Λ_M [Ω^{-1} cm^2 mol^{-1}] in methanol and DMF (concentration $1.0\cdot10^{-3}$ mol dm^{-1}) at 25°C of the Pb(II) and Cd(II) complexes with 2,4D and 2,4DP

Complex	Analysis: found (calculated)/%			$S\cdot10^{-3}$	Λ_M	
	M	C	H		methanol	DMF
Pb-2,4D	31.43 (31.14)	28.48 (28.88)	1.76 (1.82)	0.35	40.30	7.12
Pb-2,4DP	29.64 (29.88)	31.10 (31.18)	2.02 (2.33)	1.55	41.36	6.01
Cd-2,4D	19.11 (19.09)	32.84 (32.64)	2.23 (2.40)	4.96	42.13	6.26
Cd-2,4DP	18.25 (18.23)	35.91 (36.12)	2.66 (2.70)	21.14	36.97	5.45

Water solubility of the complexes under study was determined at room temperature. In the saturated water solutions of the complexes the content of the metal was determined by complexometric titration using EDTA *vs.* eriochrome black T [33] and by the spectrophotometric method with 4-(2-pyridylazo)-resorcinol (PAR) [34, 35]. The average values of water solubility of the 2,4D and 2,4DP compounds with Pb(II) and Cd(II) are presented in Table 1.

Results and discussion

The reaction of formation of complexes of 2,4-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy)-propionic acid with Pb(II) and Cd(II) may be presented as below by the following reaction schemes:

$$2(2{,}4\mathrm{D})+\mathrm{M}^{2+}+n\mathrm{H_2O}\xrightarrow{-2\mathrm{H}^+}\mathrm{M}(2{,}4\mathrm{D})_2\cdot n\mathrm{H_2O}$$

$$2(2{,}4\mathrm{DP})+\mathrm{M}^{2+}+n\mathrm{H_2O}\xrightarrow{-2\mathrm{H}^+}\mathrm{M}(2{,}4\mathrm{DP})_2\cdot n\mathrm{H_2O}$$

where M=Cd(II) and Pb(II); n=1 for Cd-2,4DP, Pb-2,4D and Pb-2,4DP; n=2 for Cd-2,4D.

The molar ratio M:2,4D and M:2,4DP (where M=Cd, Pb) in the complexes formed at pH=7 is 1:2. Table 1 presents the calculated and determined contents of carbon, hydrogen and metals in the precipitated compounds and their solubility (S[mol dm^{-3}]) in water at room temperature. The analytical results indicate the following molecular formulae for the obtained complexes: $\mathrm{Pb(C_8H_5O_3Cl_2)_2\cdot H_2O}$, $\mathrm{Cd(C_8H_5O_3Cl_2)_2\cdot 2H_2O}$, $\mathrm{Pb(C_9H_7O_3Cl_2)_2\cdot H_2O}$ and $\mathrm{Cd(C_9H_7O_3Cl_2)_2\cdot H_2O}$. All the compounds are stable in air. Their solubility in water at room temperature is of the order of 10^{-4} mol dm^{-3} for Pb-2,4D, 10^{-3} mol dm^{-3} for Cd-2,4D and Pb-2,4DP, 10^{-2} mol dm^{-3} for Cd-2,4D (Table 1). They dissolved fairly in methanol. Lead compounds dissolved readily in 1 mol dm^{-3} NaOH solution too.

The molar conductivity in DMF (Table 1) proves that the complexes are non-electrolytes. In methanol they display a behaviour intermediate between those of non- and 1:1 electrolytes [36]. The differences between the types of electrolyte may result from the displacement of phenoxy ligand by methanol molecules. For this reason the values of molar conductivity are a little higher than the values for non-electrolytes in methanol.

Powder diffraction patterns of 2,4D and 2,4DP and their complexes with Cd(II) and Pb(II) were obtained. The analysis of the diffractograms (Fig. 1) shows that Pb-2,4D, Cd-2,4D and Pb-2,4DP are crystalline, while Cd-2,4DP is either amorphous or its degree of crystallinity is very low.

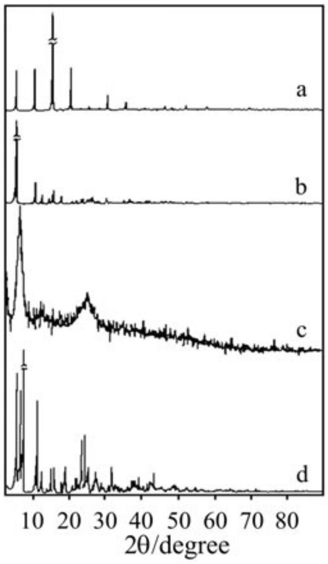


Fig. 1 Diffractograms of a – Cd-2,4D, b – Pb-2,4D, c – Cd-2,4DP and d – Pb-2,4DP

IR spectroscopy

2,4-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy)-propionic acid, due to the presence of the carboxyl group in their molecules, may coordinate with metal cations. IR spectrophotometry (over the range 4400–400 cm^{-1}) confirmed that 2,4D and 2,4DP combine with *z* Cd(II) and Pb(II) through the oxygen atoms of the carboxylate group. Table 2 presents the fundamental frequencies of vibrations of the carboxylate group for acids and for the prepared complexes [37, 38].

The stretching bands of the undissociated carboxyl group ν(C=O), present at 1735.8 and 1716.5 cm^{-1} in the spectrum of 2,4D and 2,4DP, respectively, does not appear in the spectra of their complexes. Instead, two new stretching bands, $\nu(C{=}O)_{sym}$ and $\nu(C{=}O)_{asym}$ appear, representing the vibrations of the dissociated carboxylate group. Moreover, in the spectra of the complexes there are no bands representing the vibrations of the hydroxyl group of 2,4D and 2,4DP: δ(C-OH), ν(C-OH), δ(OH) and ν(OH).

On the basis of Δν value calculated as the difference between the frequencies of the symmetric and asymmetric vibrations of the dissociated carboxylate group and its comparison with the results obtained for the sodium salts of 2,4D and 2,4DP, the type of coordination of the carboxylate group was established [39–41].

Kennard *et al.* studied crystal and molecular structures of Ag(I), Zn(II) and Cu(II) complexes of 2,4-dichlorophenoxyacetic acid [12–14]. They found out that 2,4D reacts with Ag^+ forming $[Ag(2,4D)]_n$. This complex is the chain polymer and contains only 2-coordinate linear bonds to Ag. The authors confirmed that it is isomorphous. The molecular units in the Zn-2,4D consist of both octahedral $[Zn(H_2O)_4(2,4D)_2]$ and tetrahedral $[Zn(H_2O)_2(2,4D)_2]$ complexes linked only by hydrogen bonding between the non-complexed carboxyl oxygens and the complexed aqua ligands. The carboxylate groups are unidentate in these complexes. In the case of Cu compound, 2,4D acid forms $[Cu_2(2,4D)_4(H_2O)_2{\cdot}2H_2O]$ – centrosymmetric dimeric units with two copper centres bridged by four carboxylate groups of 2,4-dichlorophenoxyacetic acid.

Therefore the carboxylate group in 2,4D compounds may be both unidentate and bidentate and also may be both dimeric and polymeric.

Unequivocal identification of the nature of carboxylate group is very difficult without supplementary structural studies. The absorption bands arising from asymmetric $\nu(OCO)_{asym}$ and symmetric $\nu(OCO)_{sym}$ vibration of OCO-groups appear at 1618.2–1529.4 and 1417.6–1338.5 cm^{-1}, respectively. The analysis of band frequencies of OCO group allowed the determination of separation of $\nu(OCO)_{asym} - \nu(OCO)_{sym} = \Delta\nu$, whose value is used as a criterion of the carboxylate bonding with metal ions. In this paper separations Δν for Pb and Cd complexes are in the range 111.8–277.7 cm^{-1}; they are less than those of the sodium salts (281.6 and 206.4 cm^{-1} for Na-2,4D and Na-2,4DP, respectively). On the basis of Δν it is possible to assume that the carboxylate ion is bonded as a bidentate chelating or bridging ligand [39–41]. The $\nu(OCO)_{asym}$ bands of Cd-2,4D, Pb-2,4D and Pb-2,4DP and $\nu(OCO)_{sym}$ band of Pb-2,4D are split into doublet. It may be connected with the presence of two non-equivalent carboxylate groups in the molecules of complexes. Then one of OCO group can be chelating the other–bridging. In case of

Table 2 The frequencies of group vibrations [cm^{-1}] present in the spectra of 2,4D and 2,4DP acids and their complexes with Pb(II) and Cd(II)

Compound	ν(C=O)	$\nu(OCO)_{asym}$	$\nu(OCO)_{sym}$	Δν*	ν(MO)+δ(OCO)	δ(C–OH)	ν(C–OH)
2,4D	1735.8vs	–	–	–	–	1392.5s	1492.2s
Na-2,4D	–	1620.1vs	1338.5s	281.6	–	–	–
Pb-2,4D	–	1616.2vs	1338.5s	227.7			
	–	1573.8dvs	1417.6s	198.6	621.0	–	–
		1564.2dvs		146.6			
Cd-2,4D	–	1604.7vs	1342.4s	262.3	615.2w	–	–
		1556.4vs		214.0	578.6w		
2,4DP	1716.5vs	–	–	–	–	1392.5s	1434.9s
Na-2,4DP	–	1618.2vs	1411.8s	206.4	–	–	–
Pb-2,4DP	–	1591.2vs	1417.6s	173.6	690.5w	–	–
		1529.4vs		111.8			
Cd-2,4DP	–	1602.7vs	1415.7s	187.0	576.7w	–	–

[*] $\Delta\nu=\nu(OCO)_{asym}-\nu(OCO)_{sym}$; v – very; s – strong; w – weak; d – double

Pb-2,4D, one of the ν(OCO)$_{asym}$ bands is additionally split into doublet. This suggests that one of carboxylate groups is asymmetric chelating.

The obtained values of molar conductivity in DMF and methanol confirm our presumptions with regard to coordination of carboxylate groups in studied compounds. The ν(M–O)+δ(OCO) vibrations are observed within the interval ca 690.5–576.7 cm^{-1}.

The spectra of all the complexes of 2,4D and 2,4DP show strong and broad bands in the water streching region (ca 3600–3100 cm^{-1}). The bands in the water bending region (1650–1620 cm^{-1}) overlap the streching bands (ν(OCO)$_{asym}$) of the carboxylate group. The presence of these bands in the spectra of the complexes confirms that they contain crystalline or coordinated water in their molecules.

Thermal analysis

The results of the thermal analysis are listed in Table 3. Figures 2 and 3 present the thermoanalytical curves (TG, DTG, DTA) of Pb(II) and Cd(II) complexes with 2,4D and 2,4DP.

The TG curves exhibit multiple, overlapping mass loss steps. Cd-2,4D, Pb-2,4D and Pb-2,4DP decompose in four stages while Cd-2,4DP in six stages.

All the complexes are hydrated. They are thermally unstable and lose water molecules between 80 and 250°C. The dehydration processes of the compounds are connected with endothermic effects between 80 and 220°C. The mass losses which occur in the course of dehydration vary from 1 to 6.5%. The water molecules of Pb-2,4D and Cd-2,4DP are liberated in one stage while those of Pb-2,4DP and Cd-2,4D are lost in two stages. On the DTG curve of Cd-2,4D one splitting peak within the temperature range 50–170°C and peaks at 110 and 140°C on the DTA curve are ob-

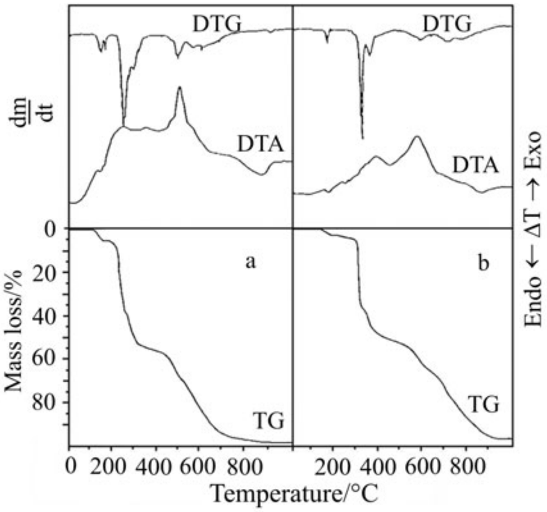


Fig. 2 Thermoanalytical curves (TG, DTG, DTA) of a – Cd-2,4D and b – Pb-2,4D (mass sample 100 mg)

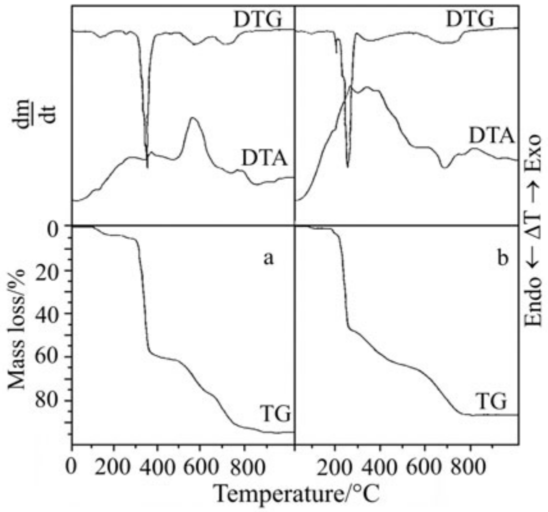


Fig. 3 Thermoanalytical curves (TG, DTG, DTA) of a – Cd-2,4DP and b – Pb-2,4DP (mass sample 100 mg)

served. It shows that dehydration takes place in two steps. In the case of Pb-2,4DP the first stage of dehydration involves the release of 0.5 molecule of water. It is associated with a weak endothermic effect. The release of the remaining half of the water molecule is accompanied by partial thermal decomposition of anhydrous complexes. Therefore the summary thermal effect observed in this stage is slightly exothermic with a DTA peak at 220°C. The peaks at 120 and 80°C on DTA curves of Pb-2,4D and Cd-2,4DP, respectively, are associated with the release of water molecules present in those compounds. Water release is observed in the mass spectra of the gaseous products of pyrolysis of these complexes.

X-ray analysis let us identify only the final product of thermal decomposition of Cd-2,4DP – it is CdO. All the complexes decompose progressively via chlorine compounds ($PbCl_2$, $CdCl_2$, PbOHCl, $Cd_3Cl_2O_2$).

On the TG curve of Cd-2,4DP a slight loss of mass (1.5%) takes place within the temperature range 180–210°C. The mass spectrum indicates that within this temperature range CH_3^+ starts to liberate.

The further mass loss observed on the TG curves within the temperature ranges 160–420°C (Pb-2,4D), 200–370°C (Pb-2,4DP), 170–390°C (Cd-2,4D) and 210–410°C (Cd-2,4DP) is caused by the pyrolysis of organic ligands. In these stages several broad and weak partly overlapping exothermic peaks on the DTA curves are observed.

The next stages of pyrolysis between 390 and 770°C (Cd-2,4D), 420 and 620°C (Pb-2,4D), 410 and 630°C (Cd-2,4DP) and 370 and 580°C (Pb-2,4DP) are caused by farther oxidation of organic fragments. The very strong and broad exothermic effects accompany those steps on the DTA, probably caused by the oxidation of the products of decomposition of carboxylate anions and destruction of benzene rings (TG/MS measurements). The last stages of decomposition within the temperature range 580–820°C

Table 3 Thermal decomposition data of Pb(II) and Cd(II) complexes with 2,4D and 2,4DP acids (sample mass 100 mg)

Compound	Temp. range of pyrolysis/°C	Mass loss/%	DTA peaks/° C	Intermediate solid products
$Cd(C_8H_5O_3Cl_2)_2\cdot 2H_2O$	50–170	6.5	Endo/110, 140	$Cd(C_8H_5O_3Cl_2)_2$
	170–390	55.0	Exo/270, 380	organic fragments, $CdCl_2$, $Cd_3Cl_2O_2$
	390–770	96.0	Exo/540	unidentified
	770–940	99.0	Endo/880	unidentified
$Pb(C_8H_5O_3Cl_2)_2\cdot H_2O$	80–130	3.0	Endo/120	$Pb(C_8H_5O_3Cl_2)_2$
	160–420	52.5	Exo/230, 290, 380	organic fragments, $PbCl_2$
	420–620	69.0	Exo/550	$PbCl_2$
	620–920	92.0	Endo/820	unidentified (amorphous)
$Cd(C_9H_7O_3Cl_2)_2\cdot H_2O$	40–140	3.5	Endo/80	$Cd(C_9H_7O_3Cl_2)_2$
	180–210	5.0	–	unidentified (amorphous)
	210–410	60.0	Exo/310, 360	organic fragm., $CdCl_2$, Cd, $Cd_3Cl_2O_2$
	410–630	77.0	Exo/560	$Cd_3Cl_2O_2$, CdO
	630–800	92.0	Endo/720; Exo/760	CdO
	800–930	95.0	Endo/830	CdO
$Pb(C_9H_7O_3Cl_2)_2\cdot H_2O$	50–100	1.0	–	$Pb(C_9H_7O_3Cl_2)_20.5H_2O$
	200–370	3.5	Exo/220, 350	unidentified (amorphous)
	370–580	63.5	Exo/430, 480	$PbCl_2$, PbClOH
	580–820	86.5	Endo/730	unidentified (amorphous)

(Pb-2,4DP), 800–930°C (Cd-2,4DP), 620–920°C (Pb-2,4D) and 770–940°C (Cd-2,4D) are endothermic and probably involve melting and evaporation of the final products.

Table 3 presents intermediate and final solid products of thermal decomposition of Cd(II) and Pb(II) complexes with 2,4D and 2,4DP. These compounds were identified on the basis of powder diffraction patterns of products of decomposition obtained under conditions similar to those used in derivatograph. Using the crystallographic database of inorganic compounds [32] we were able to find out that the intermediate products are usually metal hydroxychlorides (Pb(OH)Cl), metal oxychlorides ($Cd_3O_2Cl_2$) and metal chlorides ($CdCl_2$, $PbCl_2$). The final products are unidentified for Cd-2,4D, Pb-2,4D and Pb-2,4DP. The final product of Cd-2,4DP is CdO. In connection with sublimation of intermediate solid products of decomposition (chlorine compounds) the summary loss of mass is larger than expected for all studied compounds.

In this study a coupled TG/MS system was used to analyse of gaseous products liberated during the thermal decomposition of Pb(II) and Cd(II) complexes under study in air atmosphere. MS data of these compounds are similar. Figure 4 presents, by way

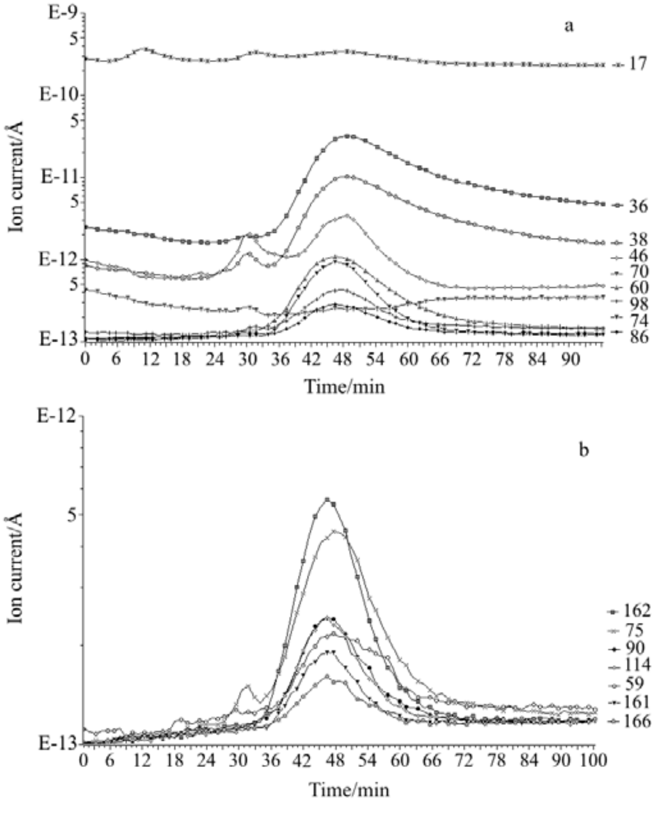


Fig. 4 Ion current for a – m/z=17, 36, 38, 46, 60, 70, 74, 86, 98 and b – m/z=59, 75, 90, 114, 161, 162, 166 detected in the mass spectrometer *vs.* time for Cd-2,4DP (mass sample 6.40 mg, heating rate 10°C min^{-1}), original record

of example, the relationship of the ion current for *m*/*z* detected in the mass spectrometry *vs.* time of decomposition (heating rate=10°C min^{-1}) for Cd-2,4DP. In this figure the profiles for MS are not presented, which are shown in Fig. 5, where TG/MS data are listed. In the mass spectra different intensities of signal ions are detected.

In all causes, the first gaseous products detected was H_2O^+ (*m*/*z* =17, 18). The strong peak connected with the elimination of H_2O^+ (crystalline or coordinated) occurs at 140, 130, 105 and 125°C for Cd-2,4D, Pb-2,4D, Cd-2,4DP and Pb-2,4DP, respectively. Next, the H_2O is a product of oxidation of organic ligands at 280, 310, 325 and 500°C for Pb-2,4D, Pb-2,4DP and Cd-2,4DP, respectively.

Peaks of CH_2O^+ (*m*/*z*=30) and CH_3^+ (*m*/*z*=15) appear from 210 to 310°C. At 380°C (Cd-2,4D), 320°C (Cd-2,4DP and Pb-2,4D) and 260°C (Pb-2,4DP) the several gaseous products start to liberate: CO_2^+, C^+, CH^+, CH_2^+, Cl^+, HCl^+, Cl_2^+, H_2^+ (*m*/*z*=44, 46, 12, 13, 14, 35, 37, 36, 38, 70, 74, 2, respectively). In air atmosphere CO^+ was not detected. The profiles observed for *m*/*z*=44, 46 (CO_2^+ and its isotope) are similar. CO_2^+ is mainly formed as a result of decomposition of carboxylate groups. At the same time, mass fragments *m*/*z*=12 and 13 are liberated. The chlorine compounds

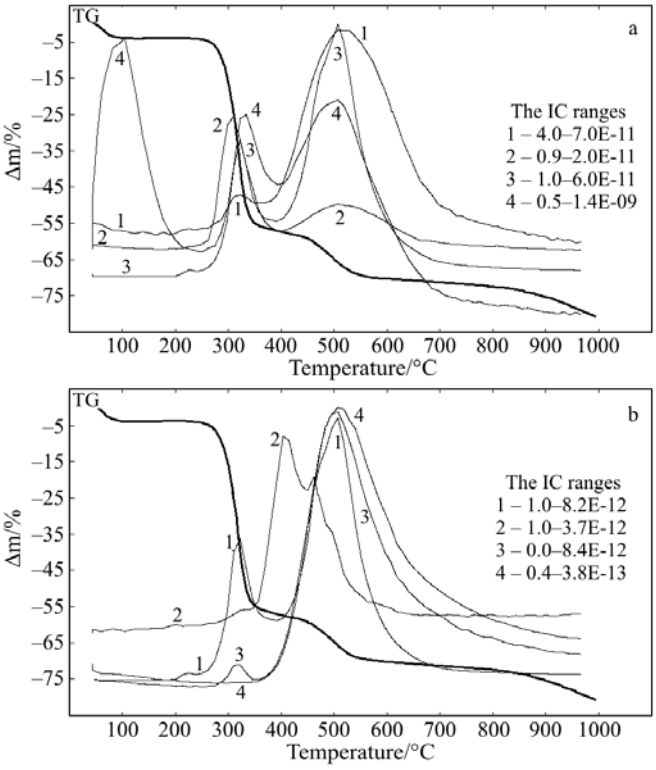


Fig. 5 TG curve for Cd-2,4DP and ion current detected by the mass spectrometer for mass fragments a – *m*/*z*=1 – 1, 2 – 2, 3 – 12, 4 – 18, b – *m*/*z*=1 – 35, 2 – 37, 3 – 44, 4 – 78

Cl^+, HCl^+, Cl_2^+ and Cl_2O^+ (*m*/*z*=35, 36, 37, 38, 70, 74, 86, 90) start to appear above 400°C (Cd-2,4D), 380°C (Pb-2,4DP), 320°C (Pb-2,4D) and at 320 and 510°C (Cd-2,4DP). Benzene $C_6H_6^+$ (*m*/*z*=78) and its products of destruction liberate at 380, 420, 360, 400 and 460°C for Cd-2,4D, Pb-2,4D, Pb-2,4DP and Cd-2,4DP, respectively. Additionally the mass spectrometer detected: CH_3OH^+, CH_2COOH^+, CH_3COOH^+, OCH_2COOH^+, $C_6H_5OH^+$, $C_6H_{10}O^+$, $C_6H_5Cl^+$, $C_6H_5COOH^+$, $C_6H_4OCl^+$, $C_6H_4ClOH^+$, $C_6H_9OCl^+$, $C_6H_4Cl_2^+$, $C_6H_5OCH_2COOH^+$, $C_6H_3OCl_2^+$, $C_6H_3Cl_2OH^+$ (*m*/*z*=32; 59; 60; 75; 94; 98; 112, 114; 122; 127, 129; 129, 131; 132, 134; 146, 148, 150; 152; 161, 163, 165; 162, 164, 166, respectively).

TG coupled with MS data of some gaseous products of decomposition are shown (for Cd-2,4DP) in Fig. 5.

Conclusions

2,4-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy)-propionic acid form with lead(II) and cadmium(II) complexes of the molar ratio M:2,4D and M:2,4DP=1:2 (where *M*=Cd(II), Pb(II)). The complexes contain crystallisation or coordinated water and have the following molecular formulae: $Pb(C_8H_5O_3Cl_2)_2{\cdot}H_2O$, $Cd(C_8H_5O_3Cl_2)_2{\cdot}2H_2O$, $Pb(C_9H_7O_3Cl_2)_2{\cdot}H_2O$ and $Cd(C_9H_7O_3Cl_2)_2{\cdot}H_2O$. The complexes are sparingly soluble in water at room temperature and their solubility increases in the orders:

$$\text{Pb-2,4D}<\text{Pb-2,4DP}<\text{Cd-2,4D}<\text{Cd-2,4DP}$$

The 2,4DP complexes are more readily soluble in water than 2,4D complexes (for the same metal).

The powder X-ray diffraction patterns of the studied compounds demonstrate that Pb-2,4D, Cd-2,4D and Pb-2,4DP have a crystalline structure, while Cd-2,4DP is either amorphous or its degree of crystallinity is very low. The IR spectroscopy confirms that 2,4D and 2,4DP acids combine with Pb and Cd through the oxygen atoms of the carboxylate group. On the basis of $\Delta\nu=\nu(OCO)_{asym}-\nu(OCO)_{sym}$ values and conductance measurements a conclusion can be drawn that in the compounds the carboxylate groups are bidentate chelating but the splitting of ν(OCO) bands suggest presence of two non-equivalent carboxylate groups in the molecules of the complexes. It is possible, then, that one of OCO groups can be chelating the other–brinding. Conductivity measurements in DMF and methanol confirm our presumptions concerning the coordination of the carboxylate groups.

The thermal decomposition of all the hydrated complexes begins with the release of water. Thermal stability of anhydrous compounds increases in the following order:

$$\begin{array}{cccc}\text{Pb-2,4D}< & \text{Cd-2,4D}< & \text{Cd-2,4DP}< & \text{Pb-2,4DP}\\ (160°\text{C}) & (170°\text{C}) & (180°\text{C}) & (200°\text{C})\end{array}$$

The anhydrous 2,4DP complexes are thermally more stable than 2,4D complexes. All the complexes decompose via chlorine compounds. The final product of Cd-2,4DP is CdO. The other final products are unidentified. The gaseous products liberated during pyrolysis of the studied complexes are similar. During the heating of the complexes the decomposition of the organic ligands and oxidation processes take place. Using TG/MS technique molecular ions: H_2O^+, CO_2^+, HCl^+, Cl_2^+, CH_2O^+, $C_6H_6^+$, C^+, CH^+, CH_3^+, Cl^+, Cl_2O^+, $C_6H_5Cl^+$, $C_6H_5OH^+$, $C_6H_4ClOH^+$ CH_2COOH^+, CH_3COOH^+, $C_6H_4OCl^+$, $C_6H_3OCl_2^+$, $C_6H_3Cl_2OH^+$, $C_6H_5COOH^+$, $C_6H_5OCH_2COOH^+$ were detected.

* * *

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