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# Phenoxyalkanoic acid complexes Part II. Complexes of selected bivalent metals with 2,4-dichlorophenoxyacetic acid (2,4D) and 2-(2,4-dichlorophenoxy)propionic acid (2,4DP)

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ABSTRACT

Seven new solid complexes have been obtained: Hg(II), Fe(II), Ca(II) and Mg(II) complexes with 2,4D and Hg(II), Fe(II) and Ca(II) complexes with 2,4DP as well as previously described Cu(II), Zn(II), Cd(II), Pb(II), Mn(II), Co(II) and Ni(II) complexes with both ligands. The composition of $ML_2{\cdot}nH_2O$ complexes, where $n = 0–6$, was established by chemical analysis methods. Their water solubility has been determined and X-ray, IR and thermal analyses have been carried out. It has been found out that the most sparingly soluble mercury, lead, copper and cadmium compounds precipitate also from a solution of a herbicide which contains 2,4-dichlorophenoxyacetic acid (2,4D) as an active substance. The analysis of powder diffraction patterns of the complexes under study shows that they are crystalline, but have different structures. Their IR spectra have been interpreted in relation to the structural data available. It has been found out that metals are coordinated by the carboxylate groups of the ligands. The IR analysis does not allow to establish precisely the mode of coordination of the metals with the carboxylate groups. The thermal decomposition of all the compounds proceeds in a similar way. In the case of the hydrated complexes first the 1–3 step dehydration process takes place. The decomposition of the anhydrous compounds is a two step process with a complicated course. Total mass losses for the mercury, lead and cadmium complexes are close to 100%, thus in the process of thermal decomposition the metals form volatile compounds.

## 1. Introduction

Phenoxyalkanoic acids, containing chlorine and/or methyl group in 2 and 4 position of benzene ring, show herbicidal properties. These compounds are selective herbicides because they destruct effectively broadleaf plants whereas the monocotyledonous plants are resistant to them. 2,4-dichlorophenoxyacetic (2,4D), 2-(2,4-dichlorophenoxy)propionic (2,4DP), 4-chloro-2-methylphenoxyacetic (MCPA) and 4-chloro-2-methylphenoxypropionic (MCPP) acids are widely used for protection of crops and water plants control. Due to the presence of the carboxylate group in their structure, the compounds can react with metal ions to form complexes which are sparingly soluble in water.

In Part I, complexes of Pb(II), Cd(II) and Cu(II) with MCPA were studied [1]. Synthesis and properties of solid complexes of 2,4D with Cu(II) [2–5], Zn(II) [2,4,6–8], Cd(II) [2,4,9], Pb(II) [4,9], Mn(II) [2,7,10], Co(II) [2,11,12] and Ni(II) [2,11] have been hitherto described. Complexes of the above mentioned metals with 2,4DP are not so well known, although they have also been described in literature [5,8–11]. Since not all the literature data on complexes with 2,4D are consistent, and the complexes with 2,4DP have been investigated only by Ptaszynski and Zwolinska [5,8–11], it seemed useful to carry out their syntheses and comparative studies on the properties of these complexes.

The present work concerns complexes of 2,4D and 2,4DP with metals present in soil and water environments. Among the metals under study are microelements and macroelements Cu(II), Zn(II), Mn(II), Co(II), Ni(II), Fe(II), Ca(II), Mg(II) necessary for plants and toxic heavy metals Cd(II), Hg(II), Pb(II). The new compounds obtained in our study are mercury, iron and calcium complexes with 2,4D and 2,4DP and the magnesium complex with 2,4D. Elemental, IR, X-ray and thermal analyses were carried out to examine them.

The current interest in investigating these complexes results from the pollution of the environment with heavy metals and pesticides. It was assumed that similar complex formation can also occur between phenoxyacetic herbicides and metals present in the soils and waters. These herbicides are usually applied in the form of a suspension at the time when the crops are sprouting. After spraying, the herbicides get also into the soil where they undergo

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**Table 1**
Chemical analyses and solubility of 2,4D complexes.

| Compound | Analysis: found (calculated) (%) | | | | | $S \times 10^3$ (mol $L^{-1}$) |
|---|---|---|---|---|---|---|
| | Metal | C | H | Cl | $H_2O$ | |
| $Hg(C_8H_5O_3Cl_2)_2$ | 30.23 (31.31) | 29.26 (29.97) | 1.78 (1.56) | | | 0.01 |
| $Mn(C_8H_5O_3Cl_2)_2\cdot 4H_2O$ | 9.81 (9.69) | 34.07 (33.89) | 3.26 (3.20) | 25.29 (25.01) | 12 (12.70) | 11 |
| $Fe(C_8H_5O_3Cl_2)_2\cdot 4H_2O$ | 9.84 (9.83) | 33.45 (33.83) | 3.01 (3.19) | 25.47 (24.97) | 12 (12.68) | 4.2 |
| $Co(C_8H_5O_3Cl_2)_2\cdot 6H_2O$ | 9.99 (9.71) | 32.18 (31.66) | 3.58 (3.65) | 23.23 (23.36) | 18 (17.8) | 5.3 |
| $Ni(C_8H_5O_3Cl_2)_2\cdot 6H_2O$ | 9.68 (9.67) | 32.16 (31.47) | 3.96 (3.62) | 22.81 (23.37) | 17 (17.8) | 6.0 |
| $Ca(C_8H_5O_3Cl_2)_2\cdot 2H_2O$ | 8.06 (7.78) | 36.92 (37.20) | 2.55 (2.71) | 25.06 (27.47) | 7 (6.97) | 8.6 |
| $Mg(C_8H_5O_3Cl_2)_2\cdot 5H_2O$ | 4.56 (4.38) | 35.59 (34.63) | 4.15 (3.61) | 26.04 (25.58) | 17 (16.23) | |
| $Cu(C_8H_5O_3Cl_2)_2\cdot 4H_2O$[a] | 10.66 (11.04) | 33.05 (33.39) | 2.88 (3.13) | 23.84 (24.64) | 13 (12.51) | 1.1 |
| $Zn(C_8H_5O_3Cl_2)_2\cdot 3H_2O$[a] | 11.48 (11.69) | 34.33 (34.35) | 2.80 (2.86) | 25.85 (25.35) | 10 (11.89) | 7.0 |
| $Cd(C_8H_5O_3Cl_2)_2\cdot 2H_2O$[a] | 19.73 (19.10) | 31.50 (32.66) | 2.26 (2.38) | 21.46 (24.11) | 5.5 (5.23) | 2.8 |
| $Pb(C_8H_5O_3Cl_2)_2\cdot H_2O$[a] | 30.88 (31.15) | 27.65 (28.89) | 1.75 (1.80) | 18.25 (21.32) | 3 (2.71) | 0.15 |

[a] As published in ref. [4].

complex reactions leading to their complete biodegradation. The half-life period in soil of 2,4D and MCPA is considered to be 2–4 weeks [13]. The solubility of metal–herbicide complexes may affect the mobility of the metal in the soil and resistance of herbicides to biodegradation. Our experiments indicate that spraying of the wheat with 2,4D and MCPA decreases the uptake of Cu, Zn and Mn by the wheat stems [14]. Widespread use of phenoxylic herbicides causes accumulation of hazardous waste (unused and outdated herbicides, pesticide packaging). This waste has to be disposed of in a suitable way, for instance in the processes of thermal decomposition. The results of our thermal analyses may be used to develop safe technologies to utilize mixed waste containing herbicides and heavy metal compounds.

## 2. Experimental

### 2.1. Chemicals

2,4-dichlorophenoxyacetic acid (2,4D) and 2-(2,4-dichlorophenoxy)propionic acid (2,4DP), (98% and 95%, respectively) were obtained from Aldrich. They were purified by double crystallization from toluene. Their melting temperatures after purification were 141 °C (theoretical melting point 140.5 °C) and 118 °C (theoretical melting point 117.5–118.1 °C), respectively [15]. Pesticide preparation "Aminopielik 450 SL" (Rokita S.A. Poland). Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Mn(II), Co(II), Ni(II), Ca(II), Mg(II) nitrates(V) and Fe(II) chloride (GR for analysis, Merck). Stock solutions of the same metals (1000 mg $L^{-1}$ as nitrate salts in 0.5 mol $L^{-1}$ nitric acid) were purchased from Merck. Working solutions were prepared by appropriate dilution of standard solutions. The other chemicals are p.a. from POCh-Poland or GR for analysis from Merck.

### 2.2. Synthesis and chemical analysis

The complexes under study were prepared by reaction of sodium salts of 2,4D or 2,4DP with metal nitrates in a molar ratio 2:1. The 2,4D and 2,4DP acids are sparingly soluble in water and they were used in the synthesis after transformation into soluble sodium salts. Samples of 2,4D or 2,4DP (0.01 mol) were mixed with 80 mL of distilled water and then a 1 mol $L^{-1}$ NaOH solution was added dropwise while stirring to complete dissolution of acid. If the pH of obtained solutions was alkaline it was adjusted to pH about 7 with a 1 mol $L^{-1}$ $HNO_3$ (pH-meter Mettler Delta 350). Samples of metal nitrates (0.005 moles) were dissolved in 20 mL of distilled water (in the case of mercury in 1 mol $L^{-1}$ $HNO_3$) and added to Na-2,4D or Na-2,4DP solutions, which causing precipitation of the compounds under study. The precipitates were filtered after 24 h, washed with a small amounts of distilled water and dried in air at room temperature. The complexes were obtained with yields 60–90%.

The composition of the complexes was established on the basis of metal, carbon, hydrogen, chlorine and water contents determination (Tables 1 and 2). The metals (except mercury) were determined by complexometric titration [16] after decomposition of complexes using concentrated $HNO_3$ (UniClever BM-1z mineralizer, Plazmatronika) while carbon, hydrogen and chlorine by elemental analysis methods (CHN analyser, Carlo Erba 1108). To determine the content of mercury, weighed samples of the complexes were decomposed by means of 1 mol $L^{-1}$ NaOH, the released HgO was dissolved in 1 mol $L^{-1}$ $HNO_3$ and mercury was determined in the obtained solution by complexometric back-titration.

Attempts were also made to precipitate the compounds under study from the herbicidal preparation "Aminopielik" which contains 2,4-dichlorophenoxyacetic acid in the form of the ammonium salt. Solutions of the metals were added to the 100 times diluted

**Table 2**
Chemical analyses and solubility of 2,4DP complexes.

| Compound | Analysis: found (calculated) (%) | | | | | $S \times 10^3$ (mol $L^{(1)}$) |
|---|---|---|---|---|---|---|
| | Metal | C | H | Cl | $H_2O$ | |
| $Hg(C_9H_7O_3Cl_2)_2$ | 29.25 (29.99) | 32.69 (32.30) | 2.08 (2.09) | | | 0.03 |
| $Mn(C_9H_7O_3Cl_2)_2\cdot 6H_2O$ | 9.03 (8.70) | 34.02 (34.25) | 4.03 (4.15) | 22.32 (23.46) | 16.5 (17.11) | 24 |
| $Fe(C_9H_7O_3Cl_2)_2\cdot 4H_2O$ | 9.31 (9.36) | 35.30 (36.27) | 3.51 (3.72) | 22.69 (23.79) | 10 (12.08) | 2.4 |
| $Co(C_9H_7O_3Cl_2)_2\cdot 6H_2O$ | 9.40 (9.28) | 34.66 (34.04) | 3.99 (4.13) | 22.18 (22.30) | 18 (17.01) | 5.8 |
| $Ni(C_9H_7O_3Cl_2)_2\cdot 6H_2O$ | 9.19 (9.25) | 33.55 (34.06) | 4.04 (4.13) | 20.97 (22.34) | 17.5 (17.01) | 7.0 |
| $Ca(C_9H_7O_3Cl_2)_2\cdot 2H_2O$ | 7.64 (7.37) | 38.98 (39.70) | 3.24 (3.31) | 23.25 (26.05) | 7 (6.61) | 4.6 |
| $Cu(C_9H_7O_3Cl_2)_2\cdot H_2O$ | 11.38 (11.56) | 38.41 (39.33) | 2.74 (2.93) | 24.04 (25.80) | 2.5 (3.27) | 6.4 |
| $Zn(C_9H_7O_3Cl_2)_2\cdot 4H_2O$ | 10.82 (10.80) | 34.42 (35.69) | 3.02 (3.63) | 21.96 (23.43) | 14 (11.89) | 15 |
| $Cd(C_9H_7O_3Cl_2)_2\cdot 2H_2O$ | 17.78 (18.24) | 34.58 (35.69) | 2.94 (2.92) | 20.82 (23.00) | 7 (5.22) | 8.6 |
| $Pb(C_9H_7O_3Cl_2)_2$ | 29.07 (30.69) | 33.40 (32.00) | 2.29 (2.07) | 18.66 (21.01) | | 1.0 |

**Table 3**
Yield of the synthesis and metal contents in the precipitates obtained in the reaction of metal nitrate with “Aminopielik”.

| Metal | Yield (%) | Metal content (%) | |
|---|---|---|---|
| | | Found | Calculated |
| Hg | 100 | 29.75 | 31.33 |
| Cu | 100 | 8.58 | 11.04 |
| Cd | 60 | 19.40 | 19.10 |
| Pb | 100 | 31.73 | 31.15 |

“Aminopielik” solution (pH about 7) recommended for spraying plants maintaining 2:1 molar ratio. The precipitates appeared immediately in the case of Cu(II), Pb(II) and Hg(II) and after a week in the case of Cd(II). Metal content was determined in the precipitates (Table 3). The compounds of Cu(II), Pb(II) and Hg(II) precipitated also from more diluted (250, 500 and 1000 times) “Aminopielik” solutions.

Water solubility of the complexes (at 293 K) was established on the basis of the content of metal determined by complexometric [16], spectrophotometric [17] or CV-AAS (mercury) methods in the saturated water solutions (Tables 1 and 2).

### 2.3. X-ray analysis

Powder diffraction patterns of the complexes under study were recorded on a Siemens 5000 diffractometer using $CuK_\alpha$ radiation monochromatized by means of a secondary graphite monochromator within the $2\theta$ range 2–90°.

### 2.4. IR spectra

IR spectra of 2,4D or 2,4DP, their sodium salts and complexes under study were recorded on a FTIR-8501 spectrometer (Shimadzu), within frequency range 4000–400 $cm^{-1}$ in KBr discs (Table 4).

### 2.5. Thermal analysis

The thermal decomposition curves of complexes under study were obtained on OD-102/1500 derivatograph. The samples of 100 mg were heated in corundum crucible in static air atmosphere. $\alpha$-$Al_2O_3$ was used as standard material. All thermal investigations were carried out within the temperature range 20–1000 °C at a heating rate of 10°/min.

## 3. Results and discussion

### 3.1. Composition and solubility of the complexes

Twenty one solid compounds of the general formula $ML_2 \cdot nH_2O$, where M = Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Mn(II), Fe(II), Co(II), Ni(II), Ca(II), Mg(II), L = 2,4D or 2,4DP and $n = 0$–6 were obtained. The series with 2,4D consists of 11 complexes (Table 1) and that with 2,4DP – 10 (Table 2), because it was not possible to obtain the magnesium complex with this ligand in the solid form. The complexes of Hg(II), Fe(II) and Ca(II) with 2,4D and 2,4DP and the complex of Mg(II) with 2,4D were obtained for the first time so more attention will be given to them in the discussion. Analogous general composition of the complexes was reported in literature [1–12], with the exception of [8], where the composition of zinc complex with 2,4D was found to be $M_2L_3$. In some cases differences also appear in the number of water molecules attached.

All of the compounds were precipitated from neutral solutions of sodium salts of 2,4D or 2,4DP, to which water solutions of nitrates of respective metals were added maintaining the molar ratio ligand: metal = 2:1. In the case of the mercury compounds it was necessary to acidify the solution of mercury nitrate to avoid precipitation of HgO. The hydration state of the compounds is different. Both complexes of mercury and the complex of lead with 2,4DP are anhydrous and one water molecule is attached to Pb-2,4D and Cu-2,4DP. The other compounds contain from 2 to 6 water molecules.

Water solubility of the obtained complexes varies considerably (Tables 1 and 2) and according to the increasing *S* value they can be put in the following way:

2,4D Hg < Pb < Cu < Cd < Fe < Co < Ni < Zn < Ca < Mn < Mg
2,4DP Hg < Pb < Fe < Ca < Co < Cu < Ni < Cd < Zn < Mn

In both series the compounds of mercury and lead are definitely the most sparingly soluble and the manganese compound – the most readily soluble. The compound of magnesium with 2,4D exhibits the highest solubility. Its analogue with 2,4DP was not obtained, probable because it is more soluble than magnesium compound with 2,4D. In most cases the salts of the same metals with 2,4DP were more readily soluble than those with 2,4D. Similar observations were made in refs. [9,11]. The complexes of iron and calcium are an exception.

The above presented series of solubility of the 2,4D complexes explains the result of the experiment with the use of the herbicide “Aminopielik” which contains 2,4D. In solution of “Aminopielik” precipitates appear immediately after the addition of mercury, lead and copper salts and after a week in the case of cadmium salt. The content of Hg, Pb and Cd determined in these precipitates is similar to the content established in the complexes under study (Table 3). The solid obtained with “Aminopielik” contained a low percentage of copper in comparison with $Cu(2,4D)_2 \cdot 4H_2O$. It can be caused by co-precipitation of the “Aminopielik” components. Under the same conditions the other metals did not appear in the form of precipitates.

### 3.2. X-ray analysis

Powder diffraction patterns indicate that the obtained complexes are crystalline and have different structures. The number of the peaks proves that the complexes of Zn(II), Cd(II), Pb(II), Mn(II), Co(II), Ni(II), Ca(II) and Mg(II) have higher degree of crystallinity than the Cu(II), Hg(II) and Fe(II). Fig. 1 presents examples of diffraction patterns of new Ca complexes with 2,4D and 2,4DP and the Mg complex with 2,4D.

Monocrystals of Co, Ni, Ca and Mg compounds with 2,4D and Mn with 2,4DP sufficient for structural studies were obtained and their structures were resolved [18]. The crystallographic structures of Cu and Zn complexes with 2,4D have been described earlier by Smith and Kennard [3,6]. The structures of the other complexes under study are unknown. The copper complex is a dimer of a formula $[Cu_2(2,4D)_4(H_2O)_2] \cdot 2H_2O$, in which bidentate bridging carboxylate groups are present [3]. The zinc complex is also a dimer $\{[Zn(2,4D)_2(H_2O)_4]\ [Zn(2,4D)_2(H_2O)_2]\}$, in which an octahedral and tetrahedral complexes are bound by hydrogen bonds and carboxylate groups are unidentate ligands [6]. The Co, Ni and

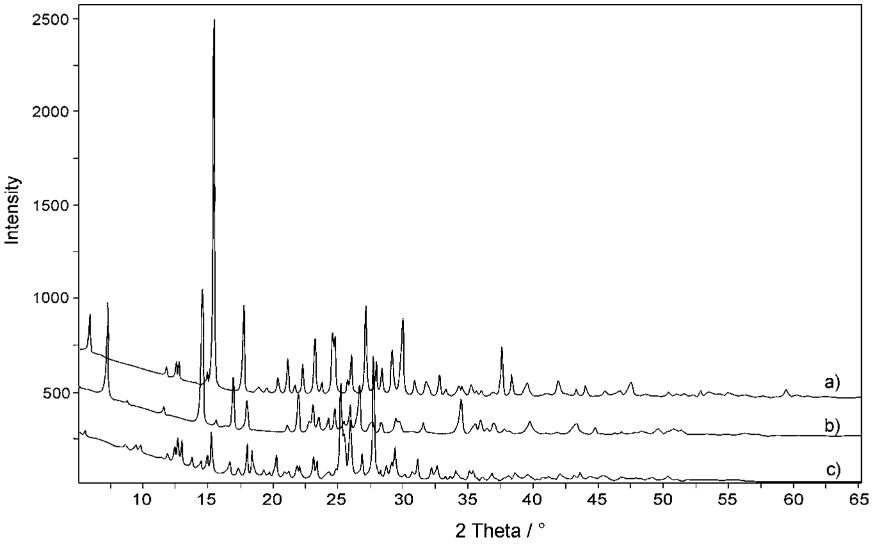

**Fig. 1.** X-ray diffraction patterns of: (a) $Mg(2,4D)_2{\cdot}5H_2O$, (b) $Ca(2,4DP)_2{\cdot}2H_2O$, (c) $Ca(2,4D)_2{\cdot}2H_2O$.

Mg compounds with 2,4D which we investigated are complex salts containing two unidentate carboxylate groups and water molecules in their coordination spheres. The Co and Ni complexes are polymeric structure with bridges formed by one of the water molecules and Mg compound is monomer. In the Ca complex with 2,4D each carboxylate group is bidentate chelating in relation to one metal atom and unidentate in relation to the other. The bonds with carboxylate groups acting as unidentate ligands cause formation of polymer chains which are connected by hydrogen bonds, thus giving a lamellar structure. An analogous structure of $Pb(MCPA)_2{\cdot}H_2O$ was established by Kruszynski et al. [19]. The ligand in this complex is 4-chloro-2-methylphenoxyacetic acid which differs from 2,4D with one substituent in the benzene ring. The structures of several other metals with MCPA have also been determined. Kruszynski and Turek [20] found that $Cd(MCPA)_2{\cdot}2H_2O$ is a polymer whose chains are formed by bidentate bridging carboxylate groups and polymer net is stabilized by hydrogen bonds. Shulgin and Konnik [21] found out that $Cu(MCPA)_2{\cdot}4H_2O$ has an analogous polymer structure but postulated a formation of a bond between copper and ether oxygen. Smith et al. [22] examined the structure of the magnesium compound and found it to be a monomer of the formula $[Mg(MCPA)_2{\cdot}4H_2O]{\cdot}2H_2O$ and ruled out a bond of the metal with ether oxygen. Tangoulis et al. [23] pointed out that the manganese complex is a polymer with a layer structure in which bidentate bridging carboxylate groups are bound with manganese atoms $[Mn(MCPA)_2{\cdot}(H_2O)_2]_n$. The only metal complex with 2,4DP, whose structure is known and was solved by us, is a polymeric manganese compound of a formula $[Mn(2,4DP)_2{\cdot}(H_2O)_3]{\cdot}3H_2O)]_n$ [18], where manganese is attached to two unidentate carboxylate groups and four water molecules. In the polymer chain there are

**Table 4**
Principal IR bands for OCO groups in sodium salts and obtained complexes.

| Compound | $\nu_{COOH}$ ($cm^{-1}$) | $\nu(OCO)_{as}$ ($cm^{-1}$) | $\nu(OCO)_s$ ($cm^{-1}$) | $\Delta\nu = \nu_{as} - \nu_s$ ($cm^{-1}$) |
|---|---|---|---|---|
| 2,4D | 1738.9 | | | |
| Na(2,4D) | | 1622.0 | 1429.2 | 192.8 |
| $Hg(2,4D)_2$ | | 1618.2 | 1427.2 | 191.0 |
| $Mn(2,4D)_2{\cdot}4H_2O$ | | 1589.2 | 1423.4 | 160.6 |
| $Fe(2,4D)_2{\cdot}4H_2O$ | | 1584.0 | 1425.3 | 158.7 |
| $Co(2,4D)_2{\cdot}6H_2O$ | | 1575.7 | 1415.7 | 160.0 |
| $Ni(2,4D)_2{\cdot}6H_2O$ | | 1580.2 | 1416.0 | 164.2 |
| $Ca(2,4D)_2{\cdot}2H_2O$ | | 1591.2 | 1430.1 | 161.1 |
| $Mg(2,4D)_2{\cdot}5H_2O$ | | 1595.0 | 1427.2 | 167.8 |
| $Cu(2,4D)_2{\cdot}4H_2O$ | | 1635.5 | 1429.2 | 206.3 |
| $Zn(2,4D)_2{\cdot}3H_2O$ | | 1616.2 | 1425.3 | 190.9 |
| $Cd(2,4D)_2{\cdot}2H_2O$ | | 1618.2 | 1429.2 | 198.0 |
| $Pb(2,4D)_2{\cdot}H_2O$ | | 1618.2 | 1438.8 | 179.4 |
| 2,4DP | 1716.5 | | | |
| Na(2,4DP) | | 1616.0 | 1417.6 | 198.4 |
| $Hg(2,4DP)_2$ | | 1608.5 | 1408.0 | 200.5 |
| $Mn(2,4DP)_2{\cdot}6H_2O$ | | 1589.2 | 1415.7 | 173.5 |
| $Fe(2,4DP)_2{\cdot}4H_2O$ | | 1591.2 | 1419.5 | 171.7 |
| $Co(2,4DP)_2{\cdot}6H_2O$ | | 1591.2 | 1413.7 | 177.5 |
| $Ni(2,4DP)_2{\cdot}6H_2O$ | | 1587.3 | 1419.5 | 167.8 |
| $Ca(2,4DP)_2{\cdot}2H_2O$ | | 1575.7 | 1432.0 | 143.7 |
| $Cu(2,4DP)_2{\cdot}H_2O$ | | 1624.0 | 1419.5 | 204.5 |
| $Zn(2,4DP)_2{\cdot}4H_2O$ | | 1590.0 | 1417.6 | 172.4 |
| $Cd(2,4DP)_2{\cdot}2H_2O$ | | 1568.5 | 1418.5 | 150.0 |
| $Pb(2,4DP)_2{\cdot}H_2O$ | | 1593.1 | 1417.6 | 175.5 |

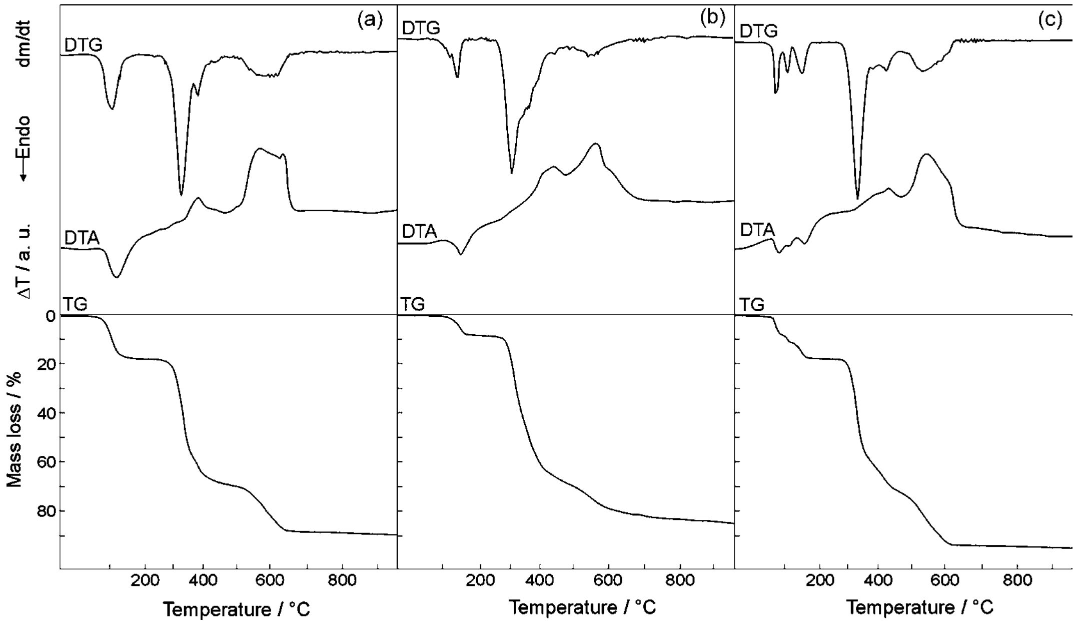

**Fig. 2.** Thermal analysis curves of metal complexes with 2,4D: (a) Ni, (b) Ca, (c) Mg.

bridges formed by one of the water molecules between manganese atoms.

### 3.3. *IR spectra*

In the spectra of metal complexes with carboxylic acid, bands of the valence vibrations of nondissociated COOH group (over the range 1760–1690 $cm^{-1}$) are not observed. On the contrary there are bands of asymmetrical (1610–1550 $cm^{-1}$) and symmetrical (1420–1300 $cm^{-1}$) vibrations of dissociated OCO groups [24]. The magnitude of separation $\Delta\nu = \nu(OCO)_{as} - \nu(OCO)_s$ and the direction of the shifts of these bands in relation to the respective frequencies in the spectrum of the sodium salt of the acid are often used as spectroscopic criteria to determine the mode of carboxylate binding [25,26]. According to these criteria, the highest $\Delta\nu$ values should accompany unidentate coordination, lower-bidentate bridging and the lowest-bidentate chelating. The direction of shifts of $\nu(OCO)_{as}$ and $\nu(OCO)_s$ frequencies in relation to ionic bond in sodium salts should be successive:

(1) unidentate – $\nu(OCO)_{as}$ higher, $\nu(OCO)_s$ lower;
(2) unsymmetrical bidentate bridging – $\nu(OCO)_{as}$ higher, $\nu(OCO)_s$ almost the same;
(3) symmetrical bidentate bridging – $\nu(OCO)_{as}$ higher, $\nu(OCO)_s$ higher;
(4) unsymmetrical bidentate chelating – $\nu(OCO)_{as}$ almost the same, $\nu(OCO)_s$ higher;

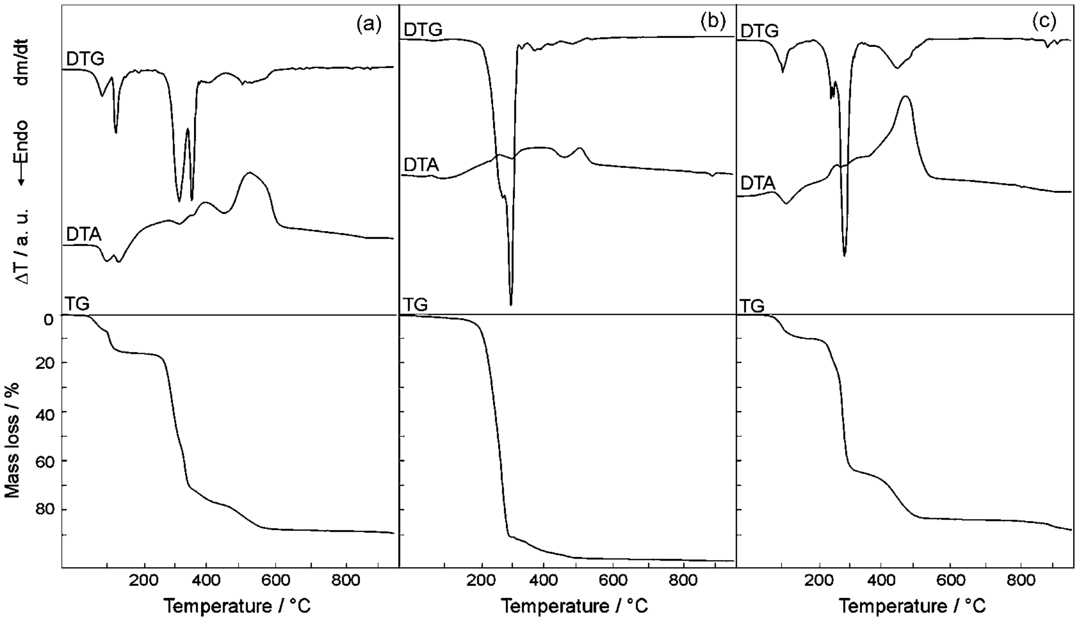

**Fig. 3.** Thermal analysis curves of metal complexes with 2,4DP: (a) Zn, (b) Hg, (c) Fe.

(5) symmetrical bidentate chelating – $\nu(OCO)_{as}$ lower, $\nu(OCO)_s$ higher.

In the IR analysis of the complexes under study (Table 4), the information resulting from the above-discussed X-ray analyses was taken into account. The structures of six of the metal complexes with 2,4D (Cu, Zn, Co, Ni, Ca, Mg) and three metal complexes with its analogue MCPA (Cd, Pb, Mg) are known. The spectroscopic criterion could be used to determine the mode of coordination in only a few of the 21 investigated complexes. In the spectrum of Cu complex with 2,4D, $\nu(OCO)_{as}$ is shifted towards higher frequencies and $\nu(OCO)_s$ remains the same, so it can be supposed to be unsymmetrical bidentate bridging coordination, which is in agreement with the structure of the compound [3]. It is similar in the spectrum of Cu complex with 2,4DP, but the $\nu(OCO)_s$ band is shifted toward higher frequencies, which may indicate symmetrical bidentate bridging coordination. In the spectra of Ca complexes with 2,4D and 2,4DP a big shift of $\nu(OCO)_{as}$ in the direction of lower frequencies is observed while $\nu(OCO)_s$ shifts toward higher frequencies. It follows that coordination in both complexes is symmetrical bidentate chelating. A similar carboxylate group coordination mode follows from the spectrum of Pb complex with 2,4D, where the directions of shifts of the bands are the same as in the Ca complexes but $\nu(OCO)_{as}$ shift is much smaller. This is partly in agreement with the results of the structural analysis of Ca compounds with 2,4D [18] and Pb compounds with MCPA [19], which show that they are polymers with a unsymmetrical bidentate chelating and unidentate carboxylate group. In the spectra of Co, Ni and Zn complexes with 2,4D $\nu(OCO)_{as}$ bands appear at lower and $\nu(OCO)_s$ bands at higher frequencies than in the case of the sodium salt, which results in low values $\Delta\nu$ and indicates the presence of bidentate chelating carboxylate groups. This disagrees with the results of structural analysis which indicate that Co and Ni salts are polymers and the Zn compound is a dimer with unidentate carboxylate groups. In the spectra of the other complexes under study, $\nu(OCO)_{as}$ bands are shifted in the direction of lower frequencies and $\nu(OCO)_s$ bands also in the direction of lower values or remain the same as for the sodium salt. This is against the assumptions of the spectroscopic criterion. The structures of only two complexes: a Mg monomer with 2,4D [18] and a Mn polymer with 2,4DP [18] are known. Both compounds contain unidentate carboxylate groups. Zn(II), Pb(II), Fe(II), Co(II) and Ni(II) complexes with 2,4DP exhibit $\nu(OCO)_{as}$ and $\nu(OCO)_s$ vibration frequencies similar to those of Mn complex with 2,4DP and similar $\Delta\nu$ values. It can be supposed that their structures are analogous to the

**Table 5**
Thermal analysis of 2,4D complexes.

| Compound | Temperature range of decomposition stages (°C) | Mass loss (%) | | Temperature of DTA peaks and thermal effects (°C) |
|---|---|---|---|---|
| | | Found (calc.)[a,b] | Total | |
| $Hg(2,4D)_2$ | 160–335 | 86 (50.55)[b] | 100 | |
| | 335–800 | 14 | | 590 exo |
| $Mn(2,4D)_2{\cdot}4H_2O$ | 60–85 | 6 (6.35)[a] | 87 | 80 endo |
| | 85–130 | 6 (6.35)[a] | | 130 endo |
| | 240–360 | 41 (57.11)[b] | | 390 exo |
| | 360–660 | 34 | | 520 exo |
| $Fe(2,4D)_2{\cdot}4H_2O$ | 45–100 | 12 (12.68)[a] | 85.5 | 95 endo |
| | 180–300 | 55 (57.02)[b] | | 440 exo |
| | 300–550 | 18.5 | | 500 exo |
| $Co(2,4D)_2{\cdot}6H_2O$ | 40–90 | 12.5 (11.86)[a] | 89 | 90 endo |
| | 90–140 | 5.5 (5.93)[a] | | 140 endo |
| | 260–340 | 42 (53.25)[b] | | 350 exo |
| | 340–640 | 29 | | 560 exo |
| $Ni(2,4D)_2{\cdot}6H_2O$ | 50–110 | 17 (17.79)[a] | 88 | 90 endo |
| | 280–500 | 51 (53.25)[b] | | 390 exo |
| | 500–650 | 18 | | 570 exo |
| $Ca(2,4D)_2{\cdot}2H_2O$ | 80–140 | 7 (6.97)[a] | 83 | 130 endo |
| | 270–480 | 60 (62.74)[b] | | 440 exo |
| | 480–700 | 16 | | 570 exo |
| $Mg(2,4D)_2{\cdot}5H_2O$ | 60–90 | 7.0 (6.50)[a] | 95 | 80 endo |
| | 90–120 | 3.5 (3.25)[a] | | 110 endo |
| | 120–170 | 6.5 (6.50)[a] | | 160 endo |
| | 280–470 | 56 (58.41)[b] | | 430 exo |
| | 470–740 | 22 | | 540 exo |
| $Cu(2,4D)_2{\cdot}4H_2O$ | 60–100 | 13 (12.51)[a] | 91 | 105 endo |
| | 220–340 | 55 (56.26)[b] | | 270 exo |
| | 340–880 | 23 | | 470 exo |
| $Zn(2,4D)_2{\cdot}3H_2O$ | 60–100 | 10 (11.89)[a] | 88 | 90, 250 endo |
| | 260–340 | 58 (57.88)[b] | | 340 exo |
| | 340–620 | 20 | | 580 exo |
| $Cd(2,4D)_2{\cdot}2H_2O$ | 95–130 | 5.5 (5.23)[a] | 99 | 130 endo |
| | 235–360 | 43.5 (55.00)[b] | | 380 exo |
| | 360–770 | 50 | | 540 exo |
| $Pb(2,4D)_2{\cdot}H_2O$ | 100–140 | 3 (2.71)[a] | 99 | 130, 220 endo |
| | 210–360 | 49 (48.68)[b] | | 380 exo |
| | 360–810 | 47 | | 570 exo |

[a] Calculated for the number of water molecules as found in the complex structure.
[b] Calculated for two –O–$C_6H_3Cl_2$ leaving groups.

structure of the manganese compound. However, full interpretation of the mode of coordination between metal(II) and carboxylates in the obtained compounds will be possible after the determination of their crystal structure.

### 3.4. Thermal analysis

TG, DTG and DTA curves (Figs. 2 and 3 and Tables 5 and 6) show that the thermal decomposition of the complexes proceeds in a similar way. The first step of the decomposition of the hydrated compounds is dehydration. Thermal decomposition of anhydrous compounds consists of two steps with a complex course.

#### 3.4.1. Dehydration

As they are heated, most of the compounds lose water in one step, but dehydration of $Mn(2,4D)_2{\cdot}4H_2O$, $Co(2,4D)_2{\cdot}6H_2O$, $Zn(2,4DP)_2{\cdot}4H_2O$ and $Cd(2,4DP)_2{\cdot}2H_2O$ proceeds in two, and that of $Mg(2,4D)_2{\cdot}5H_2O$ in three steps. On the basis of loss in mass in the process, the number of water molecules in the obtained complexes was determined. The loss in mass showing in the TG curve corresponds with an appropriate number of endothermic peaks in the DTA curve and distinct peaks in the DTG curve. The number of dehydration steps does not depend on the number of water molecules in the complex. Thus, for instance, Ni and Ca complexes with 2,4D, containing 6 and 2 $H_2O$ molecules, respectively, lose water in one step while dehydration of the Mg pentahydrate complex is a process consisting of three steps, in which the compound loses first two, then one, and finally the other two molecules of water (Fig. 2). Similarly, the complex of Fe with 2,4DP which contains 4 molecules of $H_2O$ is dehydrated in a one step process, while the dehydration of the tetrahydrous Zn compound with 2,4DP proceeds in two steps and the compound loses two water molecules in each of them (Fig. 3). Fig. 3 also presents thermal analysis curves of the anhydrous Hg complex with 2,4DP.

The temperature ranges at which the compounds under study are dehydrated are different. The one step dehydration of Cu, Fe and Ni with either ligand, Zn with 2,4D and Mn and Co with 2,4DP begins at 45–60 °C and ends at 100–110 °C, whereas the dehydration of Cd, Pb and Ca complexes with 2,4D and Ca complex with 2,4DP occurs at higher temperatures, from 80–100 °C to 130–140 °C. In the case of complexes of Zn and Cd with 2,4DP and Mn and Co with 2,4D which release water in two steps, the first step of dehydration begins at 20–60 °C and ends at 70–95 °C and the second step ends at 120–150 °C. The three step dehydration of the Mg complex with 2,4D ends at the highest temperature (170 °C), which indicates a strong bond with two water molecules in the complex.

#### 3.4.2. Decomposition of the anhydrous compounds

The course of TG and DTG curves indicates that the thermal decomposition of all the anhydrous complexes can be divided into two steps (Figs. 1 and 2, Tables 4 and 5). In the first step the compounds decompose rapidly with mass losses within the range 40–60% and in the case of the mercury complexes reaching up

**Table 6**
Thermal analysis of 2,4DP complexes.

| Compound | Temperature range of decomposition stages (°C) | Mass loss (%) | | Temperature of peaks and thermal effects (°C) |
|---|---|---|---|---|
| | | Found (calc.) | Total | |
| $Hg(2,4DP)_2$ | 180–320 | 85 (48.42)[a] | 100 | 265 exo |
| | 320–800 | 15 | | 510 exo |
| $Mn(2,4DP)_2{\cdot}6H_2O$ | 50–100 | 16 (17.11)[b] | 87 | 90 endo |
| | 240–370 | 50 (51.31)[a] | | 380 exo |
| | 370–740 | 21 | | 510 exo |
| $Fe(2,4DP)_2{\cdot}4H_2O$ | 50–130 | 11 (12.08)[b] | 84 | 90 endo |
| | 200–310 | 54 (54.33)[a] | | |
| | 310–505 | 19 | | 580 exo |
| $Co(2,4DP)_2{\cdot}6H_2O$ | 50–110 | 16.5 (17.01)[b] | 86.5 | 105 endo |
| | 280–370 | 49 (50.99)[a] | | 360 exo |
| | 370–560 | 21 | | 480, 540 exo |
| $Ni(2,4DP)_2{\cdot}6H_2O$ | 50–110 | 17.5 (17.01)[b] | 89.5 | 100 endo |
| | 285–375 | 48 (50.99)[a] | | 350 exo |
| | 375–655 | 24 | | 580, 630 exo |
| $Ca(2,4DP)_2{\cdot}2H_2O$ | 100–140 | 7 (6.4)[b] | 83 | 150 endo |
| | 270–445 | 58.5 (59.5)[a] | | 420 exo |
| | 445–840 | 17.5 | | 585 exo |
| $Cu(2,4DP)_2{\cdot}H_2O$ | 60–95 | 3 (3.27)[b] | 90 | 80 endo 280 exo |
| | 230–310 | 60 (58.91)[a] | | 460 exo |
| | 310–940 | 27 | | |
| $Zn(2,4DP)_2{\cdot}4H_2O$ | 40–85 | 6.5 (5.95)[b] | 85.5 | 70 endo |
| | 85–120 | 7.5 (5.95)[b] | | 100 endo |
| | 260–350 | 54.5 (53.43)[a] | | 400 exo |
| | 350–610 | 17 | | 530 exo |
| $Cd(2,4DP)_2{\cdot}2H_2O$ | 50–95 | 3 (2.61)[b] | 91 | 80 endo |
| | 95–120 | 3.5 (2.61)[b] | | 110 endo |
| | 260–320 | 47.5 (52.52)[a] | | 350 exo |
| | 320–760 | 36 | | 535 exo |
| $Pb(2,4DP)_2$ | 235–350 | 49 (47.95)[a] | 99 | 190 endo |
| | 350–950 | 50 | | 320, 590 exo |

[a] Calculated for two $–O–C_6H_3Cl_2$ leaving groups.

[b] Calculated for the number of water molecules as found in the complex structure.

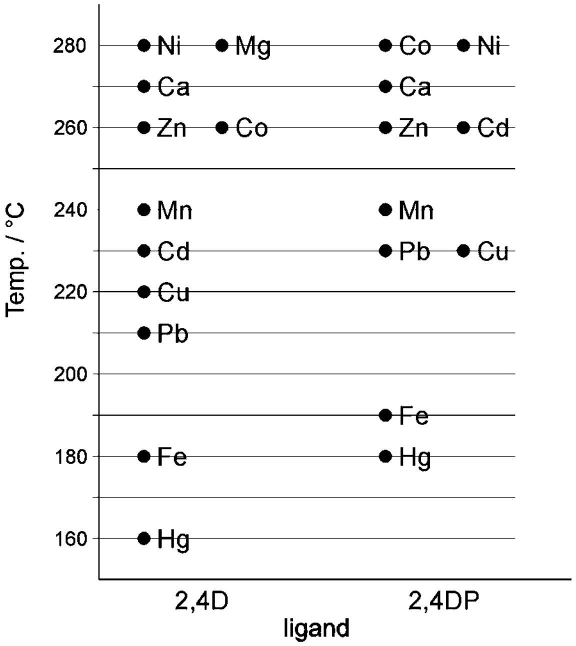

**Fig. 4.** Thermal stabilities of all anhydrous complexes under study.

to 86%. The peaks in the DTG curves are intensive and sharp, but also unsymmetrical or split, which indicates the complexity of the decomposition process. In this step pyrolysis of the organic ligands probably proceeds and chlorophenoxy groups $–O–C_6H_3Cl_2$ or phenyl groups $–C_6H_3Cl_2$ are split off. It is known from the available structural studies that the ether group oxygen bond with the benzene ring in 2,4D and 2,4DP and their complexes with metals are shorter than the bond with the carbon of a respective alkane acid [3,6,18]. Thus $–O–C_6H_3Cl_2$ groups are more likely to split off. The mass losses in the first step of decomposition, calculated with the assumption that the complex molecule loses two chlorophenoxy groups, are in agreement (within the range ± 5%) with the experimental data (Tables 5 and 6), except for the mercury complexes for which they are almost twice higher and the compounds of Cd, Mn and Co with 2,4D and of Cd with 2,4DP for which they are lower by about 10–30%. The split off organic fragments are combusted. In the DTA curves a broad exothermic peak begins from the start of the first step of decomposition and ends as the second is finished. It has two maxima and that corresponding with the second decomposition step is usually more intensive. The second step of decomposition is slower, the mass losses are smaller and the corresponding DTG peaks are broad and not intensive. The remaining organic substance is released, and the gaseous decomposition products are combusted. The final decomposition products are oxides of respective metals (identified by X-ray diffractometry), with the exception of mercury, cadmium and lead, for which mass losses are close to 100%. It follows that under the conditions of thermal decomposition, Hg, Cd and Pb form volatile compounds. In the case of Cd and Pb complexes, they can be volatile chlorides, while in the case of decomposing Hg compounds, the release of mercury vapour, the formation of volatile chlorides and metaloorganic volatile derivatives, such as the very toxic methylmercury $CH_3Hg^+$, have to be taken into account. The thermal analysis curves of the mercury complexes show a considerably bigger loss of mass in the first step of decomposition and less visible exothermic effects than the derivatograms of the other compounds under study (Fig. 3). It follows that volatile mercury derivatives are oxidized gradually during the whole decomposition process and do not undergo complete combustion.

The temperature of the beginning of the DTG peak associated with the first decomposition step was taken as the criterion of thermal stability of the complexes under investigation. Fig. 4 presents the respective comparison for the two series of metal complexes with 2,4D and 2,4DP. Mercury complexes are characterized by the lowest thermal stability and it should be stressed that already at 160–180 °C highly toxic compounds appear in the air. A correlation was also observed between the temperature of the onset of the decomposition of the anhydrous compounds and the solubility of the complexes. The complexes of the metals under study with 2,4DP which were found to be more readily soluble in water than the complexes with 2,4D, usually show higher thermal stability. The least stable Hg complexes, on the other hand, exhibit also the lowest solubility.

### *3.5. Conclusions*

In the metal complexes with phenoxyalkanoic acids the carboxylate group may be either unidentate or bidentate bridging or chelating. The complexes may be monomers, dimers or polymers. Dimeric and polymeric structures are formed by bidentate bridging carboxylate groups, but metal atoms may be bridged by water molecules and dimers may be formed by hydrogen bonds. Hydrogen bonds are present in all complexes with phenoxyalkanoic acid anions and they stabilize their structure. Due to such great diversity of the structures of the complexes under study: (i) spectroscopic criterion $\Delta$ cannot be used for explicit determination of the mode of coordination between metal ions and carboxylate groups; (ii) thermal stability of these complexes does not depend on the properties of the central ion.

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