Journal of Thermal Analysis and Calorimetry, Vol. 74 (2003) 237–250

Ni(II) AND Co(II) COMPLEXES WITH 2,4-DICHLOROPHENOXYACETIC ACID AND 2-(2,4-DICHLOROPHENOXY)-PROPIONIC ACID
Synthesis, properties and thermal decomposition

B. Ptaszyński[*] *and A. Zwolińska*

Institute of General and Ecological Chemistry, Technical University, 90-924 Łódź, Poland

(Received November 8, 2002; in revised form March 11, 2003)

Abstract

Nickel(II) and cobalt(II) complexes with the commercial herbicides 2,4-dichlorophenoxyacetic acid (2,4D; $C_8H_6O_3Cl_2$) and 2-(2,4-dichlorophenoxy)-propionic acid (2,4DP; $C_9H_8O_3Cl_2$) were prepared and characterized. On the basis of the results of elemental analysis and Ni and Co determination, the following molecular formulae were proposed for the obtained compounds: $Ni(C_8H_5O_3Cl_2)_2 \cdot 6H_2O$, $Co(C_8H_5O_3Cl_2)_2 \cdot 6H_2O$, $Ni(C_9H_7O_3Cl_2)_2 \cdot 2H_2O$ and $Co(C_9H_7O_3Cl_2)_2 \cdot 2H_2O$. X-ray powder analysis was carried out. The IR, electronic (VIS) spectra and conductivity data were discussed. Water solubility of the synthesized complexes at room temperature was examined. Thermal decomposition of the compounds was studied. Dehydration processes occur during heating in air. The anhydrous compounds decompose *via* different intermediate products to oxides. TG/MS studies indicate formation of gaseous mass fragments of decomposition including H_2O^+, OH^+, CO_2^+, HCl^+, Cl_2^+, CH_3Cl^+, CH_2O^+, $C_6H_6^+$ and other.

Keywords: complexes, 2,4-dichlorophenoxyacetic acid, 2-(2,4-dichlorophenoxy)-propionic acid, IR spectra, mass spectrometry, thermal decomposition, VIS spectra, 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 which belong to the group of arylcarboxyl agents. 2,4D and 2,4DP may, due to the presence of the carboxyl group in their molecules, coordinate with metal cations.

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

---

[*] Author for correspondence: E-mail: ptaszynski@lodz.msk.pl

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The metal(II) compounds of 2,4-dichlorophenoxyacetic acid and its mixed complexes with N-bases [2–7], α-aminoacids [6] and bovine serum albumin [8] were described.

Few papers concern investigation of simple complexes of 2,4D with metals(II) [9–15]. The thermal properties of their compounds have not been extensively studied so far. The thermal decomposition of 2,4D complexes with Mn(II), Zn(II), Co(II), Cu(II), Ni(II), Cd(II) and Fe(III) was carried out by Shulgin *et al.* [13, 14] and Ristici [15].

The present paper describes the preparation, water solubility at room temperature, IR and VIS spectra, X-ray powder studies, molar conductivity investigations and thermal decomposition of $Ni(C_8H_5O_3Cl_2)_2{\cdot}6H_2O$ (**Ni-2,4D**), $Co(C_8H_5O_3Cl_2)_2{\cdot}6H_2O$ **(Co-2,4D)**, $Ni(C_9H_7O_3Cl_2)_2{\cdot}2H_2O$ (**Ni-2,4DP**) and $Co(C_9H_7O_3Cl_2)_2{\cdot}2H_2O$ (**Co-2,4DP**). The thermal decomposition was studied in air. A coupled TG/MS system was used to analyse the principal gaseous products involved during pyrolysis of the obtained compounds [16–19]. The solid intermediate and final products of decomposition were identified by X-ray diffraction.

Experimental

Chemicals

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

Cobalt(II) nitrate ($Co(NO_3)_2{\cdot}H_2O$) and nickel(II) nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) p.a. were obtained from Fluka; methanol (anhydroscan) was from Lab-Scan. Other chemicals were analytically pure products from POCh–Gliwice.

Physical measurements: techniques and apparatus

X-ray powder diffraction patterns were recorded on a Siemens D5000 diffractometer, using CuK_α radiation monochromatized by means of a secondary graphite monochromator. The curves were recorded over the 2θ range 2–90° with 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.

The VIS spectra were obtained in a Nujol mull by means of M-40 Specord Instrument over the range 29500–11500 cm^{-1}.

Conductivity measurements were performed at 25±0.05°C on an OK-102/1 conductometer with an OK902 electrode. The cell constant was determined by use of KCl standard aqueous solution. The molar conductivity (Λ_M) of the complexes was measured using $1.0{\cdot}10^{-3}$ mol dm^{-3} solution in methanol.

The thermal decomposition processes of the prepared complexes were studied by thermogravimetry (TG, DTG, DTA) and TG/MS technique. Thermal curves were obtained on derivatograph OD-102/1500 in air over the temperature ranges 25–1000°C at a heating rate 10°C min^{-1}. The mass of the samples was 100 mg. $\alpha\text{-Al}_2\text{O}_3$ was used as a reference material.

The TG/MS system (thermoanalyser TG/DTA-SET SYS-16/18, mass spectrometer ThermoStar from Balzers, corundum crucible) was used for the characterization of gaseous products thermal decomposition of the Ni and Co complexes (mass of the samples of Ni-2,4D, Ni-2,4DP, Co-2,4D and Co-2,4DP were 4.01, 2.19, 3.34 and 5.27 mg, respectively). The solid intermediate products of decomposition obtained under conditions similar to those used in thermal analysis were identified by X-ray diffraction (using Powder Diffraction File) [20].

Synthesis of the complexes

The reaction of 2,4D and 2,4DP with cobalt(II) and nickel(II) nitrates(V) were performed using amounts of substrates corresponding with molar ratio M:2,4D and M:2,4DP=1:2 (where *M*=Ni and Co) and at pH=7.

As 2,4D and 2,4DP are sparingly soluble in water, whereas their sodium salts are readily soluble, the water solutions of these compounds (20 mmol in 150 mL 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 pH=7 by adding 1 mol dm^{-3} NaOH. The solutions were filtered and slowly, while stirring vigorously added to a solution containing Co(II) or Ni(II) (10 mmol in 80 mL of the water). The precipitates formed immediately. The Ni compounds were green while these of Co – pink. The precipitated complexes were filtered off after 30 min and dried in air at room temperature.

Analyses of the complexes

The composition of the synthesized complexes was established on the basis of determination of the metals, carbon, hydrogen and chlorine. Nickel and cobalt in mineralized samples were determined by complexometric titration using EDTA [21] *vs*. murexide whereas carbon, hydrogen and chlorine by elementary analysis. The analytical results are shown in Table 1.

Water solubility of the complexes under study was determined at room temperature (about 21°C). About 1.800 g of the compound was weighed, 50 mL of distilled water were added and the sample was shaken for 6 h. Next the solution was filtered. In the saturated water solution of the complex the content of the metal was determined by complexometric titration using EDTA *vs*. pyrocatechol violet [21] and by the spectrophotometric method with 4-(2-pyridylazo)-resolcinol (PAR) [22, 23]. The average values of water solubility of studied complexes are presented in Table 1.

Results and discussion

The analytical results indicate the following molecular formulae for the obtained complexes: $Ni(C_8H_5O_3Cl_2)_2\cdot6H_2O$, $Co(C_8H_5O_3Cl_2)_2\cdot6H_2O$, $Ni(C_9H_7O_3Cl_2)_2\cdot2H_2O$ and $Co(C_9H_7O_3Cl_2)_2\cdot2H_2O$. All compounds are stable in air. Their solubility in water at 21°C is of the order of 10^{-2} mol dm^{-3}. They dissolve fairly in ethanol and methanol.

The molar conductivities in methanol (Table 1) indicate that the complexes show intermediate behaviour between those of non- and 1:1 electrolytes [24].

Table 1 Analytical data, solubility S [mol dm^{-3}] in water at 21°C and molar conductivity Λ_M [Ω^{-1}cm^2 mol^{-1}] in methanol (concentration $1.0\cdot10^{-3}$) at 25°C of the nickel and cobalt complexes with 2,4D and 2,4DP

Complexes	Analysis: found (calculated)/%				$S\cdot10^{-2}$	Λ_M
	M	C	H	Cl		
Ni-2,4D	9.57(9.67)	31.40(31.66)	3.47(3.66)	23.30(23.37)	2.01	62.6
Ni-2,4DP	10.02(10.43)	38.17(38.41)	3.22(3.23)	25.44(25.19)	4.08	61.6
Co-2,4D	9.77(9.71)	31.91(31.65)	3.68(3.66)	23.36(23.36)	1.28	60.6
Co-2,4DP	9.97(10.47)	38.23(38.39)	3.26(3.23)	24.48(25.18)	5.51	65.2

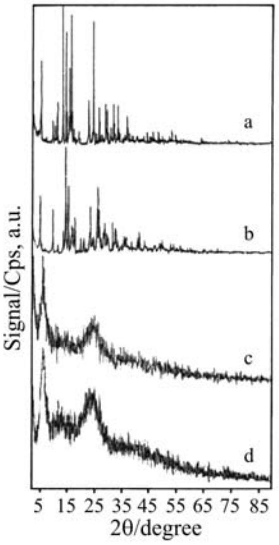

Fig. 1 Diffractograms of a – Co-2,4D; b – Ni-2,4D; c – Co-2,4DP and d – Ni-2,4DP

The analysis of the diffractograms (Fig. 1) shows that Ni-2,4D and Co-2,4D are crystalline compounds, while Ni-2,4DP and Co-2,4DP are either amorphous or their degree of crystallinity is very low.

Electronic and IR spectra

Due to the presence of carboxyl group in their molecules, 2,4-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy)-propionic acid may coordinate with metal cations. IR spectrophotometry (over the range 4400–400 cm^{-1}) confirms that 2,4D and 2,4DP combine with nickel and cobalt through the oxygen atoms of the carboxylate group. Table 2 presents only the fundamental frequencies of vibrations of the carboxylate group for acids and prepared complexes [25, 26].

The stretching band of the undissociated carboxyl group ν(C=O), present in the 2,4D and 2,4DP spectra, does not appear in the spectra of their complexes. Instead, two new stretching bands, $\nu(OCO)_{sym}$ and $\nu(OCO)_{asym}$ appear, representing the vibrations of the dissociated carboxylate group.

On the basis of Δν value calculated as the difference between the frequencies of the asymmetric and symmetric vibrations of the dissociated carboxylate group and its comparison with the results obtained for sodium salts, the type of coordination of the carboxylate group was established [27–29].

Kennard *et al.* studied crystal and molecular structures of Zn(II) and Cu(II) complexes of 2,4-dichlorophenoxyacetic acid [10, 11]. They found out that the molecular units in the Zn-2,4D compound 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-2,4D, $[Cu_2(2,4D)_4(H_2O)_2\cdot 2H_2O]$ forms 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.

Unequivocal assertion of nature of carboxylate group is very difficult without supplementary structural studies. In this paper separation (Δν) of ν(OCO) for Ni and Co complexes are lower than Δν values for sodium salts of the studied acids but difference is not large.

Waddington *et al.* [29] suggest that if difference between Δν for the complexes and Δν for the sodium salt is small, carboxylate group is bridging. If this difference is large, the carboxylate group is chelating. With Waddington's criterion accepted, the carboxylate group in our complexes is bridging. The obtained values of molar conductivity in methanol confirm our presumptions with regard to coordination of carboxylate groups.

The spectra of all the complexes of 2,4D and 2,4DP under study show strong and broad bands in the water stretching region (ca. 3600–3100 cm^{-1}). The bands in the water bending region (1650–1620 cm^{-1}) are overlaped with the streching bands ($\nu(OCO)_{asym}$) of carboxylate group. The ν(M–O)+δ(OCO) vibrations are observed within the interval ca. 516.5–466.7 cm^{-1}.

VIS spectra of the solid nickel and cobalt compounds with 2,4D and 2,4DP acids was obtained in Nujol mulls within the 29500–11500 cm^{-1} region. d-d transition bands present in the electronic spectra of the studied complexes are all consistent

Table 2 The frequencies of group vibrations [cm^{-1}] present in the spectra of 2,4D and 2,4DP acid and their complexes with Ni(II) and Co(II); Ligand field spectral data in cm^{-1} for Ni and Co complexes with 2,4D and 2,4DP

Compound	ν(C=O)/ cm^{-1}	$\nu(\mathrm{OCO})_{\mathrm{asym}}$/ cm^{-1}	ν(OCO)/$_{\mathrm{sym}}$/ cm^{-1}	$\Delta\nu^{*}$	ν(MO)+δ(OCO)/ cm^{-1}	Ligand field spectral data/ cm^{-1}	
2,4D	1735.8 vs	–	–	–	–		
Na-2,4D	–	1620.1 vs	1338.5 s	281.6	–		
Co-2,4D	–	1585.4 vs	1338.5 s	246.9	493.7 w	19100 19500	20620
Ni-2,4D	–	1581.5 vs	1342.4 s	239.1	516.5; 499.5 wd	25500	15100
2,4DP	1716.5 vs	–	–	–	–		
Na-2,4DP	–	1618.2 vs	1411.8 s	206.4	–		
Co-2,4DP	–	1596.9 vs	1419.5 s	177.4	504.6 w	18940 19340 19980	20860
Ni-2,4DP	–	1616.2 vs	1419.5 s	196.7	466.7 w	25020	14860

$^{*}\Delta\nu=\nu(\mathrm{OCO})_{\mathrm{asym}}-\nu(\mathrm{OCO})_{\mathrm{sym}}$; v – very, s – strong, w – weak, d – double with a distorted octahedral environment around the Ni(II) and Co(II) atom [16–18, 30]. Table 2 shows ligand field spectral data for Ni and Co complexes with 2,4D and 2,4DP. The nickel complexes exhibit only two bands: at ca. 15000 cm^{-1} which correspond to the transition $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ and at ca. 25000 cm^{-1} connected with $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$ transition. The ligand field spectra of cobalt complexes present multiple band at ca. 19500 cm^{-1}. This band may be assigned to the $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ transition. It is apparently asymmetrical band and has a shoulder in the region 20620 cm^{-1} for Co-2,4D and 20860 cm^{-1} for Co-2,4DP.

Thermal analysis

The thermoanalytical curves Ni(II) and Co(II) complexes are presented in Figs 2 and 3 and the thermal decomposition data are listed in Table 3.

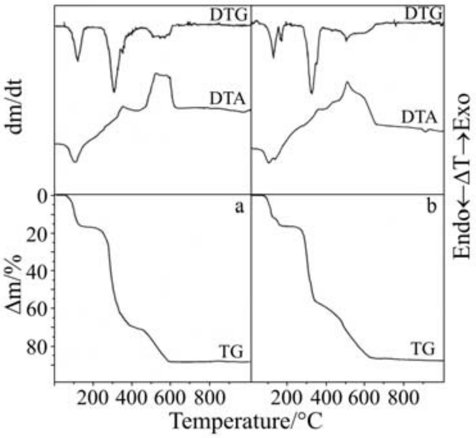

Fig. 2 Thermoanalytical curves (TG, DTG, DTA) of a – Ni-2,4D and b – Co-2,4D

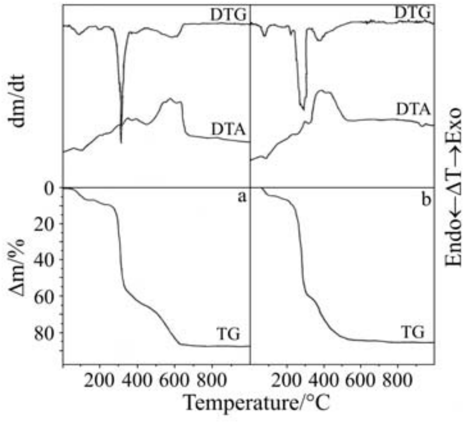

Fig. 3 Thermoanalytical curves (TG, DTG, DTA) of a – Ni-2,4DP and b – Co-2,4DP

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

Complexes	Temp. range of pyrolysis/°C	Mass loss/%		DTA peaks/°C	Intermediates solid products
		found	calcd.		
$Ni(2,4D)_2\cdot 6H_2O$	40–140	17.5	17.8	endo/100	$Ni(2,4D)_2$
	200–470	71.0		exo/390	mixture of Ni(2,4D) with Ni, $NiCl_2$, NiO
	470–650	88.0	87.7	exo/560, 600, 630	NiO
$Co(2,4D)_2\cdot 6H_2O$	50–100	13.0	13.4	endo/90	$Co(2,4D)_2\cdot 1.5H_2O$
	100–145	17.0	17.8	endo/130	$Co(2,4D)_2$
	180–370	59.0	59.0	exo/350	Co(2,4D) with ca. 15%Co_3O_4
	370–650	87.0	86.8	exo/430, 505	Co_3O_4
	650–940	88.0	87.7	exo/920	CoO
$Ni(2,4DP)_2\cdot 2H_2O$	45–130	6.5	6.4	endo/90	$Ni(2,4DP)_2$
	160–240	9.0		exo/200	organic fragments
	240–450	59.0		exo/310, 360, 410	undefined intermediate products
	450–660	86.5	86.7	exo/550, 590, 640	NiO
$Co(2,4DP)_2\cdot 2H_2O$	40–105	6.5	6.4	endo/80	$Co(2,4DP)_2$
	130–210	9.5		exo	organic fragments
	210–370	63.0		exo/250, 340	mixture of Co(2,4DP) with $CoCl_2$ and Co_3O_4
	370–600	85.5	85.7	exo/445, 495	Co_3O_4
	600–950	87.0	86.7	exo/910	CoO

All the complexes are hydrated and lose water molecules between 40–145°C in one stage (except for Co-2,4D which loses them in two steps). The dehydration processes of the compounds are connected with endothermic effects between 80–100°C.

Anhydrous complexes decompose to oxides (NiO and CoO) with formation of different intermediate products, which may be identified by the X-ray analysis. All the complexes decompose progressively. The TG curves for Ni and Co compounds with the studied acids exhibit multiple mass loss steps. Several endo- and exothermic peaks on the DTA curves are observed. The further mass loss on the TG curves within the temperature range 200–470°C (Ni-2,4D), 180–370°C (Co-2,4D), 240–450°C (Ni-2,4DP) and 210–370°C (Co-2,4DP) is caused by the pyrolysis of organic ligands. In these stages several exothermic peaks on the DTA curves are observed. The next stages are caused by farther oxidation of organic fragments and very strong and broad exothermic effects on DTA accompany those steps (probably decomposition of carboxylate anions and destruction of benzene rings take place – TG/MS measurements).

The anhydrous Ni-2,4D complex decompose in two stages connected with considerable mass losses and oxidation of organic fragments. On the DTA curve weak exothermic effects at 200–470°C and very strong at 470–650°C are observed. At 470°C the mixture of Ni-2,4D (where Ni:2,4D=1:1), Ni, $NiCl_2$ and NiO was identified. The final products of Ni-2,4D decomposition (at 650°C) is NiO.

The Ni-2,4DP complex decompose to NiO (at 660°C) via the formation of undefined intermediate products. On the TG curve three stages of pyrolysis of this compound are observed. The exothermic effects on DTA curve at 160–450°C are weak while at 450–660°C very strong and broad. Loss of mass is the largest in the range 240–450°C. In this stage, oxidation processes of intermediate products proceed very quickly.

The anhydrous Co-2,4D decompose to CoO. The first stage of thermal decomposition occurs within the range 180–370°C. In this stage 1 mol of 2,4D liberates and Co_3O_4 begins to form. The loss of mass in the range 370–650°C is attributed to the pyrolysis of the remaining 2,4D. The final product of this stage is Co_3O_4. At 650–950°C the cobalt(II) oxide CoO is formed. This process is accompanied by the endothermic peak on DTA at 920°C.

Co-2,4DP decompose in four stages. The first two stages are connected with decompositon of 1 mol 2,4DP. At 370°C the mixture of Co-2,4DP (where Co:2,4DP=1:1), $CoCl_2$ and Co_3O_4 are formed. On the DTA curve weak exothermic peaks are observed. In the range 370–600°C oxidation of the organic ligand takes place. The DTA curve shows very strong and broad exothermic effects. The final product of this stage is Co_3O_4. At 600–950°C it transforms into CoO with endothermic peak at 910°C.

In this paper, a coupled TG/MS system was used to analyse of gaseous products evolved during the thermal decomposition of Co and Ni complexes with 2,4-dichlorophenoxyacetic and 2-(2,4-dichlorophenoxy)-propionic acids in air atmosphere. Both decomposition and MS data of these compounds are similar. Figures 4 and 5 (as an example) present relationship of the ion current for *m/z* detected in the mass spectrometry *vs*. time of decomposition (heating rate=10°C min^{-1}) for Ni-2,4D and Co-2,4DP. In these figures the profiles for MS are not presented, which curves

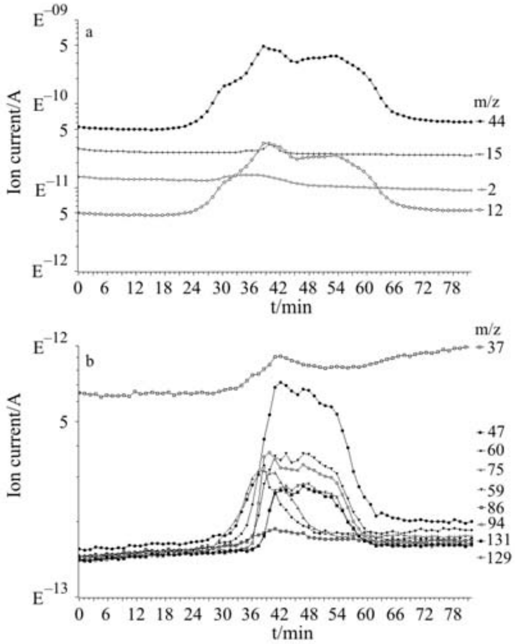

Fig. 4 Ion current for *m*/*z* detected in the mass spectrometer *vs.* time for Ni-2,4D (mass sample 4.01 mg, heating rate 10°C min^{-1})

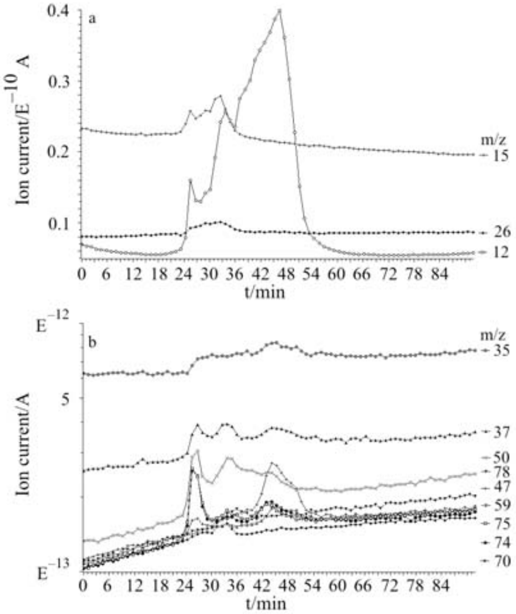

Fig. 5 Ion current for *m*/*z* detected in the mass spectrometer *vs.* time for Co-2,4DP (mass sample 5.27 mg, heating rate 10°C min^{-1})

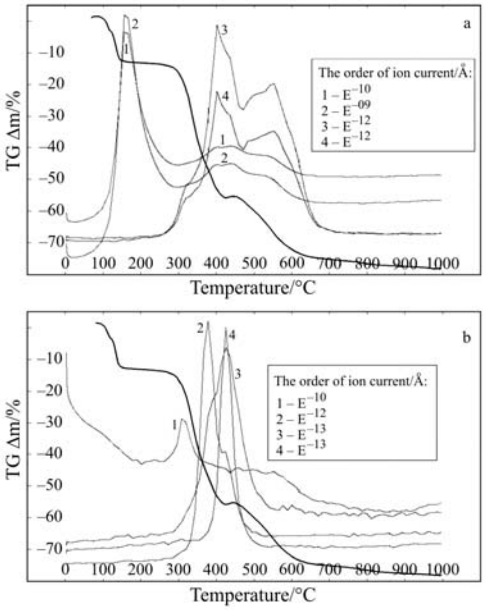

Fig. 6 TG curve for Ni-2,4D and ion current detected by the MS for mass fragments *m/z*: 1 – 17; 2 – 18; 3 – 45; 4 – 46 (a); 1 – 30; 2 –50; 3 – 74; 4 – 78 (b)

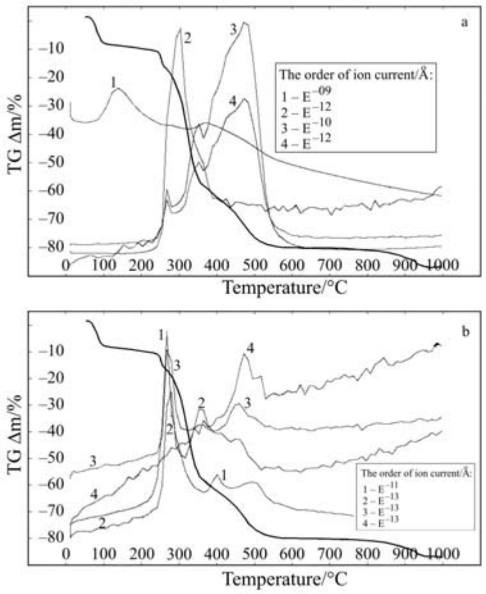

Fig. 7 TG curve for Co-2,4DP and ion current detected by the MS for mass fragments *m/z*: 1 – 18; 2 – 38; 3 – 44; 4 – 46 (a); 1 – 30; 2 –50; 3 – 74; 4 – 94 (b)

are shown in Figs 6 and 7, where TG/MS data are listed. In the mass spectrum different intensities of signal ions are detected.

In all cases, the first decomposition products detected were H_2O^+ (m/z=17, 18). The strong maximum, while the elimination of H_2O^+ appears (crystalline or coordinated), occurs at 139, 137, 157 and 130°C for Co-2,4D, Co-2,4DP, Ni-2,4D and Ni-2,4DP, respectively. Next, the H_2O is a product of oxidation of organic ligands at higher temperature.

The mass spectra suggested that at lower temperature (to 370°C) the several gaseous products are liberated: $C_2H_2^+$, CH_2O^+, CO_2^+, C^+, CH^+, CH_3^+, Cl^+, HCl^+, Cl_2^+, CH_3Cl^+, H_2^+ (m/z=26, 30, 44, 45, 46, 12, 13, 15, 35, 37, 36, 38, 70, 74, 50, 2, respectively) and CCl^+ for Co and Ni with 2,4DP. In air atmosphere CO^+ was not detected. The profiles observed for m/z=44, 45, 46 (CO_2^+ and its isotopes) are similar. CO_2^+ is mainly formed as a result of decomposition of carboxylate groups. At the same time, chlorine compounds are liberated. These compounds and CO_2^+ are presented at higher temperatures (above 370°C) too. In the range 370–570°C, benzene and its products of destruction appear additionally (among other: $C_6H_6^+$, $C_6H_5OH^+$, $C_6H_4ClOH^+$ where m/z=78, 94, 129 and 131).

Both the simple carbon chains and chlorine bonding crack at low temperatures whereas the benzene ring cracks at above 400°C.

TG coupled with MS data for some decomposition gaseous products are shown in Figs 6 and 7 (as an example) for Co-2,4DP and Ni-2,4D.

Conclusions

2,4-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy)-propionic acid form with cobalt and nickel complexes of the molar ratio M:2,4D and M:2,4DP=1:2 (where M=Co, Ni). The complexes contain crystallisation or coordinated water and have the following molecular formulae: $Ni(C_8H_5O_3Cl_2)_2\cdot 6H_2O$, $Co(C_8H_5O_3Cl_2)_2\cdot 6H_2O$, $Ni(C_9H_7O_3Cl_2)_2\cdot 2H_2O$ and $Co(C_9H_7O_3Cl_2)_2\cdot 2H_2O$. The complexes are sparingly soluble in water at room temperature and their solubility increases in the orders:

Co-2,4D<Ni-2,4D and Ni-2,4DP<Co-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 Co-2,4D and Ni-2,4D have a crystalline structure. Co-2,4DP and Ni-2,4DP are amorphous or exhibit very low degree of crystallinity. The IR spectroscopy confirms that 2,4D and 2,4DP acids combine with Co and Ni through the oxygen atoms of the carboxylate group. On the basis of the values of $\Delta\nu=\nu(OCO)_{asym}-\nu(OCO)_{sym}$ and conductance measurements in methanol a conclusion can be drawn that in compounds studied carboxylate group is bidentate bridging. The electronic spectra (VIS) indicate pseudooctahedral environment around the Co and Ni.

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

$$\underset{(130°\mathrm{C})}{\text{Co-2,4DP}}<\underset{(160°\mathrm{C})}{\text{Ni-2,4DP}}<\underset{(180°\mathrm{C})}{\text{Co-2,4D}}<\underset{(200°\mathrm{C})}{\text{Ni-2,4D}}$$

The anhydrous 2,4D complexes are thermally more stable than 2,4DP complexes. All compounds decompose via intermediate products to oxides (NiO and CoO). The gaseous products liberated during pyrolysis of studied complexes are similar. During the heating of the complexes the decomposition of the organic ligands and oxidation processes take place. Molecular ions: H_2O^+, CO_2^+, HCl^+, Cl_2^+, CH_3Cl^+, CH_2O^+, $C_6H_6^+$, $C_2H_2^+$, C^+, CH^+, CH_3^+, Cl^+, Cl_2O^+, $C_6H_5Cl^+$, $C_6H_5OH^+$, $C_6H_4ClOH^+$ were detected.

* * *

The authors wish to thank the Chemical Industrial Establishment 'Rokita S.A.' in Brzeg Dolny for providing 2,4D and 2,4DP acids used in our studies.

References

1 C. Dendrinou–Samara, G. Psomas, K. Christophorou, V. Tangoulis, C. P. Raptopoulou, A. Terzis and D. P. Kessissoglou, J. Chem. Soc. Dalton Trans., 18 (1996) 3737.
2 C. Dendrinou–Samara, G. Psomas, P. Philippakopoulos, V. Tangoulis, C. P. Raptopoulou, E. Samaras and D. P. Kessissoglou, Inorg. Chim. Acta, 272 (1998) 24.
3 A. Genske and K. Götzschel, Z. Chem., 22 (1980) 147.
4 W. Jähnig, R. Stösser, U. Ewert, K. Götzschel and G. Reck, J. Prakt. Chemie, 322 (1980) 321.
5 R. Sahai and A. K. Chaudhary, Monatsh. Chem., 113 (1982) 681.
6 R. Sahai and S. S. Kushwana, Indian J. Chem. Sect. A, 22A (1983) 778.
7 R. Sahai and S. S. Kushwana, J. Indian Chem. Soc., 61 (1984) 205.
8 R. Sahai and A. K. Chaudhary, Indian J. Chem. Sect. A, 22A (1983) 677.
9 T. C. W. Mak, Yip Wai Hing, C. H. L. Kennard, G. Smith and E. J. O'Reilly, J. Chem. Soc. Dalton Trans., 9 (1988) 2353.
10 C. H. L. Kennard, G. Smith, E. J. O'Reilly, K. M. Stadnicka and B. J. Oleksyn, Inorg. Chim. Acta, 59 (1982) 241.
11 C. H. L. Kennard, G. Smith and E. J. O'Reilly, Inorg. Chim. Acta, 49 (1981) 53.
12 R. Sahai and S. S. Kushwana, J. Ind. Chem. Soc., 58 (1981) 913.
13 W. F. Shulgin, O. W. Konnik and U. G. Timofew, Zh. Neorg. Khim., 35 (1990) 365.
14 W. F. Shulgin and O. W. Konnik, Ukr. Khim. Zh., 55 (1989) 1014.
15 J. Ristici, Buletinul Stiinttfie si Tehnic al. I. P.T., 19 (1974) 29.
16 D. Czakis-Sulikowska, A. Czylkowska and J. Radwańska-Doczekalska, J. Therm. Anal. Cal., 63 (2001) 387.
17 D. Czakis-Sulikowska, A. Czylkowska and A. Malinowska, J. Therm. Anal. Cal., 65 (2001) 505.
18 D. Czakis-Sulikowska, A. Czylkowska and A. Malinowska, J. Therm. Anal. Cal., 67 (2002) 667.
19 D. Czakis-Sulikowska and A. Czylkowska, J. Therm. Anal. Cal., in press.

20 Powder Diffraction File. International Center of Diffraction Date. ICPDS-ICDD, 1990, 1601 Park Lana Swarthmore.
21 F. J. Welcher, The Analytical Uses of Ethylenediamine Tetraacetic Acid, D. Van Nostrand Company, Princeton 1958.
22 T. Kiriyama and R. Kuroda, Fresenius Z. Anal. Chem., 288 (1977) 354.
23 M. Langova, Z. Simek, J. Chroma and L. Sommer, Collect. Czech. Chem. Commun., 52 (1987) 878.
24 W. I. Geary, Coord. Chem., 7 (1971) 81.
25 L. J. Bellamy, The Infrared Spectra of Complex Molecules, Chapman & Hill, London 1975.
26 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York 1997.
27 G. B. Deacon and R. J. Phillips, Coord. Chem. Rev., 33 (1980) 227.
28 B. S. Manhas and A. K. Trikha, J. Indian. Chem. Soc, 59 (1982) 315.
29 T. C. Waddington, N. W. Alcock and V. M. Tracy, J. Chem. Soc. Dalton Trans., 21 (1976) 2243.
30 A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam 1984.