Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 407 (2003) 25–31

thermochimica acta

www.elsevier.com/locate/tca

Phenoxyalkanoic acid complexes. Part I. Complexes of lead(II), cadmium(II) and copper(II) with 4-chloro-2-methylphenoxyacetic acid (MCPA)

J. Kobylecka, B. Ptaszynski, R. Rogaczewski, A. Turek*

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

Received 22 January 2003; received in revised form 22 April 2003; accepted 28 April 2003

Abstract

New solid heavy metal complexes with 4-chloro-2-methylphenoxyacetic acid (MCPA) of the general formulae: $Pb(MCPA)_2\cdot H_2O$ and $Cd(MCPA)_2\cdot 2H_2O$ have been prepared. Diffractometric, IR spectroscopic and thermal analyses of these complexes and the previously described $Cu(MCPA)_2$ have been performed. The complexes have different structures, a low level of crystallinity and exhibit a tendency to form polymers. An attempt has been made to explain the mode of the ligand molecule coordination on the basis of the position of the bands of the characteristic ν_{asym} and ν_{sym} vibrations of the carboxylate group. The course of the TG, DTG and DTA curves indicates that the compounds decompose in two (the copper salt) or three stages. The decomposition of the cadmium complex is preceded by dehydration. The basic gaseous products of decomposition are H_2O and CO_2. HCOOH, $HOCH_2COOH$, HCl and trace amounts of compounds containing an aromatic ring were also detected. The final solid decomposition product is a metal oxide.

Keywords: 4-Chloro-2-methylphenoxyacetic acid (MCPA) complexes; Thermal decomposition; IR analysis; X-ray diffractometry

1. Introduction

As phenoxyalkanoic acid herbicides show a considerable biological activity, their physico- and biochemical properties have been a subject of extensive studies. Phenoxy acid pesticides include 4-chloro-2-methylphenoxyacetic acid (MCPA), a component of many herbicides produced and used in Poland. MCPA is used for a number of purposes such as protection of crops or water plant control in water reservoirs, so its amounts in the soil may reach considerable levels. The properties of the following solid complexes have been hitherto described in the literature: 2,4-dichlorophenoxyacetic acid (2,4-D) with Cu [1–3], Zn [3–5], Co [3,6], Mn [3,5], Ni, Cd and Fe [3], MCPA with Cu [7], Zn [8], Co [6], Mn [9,10] and Mg [11] and 4-chloro-2-methylphenoxypropionic acid (MCPP) with Cu [7], Co [6] and Mn [9]. There have also been described studies on mixed complexes which, apart from the phenoxy acid herbicide, contain other organic ligands [12–14]. This work presents methods of synthesis and some spectroscopic and thermal properties of new solid complex compounds of MCPA with cadmium and lead, as well as additional studies on the previously described copper salt of MCPA [7].

The present work is a part of a wider study on the herbicide–soil interaction and the effect of MCPA on the bioavailability of heavy metals. It has been

---

* Corresponding author. Fax: +48-42-631-31-03.
E-mail address: akturek@p.lodz.pl (A. Turek).

0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00287-9

found that MCPA is adsorbed by mineral and organic molecules in the soil and sediment. It may also react with the metal ions present in the soil solution [15–18]. The stability and solubility of the formed MCPA–metal complexes may affect the mobility of the metal in the soil and resistance of MCPA to biodegradation. Our experiments indicate that the presence of the herbicide in the soil increases the level of bioavailable (extracted with hydrochloric acid) forms of copper, lead and manganese [19]. As a result, their bioavailability is also increased. Another problem, important from the point of view of environment protection, is waste utilization. The studies on the reactions of thermal decomposition of MCPA–lead, MCPA–cadmium and MCPA–copper complexes presented in the work may be helpful in developing technologies for simultaneous incineration of different types of waste, including those, which contain expired pesticides or heavy metal salts.

2. Experimental

2.1. Synthesis and chemical analysis

MCPA (Organika-Sarzyna, Poland) of purity 96.1% was purified by recrystallization from the water–ethanol solution (1:1 V/V). White, crystalline MCPA melted at 118 °C was obtained (theoretical melting point 118–119 °C [20]). The other reagents used for synthesis and analysis were analytically pure.

A weighed sample of MCPA was dissolved in water sufficient NaOH to bring the final pH of the solution to 6–7. An aqueous solution of the metal nitrate was added to this solution in a 2:1 molar ratio of MCPA:metal. The precipitated compounds were left in the mother liquor for 24 h, and then were collected by filtration, washed with water and dried in air at room temperature. The yields of the complexes were 75–85%. All the salts are white, except for the light green copper complex.

The content of metals in the complexes was determined by complexometric titrations with EDTA of solutions obtained after microwave decomposition of the complexes with HNO_3 solution ($d = 1.4\,g/cm^3$). Carbon, hydrogen and chlorine were determined by elemental analysis using a Carlo Erba type 1108 analyzer. The results of analyses are as follows:

$PbC_{18}\ H_{16}O_6Cl_2\cdot H_2O$				
Determined	31.70% Pb	34.57% C	2.83% H	9.35% Cl
Calculated	33.19% Pb	34.63% C	2.88% H	11.36% Cl
$CdC_{18}\cdot H_{16}O_6Cl_2\cdot 2H_2O$				
Determined	20.30% Cd	39.41% C	3.69% H	10.43% Cl
Calculated	20.53% Cd	39.49% C	3.65% H	12.95% Cl
$CuC_{18}\cdot H_{16}O_6Cl_2$				
Determined	13.63% Cu	46.68% C	3.55% H	13.84% Cl
Calculated	13.73% Cu	46.73% C	3.46% H	15.33% Cl

Water solubilities of the MCPA complexes (at 293 K), calculated on the basis of the determination of the metal ion concentration in the saturated solution are: $Pb(MCPA)_2\cdot H_2O$, $5.8 \times 10^{-4}\,mol/dm^3$; $Cd(MCPA)_2\cdot 2H_2O$, $7.2\times 10^{-3}\,mol/dm^3$; $Cu(MCPA)_2$, $1.6 \times 10^{-3}\,mol/dm^3$.

2.2. IR spectra

IR spectra of the sodium salt of MCPA and the MCPA complexes were recorded on a FTIR-8501 spectrometer (Shimadzu), within frequency range 4000–400 cm^{-1}, in KBr discs.

2.3. Thermal analysis

The TG, DTG and DTA curves of the complexes under study were recorded on TG/DTA-SET SYS-16/18 thermoanalyser connected with a ThermoStar mass spectrometer (Balzers). The measurements were made in air atmosphere over the temperature range 20–1000 °C, with heating rate 10° min^{-1}, using platinum crucibles and Al_2O_3 as reference. The mass of the samples was 5 mg. The results of the thermal analysis are presented in Table 1 and Fig. 1.

2.4. X-ray analysis

Powder diffraction patterns of the complexes under study were recorded by means of a SIEMENS D 5000 powder diffractometer within the 2Θ range 2–90° (Fig. 2). X-ray diffractometry was also used to identify the solid products of the thermal decomposition of the compounds under study.

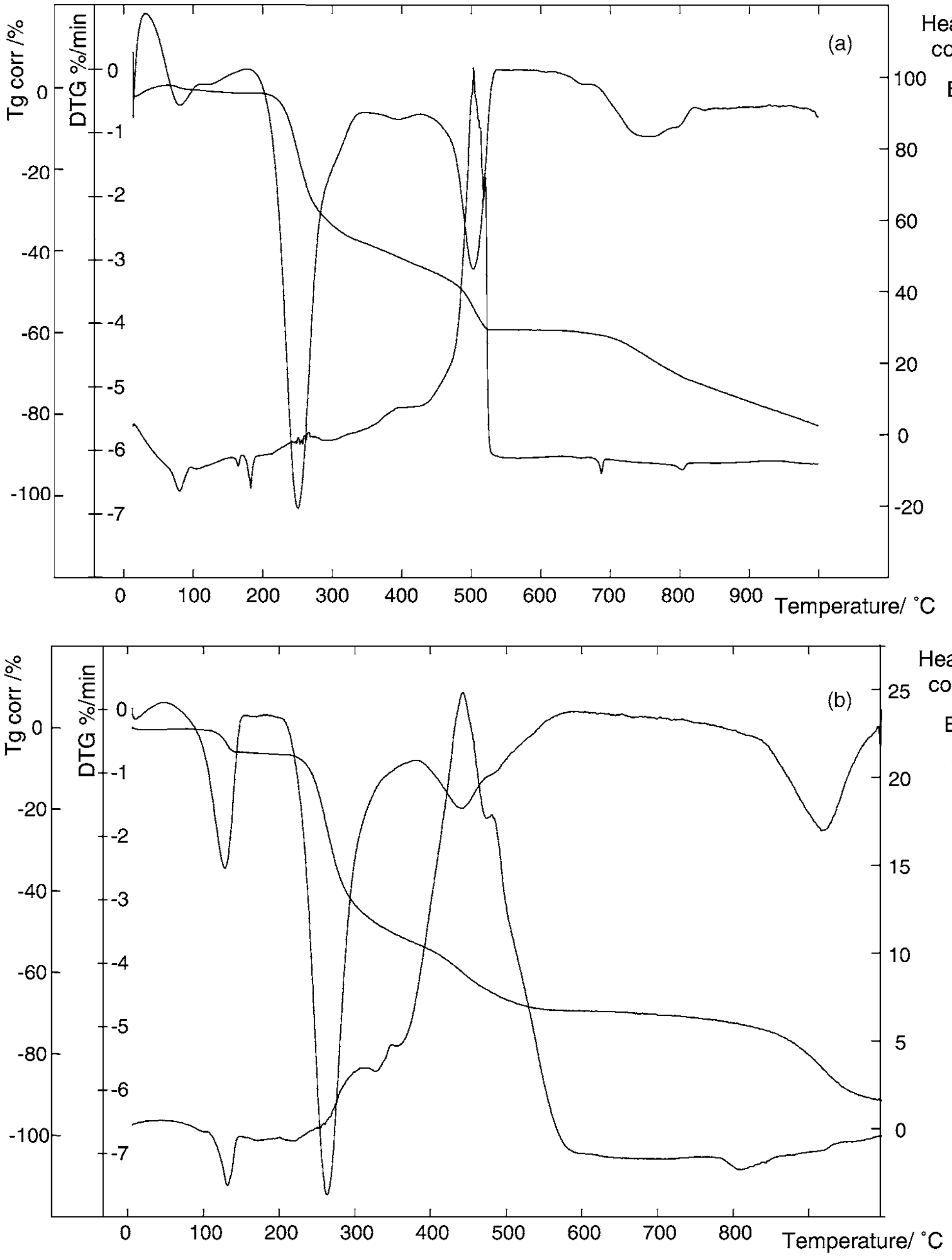

Fig. 1. Thermal analysis curves of (a) $Pb(MCPA)_2\cdot H_2O$; (b) $Cd(MCPA)_2\cdot 2H_2O$; (c) $Cu(MCPA)_2$.

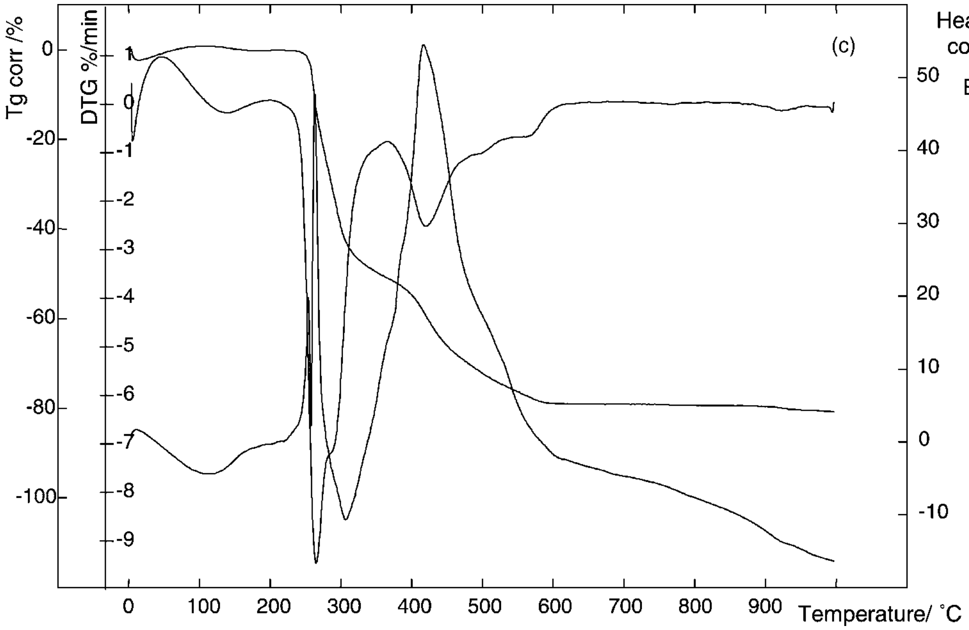

Fig. 1. (*Continued*).

Table 1
Thermal analysis of MCPA complexes

Compound	Stage	Range of decomposition stages (°C)	Mass loss (%)	DTA peaks (°C)
$Pb(MCPA)_2{\cdot}H_2O$	I + II	180–535	58.0	164, 182 (endo) 500, 518 (exo)
	III	595–1000	23.4	686, 802 (endo)
$Cd(MCPA)_2{\cdot}2H_2O$	I	100–155	5.6	132 (endo)
	II + III	200–580	63.0	312, 348, 442, 479 (exo)
	IV	580–1000	22.0	805 (endo)
$Cu(MCPA)_2$	I	205–365	51.0	254, 263 (exo)
	II	365–615	28.0	416 (exo)

3. Results and discussion

New hydrated complexes of MCPA with lead, cadmium and an anhydrous copper complex of MCPA were synthesized. The formula of the copper salt is in accordance with that proposed previously by Shul'gin [7]. All the complexes are in the form of fine powders. Their water solubilities (293 K) increase in the following order: Pb < Cu < Cd.

The analysis of the powder diffraction patterns indicates considerable differences in the structure of the complexes (Fig. 2). All of them form polymers, which was also observed before in the case of the copper salt [7]. The crystal structure of $Pb(MCPA)_2{\cdot}H_2O$ has been studied and described [21].

IR spectroscopy was carried out to establish the type of binding between the metal and the carboxylate group present in the MCPA molecule. The position of the bands corresponding with the characteristic vibrations of the carboxylate group is often a criterion which allows to solve this problem. The value of

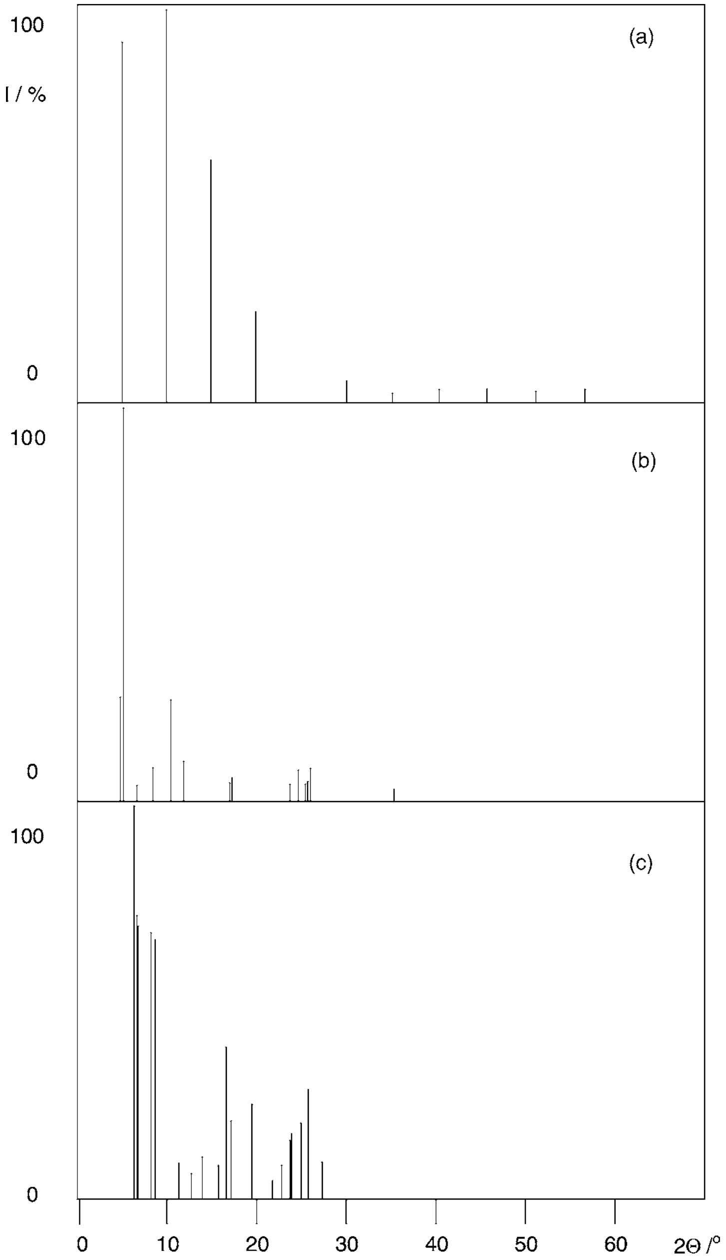

Fig. 2. X-ray diffraction patterns of (a) $Cd(MCPA)_2 \cdot 2H_2O$; (b) $Pb(MCPA)_2 \cdot H_2O$; (c) $Cu(MCPA)_2$.

Δ (equal to the difference between the frequencies of asymmetrical (ν_{asym}) and symmetrical (ν_{sym}) stretching vibrations of the carbon-oxygen bond in the carboxylate group [22,23]) and the directions of shifts of the frequencies of vibrations ν_{asym} and ν_{sym} in relation to the respective frequencies observed for the ionic bond [24] may indicate the coordination type. On these grounds five types of coordination may be attributed to the carboxylate group: unidentate, bidentate chelating symmetrical and

Table 2
Vibration frequencies of the carboxylate group in the MCPA complexes

Compound	ν_{asym} (cm^{-1})	ν_{sym} (cm^{-1})	$\Delta = \nu_{asym} - \nu_{sym}$ (cm^{-1})
NaMCPA	1608	1446	162
$Pb(MCPA)_2 \cdot H_2O$	1603 1549 1522	1445 1410	193, 77
$Cd(MCPA)_2 \cdot 2H_2O$	1605 1558	1447 1421	184, 111
$Cu(MCPA)_2$	1638	1448 1414	224, 190

unsymmetrical, bidentate bridging symmetrical and unsymmetrical.

Table 2 lists the frequencies attributed to characteristic vibrations of the –COO group in the compounds under study in comparison with analogous vibrations in Na–MCPA, which, as it is assumed, contains an ionic bond. In the sodium salt, the ν_{asym} and ν_{sym} vibrations correspond with single acute peaks, whereas in the salts under discussion, the bands are broad and split (apart from ν_{asym} of Cu–MCPA) and shifted, so they have different Δ-values. Two Δ-values which are differences between the most distant and the nearest branches of the bands corresponding with the ν_{asym} and ν_{sym} vibrations of the carboxylate group were calculated for the compounds under study. The comments on the data in Table 2 take into account also the results of our previous structural studies on the lead compound [21] and the ongoing studies on the cadmium compound.

The structural studies show that each carboxylate group in $Pb(MCPA)_2 \cdot H_2O$ is a bidentate chelating unsymmetrical ligand in relation to one metal atom and a unidentate ligand in relation to the other. The lead atom in the compound is seven-coordinate and is bound with four oxygen atoms of the two chelating carboxylate groups, one water molecule and one oxygen atom of each of the two adjacent carboxylate groups. The bonds with the –COO groups acting as unidentate ligands cause the formation of polymer chains which are connected by hydrogen bonds thus giving a lamellar structure. In the IR spectrum of the lead complex ν_{asym} and ν_{sym} frequencies are shifted towards lower values than in the sodium salt. The criterion of Δ-value confirms the presence of unidentate ($\Delta = 193\,cm^{-1}$) and bidentate chelating ($\Delta = 77\,cm^{-1}$) carboxylate group [23].

Similar directions of the shifts of the characteristic bands and Δ-values equal to 184 and $111\,cm^{-1}$ are observed in the IR spectrum of $Cd(MCPA)_2 \cdot 2H_2O$, which may suggest the binding of the carboxylate group analogous to that in the lead compound. However, the other determined Δ-value is much higher than in the case of the lead compound. This indicates the presence of the bidentate bridging symmetrical carboxylate group, although then the ν_{asym} band should be shifted towards higher frequencies than in the case of the sodium salt. The presence of the bidentate bridging carboxylate group is also indicated by preliminary structural studies.

The broad and split band in the IR spectrum of $Cu(MCPA)_2$ corresponding with ν_{asym} of the carboxylate group is clearly shifted towards higher frequencies than in the case of the ionic bond, and the calculated Δ-values are high, which strongly suggests the presence of bidentate bridging unsymmetrical carboxylate groups in the compound.

The thermal decomposition of $Pb(MCPA)_2 \cdot H_2O$ begins at 180 °C and proceeds in three stages involving a loss in mass. The stages probably consist of a number of unidentifiable processes. The dehydration of the lead compound overlaps the decomposition of the anhydrous complex (stage 1). The processes occurring in the first stage of the decomposition partly coincide with those of the second stage, so it is difficult to determine precisely the corresponding temperature ranges. The total thermal effect of the second stage is exothermic (two intense exo-peaks). In the sinters prepared at the temperature below 530 °C $Pb_3O_2Cl_2$ and lead were identified by diffractometry. Above 595 °C the next stage of the decomposition (stage 3) of the sample proceeds involving a stepwise loss of its mass. The sinters prepared at over 600 °C contain unidentified decomposition products of low crystallinity.

The thermal decomposition of $Cd(MCPA)_2 \cdot 2H_2O$ is similar to that observed for the lead salt, but the processes are preceded by dehydration at 100 °C (stage 1). The analysis of the mass spectra of the gaseous products of $Cd(MCPA)_2 \cdot 2H_2O$ decomposition confirmed that water molecules are released in the first stage of decomposition. In the temperature range 200–380 °C the anhydrous salt decomposes rapidly (the second stage), and then more slowly between 380 and 580 °C (the third stage). The processes which take place in the second and third stages are exothermic. The final product of decomposition of $Cd(MCPA)_2 \cdot 2H_2O$ (found in sinters obtained at 500 °C and at higher temperatures) is CdO. At temperatures exceeding 580 °C the decomposition of the sample is at first slow, and then at over 800 °C, its rate increases, resulting in the formation and stepwise evaporation of cadmium oxide.

On thermal curves of $Cu(MCPA)_2$ two main stages of decomposition can be distinguished, connected with continuous mass loss and strong exothermic effects. The presence of CuO and CuCl were confirmed in the sinter obtained at about 300 °C. The first and second stage overlap, and the final decomposition product, identified by X-ray diffractometry, is copper(II) oxide. Above 615 °C the mass of the sample does not change.

The main gaseous products of the decomposition of the complexes under study are CO_2, HCOOH and small amounts of H_2O. Besides, trace amounts of HCl, $HOCH_2COOH$ and compounds containing an aromatic ring (for example phenol, chlorophenol, cresol, toluene, benzoic acid, chlorobenzene) were identified. The release of different aromatic compounds, depending on the complex which is decomposed may result from the differences in the character of the metal-ligand bond, which has been discussed in the part on IR spectroscopic studies.

Acknowledgements

This work was financially supported by the State Committee for Scientific Research (Grant No. 7 T09B 109 21).

References

[1] A. Genske, K. Götzschel, Z. Chem. 22 (1982) 147.
[2] G. Smith, E.J. O'Reilly, C.H.L. Kennard, Inorg. Chim. Acta 49 (1981) 53.
[3] J. Ristici, Bull. Stiint. Teh. Inst. Politen. Timisoara 19 (1974) 229.
[4] C.H.L. Kennard, G. Smith, E.J. O'Reilly, K.M. Stadnicka, B.J. Oleksyn, Inorg. Chim. Acta 59 (1982) 241.
[5] W.F. Shul'gin, O.W. Konnik, Ukr. Khim. Zh. 55 (1989) 1011.
[6] W.F. Shul'gin, O.W. Konnik, I.G. Timofeev, Zh. Neorg. Khim. 35 (1990) 365.
[7] W.F. Shul'gin, O.W. Konnik, Ukr. Khim. Zh. 56 (1990) 887.
[8] S.J. Nefedov, J.T. Struchkov, O.W. Konnik, W.F. Shul'gin, Ukr. Khim. Zh. 57 (1991) 685.
[9] W.F. Shul'gin, O.W. Konnik, A.P. Skoblin, Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. 32 (1989) 21.
[10] V. Tangoulis, G. Psomas, C. Dendrinou-Samara, C.P. Raptopoulou, A. Terzis, D.P. Kessissoglou, Inorg. Chem. 35 (1996) 7655.
[11] G. Smith, E.J. O'Reilly, C.H.L. Kennard, Cryst. Struct. Comm. 10 (1981) 1397.
[12] R. Sahai, S.S.S. Kushwaha, J. Indian Chem. Soc. 61 (1984) 205.
[13] R. Sahai, A.K. Chaudhary, Monatsh. Chem. 113 (1982) 681.
[14] W. Jähnig, R. Stösser, U. Ewert, K. Götzschel, J. prakt. Chem. 322 (1980) 321.
[15] J. Alloway, D.C. Ayres, Chemical Principles of Environmental Pollution, PWN, Warsaw, 1999.
[16] G. Haberhauer, L. Pfeiffer, M.H. Gerzabek, J. Agric. Food Chem. 48 (2000) 3722.
[17] C. Sheng, M.A. Arshed, Can. J. Soil, Sci. 78 (1998) 181.
[18] M.M. Socias-Viciana, M. Fernanndez-Perez, M. Villafranca-Sanchez, E. Gonzalez-Pradas, F. Flores-Cespedes, J. Agric. Food Chem. 47 (1999) 1236.
[19] A. Turek, J. Kobylecka, B. Ptaszynski, XLV Meeting of Polish Chemical Society, Cracow, September 2002.
[20] L. Rozanski, Vade-mecum of pesticides 97/98, Agra-Enviro Lab., Poznañ, 1998, p. 188.
[21] R. Kruszynski, T.J. Bartczak, B. Ptaszynski, A. Turek, J. Coord. Chem. 55 (2002) 1079.
[22] N.W. Alcock, V.M. Tracy, J. Chem. Soc. Dalton Trans. 21 (1976) 2243.
[23] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.
[24] B.S. Manhas, A.K. Trikha, J. Indian Chem. Soc. 59 (1982) 315.