

Synthesis, thermal study and some properties of Zn(II), Cd(II) and Pb(II) compounds with mono-, di- and trichloroacetates

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Abstract New complexes with formulae: $Zn(CClH_2COO)_2 \cdot 2H_2O,$ $Zn(CCl_2HCOO)_2 \cdot 2H_2O$, $Zn(CCl_3COO)_2 \cdot 2H_2O$, $Cd(CCl_2HCOO)_2 \cdot H_2O$, $Cd(CCl_3COO)_2 \cdot 2H_2O$ and $Pb(CCl_3COO)_2 \cdot 2H_2O$, were prepared and characterized by chemical, elemental analysis and IR spectroscopy. The nature of metal-ligand coordination was studied. They are small crystalline. The thermal properties of compounds in the solid state were studied using TG-DTG techniques under dynamic flowing air atmosphere. Mass spectrometer was used to analyze principal volatile thermal decomposition and fragmentation products of Zn(CCl₃COO)₂·2H₂O evolved during pyrolysis in dynamic flowing air and in argon atmosphere.

Keywords Metal(II) complexes \cdot Monochloroacetates \cdot Dichloroacetates \cdot Trichloroacetates \cdot TG–DTG \cdot MS study \cdot IR spectra

Introduction

The carboxylic acids are one of the most important organic acids because of their application. They are starting compounds for the synthesis of many derivatives. Substituents of the carboxylic acids have an impact on acidity. A carboxylate group as a ligand can coordinate with metal ion in various ways [1], making it interesting. The title chloroacetic acid is widely used. It is used in medicine since it has astringent and antiseptic properties, in the

A. Czylkowska agnieszka.czylkowska@p.lodz.pl medical analysis to remove proteins from blood or serum in the determination of glucose. Sodium salt of trichloroacetic acid is used in agriculture, as one of the herbicide. It is in the fourth class of compounds known as damaging agents. In the plastics industry, it is used as a solvent for plastics, in metal industry to the surface treatment of metals, due to of the corrosive properties [2, 3]. This acid is widely present in the environment. It is characterized by very high stability. Their high solubility in water makes, that it occurs in the rain, snows, ice, fog fresh and marine waters as well as in the soil [4, 5].

To the research were selected d-block metals and lead (although it is metal of p-block). Lead and zinc are classified as non-ferrous metals. A common feature of the selected elements is the ability to create different type of complexes.

In literature there is a note about Zn(II) chloroacetate and its complexes with nicotinamide and caffeine [6]. Also, there is some information about Zn(II), Cd(II) and Pb(II) with acetic acids [7–18].

This paper investigates several solid compounds of Zn(II) and Cd(II) with mono-, di-, or trichloroacetic acids and Pb(II) with trichloroacetic acids (as the most common compound of lead with chloroacetates, which is in the soil). Their stoichiometric composition, nature of the metal–organic ligand bond, molar conductivity in various solvents and thermal behavior were studied. Thermal stability in air, information about stages of pyrolysis, intermediate and final solid products of decomposition of investigated compounds are described. In addition, for $Zn(CCl_3COO)_2 \cdot 2H_2O$ as an example, volatile species emitted during thermal decomposition in air and for comparison in argon atmosphere were studied. This compound was chosen because it is important for the environment.

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Compound	Analysis: found (calculated)/%			$\Lambda_{\rm M}/\Omega^{-1} {\rm cm}^2 {\rm mol}^{-1};$ $c = 1 \times 10^{-3} {\rm mol} {\rm L}^{-1}$		
	M(II)	С	Н	MeOH	DMF	DMSO
Zn(CClH ₂ COO) ₂ ·2H ₂ O	22.45	16.75	2.86	41.4	11.6	20.2
	(22.65)	(16.66)	(2.80)			
Zn(CCl ₂ HCOO) ₂ ·2H ₂ O	18.33	13.70	1.71	45.5	10.1	21.2
	(18.30)	(13.45)	(1.69)			
$Cd(CCl_2HCOO)_2 \cdot H_2O$	29.05	12.46	1.05	42.4	11.1	22.7
	(29.10)	(12.44)	(1.04)			
Zn(CCl ₃ COO) ₂ ·2H ₂ O	15.47	11.37	1.00	46.0	2.0	1.7
	(15.34)	(11.27)	(0.95)			
$Cd(CCl_3COO)_2 \cdot 2H_2O$	23.76	10.20	0.90	43.0	9.0	21.0
	(23.78)	(10.15)	(0.85)			
Pb(CCl ₃ COO) ₂ ·2H ₂ O	37.87	8.86	0.40	48.5	3.0	1.8
	(37.69)	(8.74)	(0.37)			

Table 1 Analytical data and molar conductivity in MeOH, DMF and DMSO for investigated compounds



Fig. 1 X-ray diffraction patterns of Pb(CCl₃COO)₂·2H₂O compound

Experimental

Materials, synthesis and analysis

CCIH₂COOH, CCl₂HCOOH and CCl₃COOH were obtained from Aldrich. Zinc(II) monochloroacetates, zinc(II) dichloroacetates, zinc(II) trichloroacetates, cadmium(II) dichloroacetates, cadmium(II) trichloroacetates and lead(II) trichloroacetates were prepared by adding 2 mol L^{-1} mono-, di- or trichloroacetic acid to freshly precipitated metal(II) carbonates (in room temperature). After obtaining saturated solutions, the excess of carbonates was filtered off. These solutions were left to crystallize.

The contents of C and H in prepared compounds were determinate by a Carlo-Erba analyzer with V_2O_5 as an oxidizing agent; the metal(II) ions in obtained solutions were determined by EDTA titration.

Methods and instruments

IR spectra were recorded with a NICOLETT 6700 Spectrometer (4000–400 cm⁻¹ with accuracy of recording 1 cm⁻¹) using KBr pellets. Molar conductance was measured on a conductivity meter of the OK-102/1 type equipped with an OK-902 electrode at 25 ± 0.5 °C, using 1×10^{-3} mol L⁻¹ solutions of complexes in methanol, dimethylformamide and dimethylsulfoxide. The thermal properties of complexes in air were studied by TG–DTG techniques in the range of temperature 25–1000 °C at a heating rate of 10 °C min⁻¹; TG and DTG curves were recorded on Netzsch TG 209 apparatus in flowing dynamic air atmosphere v = 20 mL min⁻¹ using ceramic crucibles. The mass spectra were measured on mass spectrometer ThermoStar, Balzers (Germany), in the range of temperature 25–1000 °C at a heating rate 10 °C min⁻¹ in flowing

Table 2 Principal IR bands for $CCIH_2COONa$ and for obtained compound

CClH ₂ COONa [21]	$\begin{array}{l} Compound \\ Zn(CClH_2COO)_2 \cdot 2H_2O \end{array}$	Assignments
3005	-	$v_{\rm as}(\rm CH_2)$
2975	2360	$v_{\rm s}({\rm CH_2})$
1603	1598	$v_{as}(COO)$
1418	1434	$v_{\rm s}({\rm COO})$
	1402	
1399	1388	v(CH ₂)
1260	1263	
1251	1249	$\rho_{t}(CH_{2})$
	1243	
1166	1197	$\pi(CH_2)$
	1170	
932	960	v(CC)
926	935	$\rho_t(CH_2)$
769	788	v(CCl)
682	-	$\beta_{as}(CCOO)$
185	196, 164	$\Delta v = v_{\rm as}(\rm COO) - v_{\rm s}(\rm COO)$

air and argon atmosphere v = 20 mL min⁻¹ in ceramic crucibles. The *m/z* values are given based on ¹H, ¹²C, ¹⁶O and ³⁵Cl (additionally ¹³C and ¹⁸O in case of CO₂), in the range *m/z*: 1–120. The X-ray powder diffraction patterns of synthesized complexes and final solid decomposition products in air were recorded on D-5000 diffractometer using Ni-filtered CuK_{α} radiation. The measurements were carried out in the range of 2 θ angles 2° – 80°. Obtained

Table 3 Principal IR bands for CCl₂HCOONa and for obtained compounds

results were analyzed using the Powder Diffraction File [19].

Results and discussion

In the solid state, six new compounds with formulae: $Zn(CClH_2COO)_2 \cdot 2H_2O$, $Zn(CCl_2HCOO)_2 \cdot 2H_2O$, $Zn(CCl_3COO)_2 \cdot 2H_2O$, $Cd(CCl_2HCOO)_2 \cdot H_2O$, $Cd(CCl_3COO)_2 \cdot 2H_2O$ and $Pb(CCl_3COO)_2 \cdot 2H_2O$ were obtained. Unfortunately, obtained Cd(II) compound with monochloroacetates has heterogeneous composition. Therefore, further research was discontinued.

Table 1 presents results of the elemental and chemical analysis of isolated compounds. They do not change their stoichiometric composition in solid state. The analysis of the power diffraction patterns of these compounds shows that they are small crystalline. The most crystalline is Pb(CCl₃COO)₂·2H₂O. Figure 1 presents, as an example, X-ray diffraction pattern of lead(II) compound. Table 1 shows molar conductivities values for all investigated compounds in solutions: MeOH, DMF and DMSO. All of them in DMF and also Zn(CCl₃COO)₂·2H₂O and Pb(CCl₃COO)₂·2H₂O in DMSO fall within the generally acceptable range for non-electrolytes [20]. All compounds in MeOH and Zn(CClH₂COO)₂·2H₂O, Zn(CCl₂HCOO)₂·2H₂O, Cd(CCl₂HCOO)₂·H₂O, Cd(CCl₃COO)₂·2H₂O in DMSO display behaviors intermediate between those of non-electrolytes and 1:1 electrolytes. Relatively not high molar conductance shows that they dissociate only in limited degree in these solutions.

CCl ₂ HCOONa [21]	Compounds	Assignments	
	Zn(CCl ₂ HCOO) ₂ ·2H ₂ O Cd(CCl ₂ HCOO) ₂ .H ₂ O		
2985	3012	2995	ν(CH)
	2918	2355	
	2850		
1640	1662	1624	$v_{\rm as}({\rm COO})$
	1652		
1399	1375	1391	v _s (COO)
	1338	1324	
1228	1225	_	<i>v</i> (CH)
1218			
1203	_	1194	$\delta(\text{CCOO})$
934	954	918	v(CC)
813	823	804	$v_{\rm as}(\rm CCl_2)$
807	783		
738	727	727	$\beta_{\rm as}(\rm CCOO)$
710	669		
241	324, 314, 287, 277	300, 233	$\Delta v = v_{\rm as}(\rm COO) - v_{\rm s}(\rm COO)$

CCl ₃ COONa [21]	Compounds	Assignments			
	Zn(CCl ₃ COO) ₂ ·2H ₂ O	$Cd(CCl_3COO)_2 \cdot 2H_2O$	Pb(CCl ₃ COO) ₂ ·2H ₂ O		
1671	1670	1671	1589	$v_{\rm as}({\rm COO})$	
		1656			
1353	1361	1371	1392	$v_{\rm s}({\rm COO})$	
	1346	1344	1344		
942	960	929	947	v(CC)	
833	838	846	835	$v_{\rm as}(\rm CCl_3)$	
		829			
749	757	746	762	$v_{\rm s}({\rm CCl}_3)$	
	744	713	752		
			748		
688	669	686	678	$v_{\rm s}({\rm CCl}_3)$	
318	324, 309	327, 312, 300, 285	245, 197	$\Delta v = v_{\rm as}(\rm COO) \text{-} v_{\rm s}(\rm COO)$	

Table 4 Principal IR bands for CCl₃COONa and for obtained compounds

IR spectra

Tables 2–4 show absorption bands in the region characteristic for mono- di- and trichloroacetates. For all compounds, the vibration of $v_{as}(COO)$ and $v_s(COO)$ are identified as the strong bands. The criterions of possible coordination of carboxylate groups in obtained compounds

are determined based on the separation parameter $\Delta v = v_{as}(COO)-v_s(COO)$ [22–24]. In the investigated compounds, the values of Δv ($\Delta v < \Delta v_{Na}$) indicate mainly bidentate chelating type of coordination of carboxylate groups.

In all cases, the bands $v_s(COO)$ are split into two. Additionally, for $Zn(CCl_2HCOO)_2 \cdot 2H_2O$ and

Table 5 Thermal decomposition data in dynamic air atmosphere of obtained compounds

No.	Compound	Range of decomposition/°C	DTG peaks/°C	Mass loss/%		Intermediate and residue solid products
				Found	Calc	
(I)	Zn(CClH ₂ COO) ₂ ·2H ₂ O	50-125	75	2.70	3.12	Zn(CClH ₂ COO) ₂ ·1.5H ₂ O
		125-300	250	39.30	39.55	Zn(CClH ₂ COO) _{0.5} ·Cl _{1.5}
		300-340	320	4.90	5.04	Zn(CClH ₂ COO) _{0.25} ·Cl _{1.75}
		340-525	475	42.30 ^a	_	b
(II)	$Zn(CCl_2HCOO)_2 \cdot 2H_2O$	50-175	75	7.30	7.56	$Zn(CCl_2HCOO)_2 \cdot 0.5H_2O$
		175–275	220	48.00	47.82	Zn(CCl ₂ HCOO) _{0.25} ·Cl _{1.75}
		325-500	470	43.00 ^a	_	b
(III)	Cd(CCl ₂ HCOO) ₂ ·H ₂ O	50-140	70	4.00	4.66	$Cd(CCl_2HCOO)_2$
		140-200	125, 160	35.50	35.91	$Cd(CCl_2HCOO)_{0.5} \cdot Cl_{1.5}$
		200-240	180, 210, 230	12.00	11.98	CdCl ₂
		240-660	320, 540, 600	45.00^{a}	14.21	CdO
(IV)	$Zn(CCl_3COO)_2 \cdot 2H_2O$	50–90	75	8.50	8.46	$Zn(CCl_3COO)_2$
		170–215	190, 200	59.50	59.65	ZnCl ₂
		350-475	470	30.00^{a}	_	b
(V)	$Cd(CCl_3COO)_2 \cdot 2H_2O$	50-145	125	34.50	34.44	Cd(CCl ₃ COO)·Cl
		145–190	170	27.00	26.82	CdCl ₂
		450-650	625	37.00 ^a	11.60	CdO
(VI)	Pb(CCl ₃ COO) ₂ ·2H ₂ O	100–155	140, 145	39.50	39.86	Pb(CCl ₃ COO) _{0.5} ·Cl _{1.5}
		155–180	165	20.50	20.84	PbO

^a The greater than expected mass loss is connected with the formation of volatile products containing metal(II) ions

^b Unidentified final solid product of thermal decomposition

Fig. 2 TG and DTG curves of thermal decomposition of a Zn(CClH₂COO)₂·2H₂O recorded in air atmosphere; mass sample 9.50 mg;
b Zn(CCl₂HCOO)₂·2H₂O recorded in air atmosphere; mass sample 10.64 mg;
c Zn(CCl₃COO)₂·2H₂O recorded in air atmosphere; mass sample 7.13 mg



Fig. 3 TG and DTG curves of thermal decomposition of Cd(CCl₂HCOO)₂·H₂O recorded in air atmosphere; mass sample 11.56 mg



Cd(CCl₃COO)₂·2H₂O compounds appears also separation of v_{as} (COO) band. Based on these data, we can conclude about the different coordination of organic ligands in one compounds, as well as, about formation of non-completely equivalent bands between metal(II)-carboxylate groups [25, 26].

In addition, a broad band in the water stretching region (ca $3450-3350 \text{ cm}^{-1}$) appear for all described complexes.

Thermal decomposition

Thermal decomposition of analyzed compounds in air is a multistage process. The solid intermediate products of pyrolysis were determined from TG and DTG curves. The thermal decomposition data are collected in Table 5. Figures 2–5 present the thermoanalytical curves of obtained complexes. From TG and DTG curves the solid intermediate products of decomposition were determined.

They were also confirmed by the IR spectra of sinters. In the sinters (prepared during heating of complexes up to temperatures defined from TG curves), the vibration modes of chloroacetates were analyzed as well as the presence of anions Cl⁻ was also stated. All Zn(II) and Cd(II) compounds are stable up to 50 °C. Only Pb(CCl₃COO)₂·2H₂O starts to decompose at 100 °C.

The compound of Zn(CClH₂COO)₂·2H₂O loses 0.5 mol of water in a first stage of decomposition (50–125 °C); mass founded 2.70% and calculated 3.12%. Further dehydration process is accompanied by partial destruction of monochloroacetates. In the ranges of temperature: 125–300 and 300–340 °C intermediate species Zn(CClH₂COO)_{0.5}Cl_{1.5} and Zn(CClH₂COO)_{0.25}Cl_{1.75} are created. Next, total decomposition of monochloroacetates takes place. Between 340 and 525 °C high mass loss appears (42.30%), which is probably associated with the formation of volatile decomposition products containing zinc.



Fig. 5 TG and DTG curves of thermal decomposition of Pb(CCl₃COO)₂·2H₂O recorded in air atmosphere; mass sample 11.65 mg



Dehydration of $Zn(CCl_2HCOO)_2 \cdot 2H_2O$ is in two steps. In the range 50–175 °C one and half water molecules are released. $Zn(CCl_2HCOO)_2 \cdot 0.5H_2O$ species are stable up to 175 °C. When the temperature rises on TG curves is observed the biggest mass loss (found 48.00%, calculated 47.82%), which is associated with further dehydration and partial combustion of organic ligands (175–275 °C). In the temperature range 325–500 °C volatile products containing zinc appear.

The Cd(CCl₂HCOO)₂·H₂O losses 1 mol of water above 50 °C. Next, in the interval 140–200 °C partial destruction of dichloroacetates takes place and forms intermediate specie type Cd(CCl₂HCOO)_{0.5}Cl_{1.5}. The TG curve shows a rapid mass loss between 200 and 240 °C as a result of total decomposition of organic ligands (CdCl₂ is formed). In the range 240–660 °C CdO is created. The mass loss calculated is 14.21%, but founded is 45.00%. This is probably related with the formation of volatile products with cadmium.

Thermolysis of $Zn(CCl_3COO)_2 \cdot 2H_2O$ starts with the dehydration. Zinc compound losses two water molecules in one stage (50–90 °C). When the temperature rises, decomposition of organic ligands appears and $ZnCl_2$ exists. It is accompanied by a high mass loss on TG curve (found 59.50%, calculated 59.65%). When the temperature rises (350–475 °C) volatile products containing zinc are formed.

Thermal decomposition of Cd(CCl₃COO)₂·2H₂O begins at 50 °C. On TG curve is recorded a high mass loss associate with dehydration and partial destruction of organic ligands (intermediate specie Cd(CCl₃COO)Cl is formed). Increasing temperature causes further degradation and creates CdCl₂ (145–190 °C). After this process volatile products containing cadmium are emitted. Horizontal mass level for CdO starts above 650 °C. Compound of Pb(II) starts to decompose at 100 °C. On TG curve appears rapid mass loss (found 39.50%, calculated 39.86%). Such a decrease in mass is linked with dehydration, and partial decomposition of carboxylates, $Pb(CCl_3COO)_{0.5}Cl_{1.5}$, occurs. Above 180 °C PbO forms.

MS study

Mass study was used to analyze the principal volatile products evolved during the thermal decomposition and fragmentation processes only for Zn(CCl₃COO)₂·2H₂O compound. The determination was carried out in dynamic air and argon atmospheres.

MS study in air

For Zn(CCl₃COO)₂·2H₂O major maxima for ion currents are observed in temperature range 190-220 °C. For OH⁺ and H_2O^+ (m/z = 17, 18), there is one peak around 85 °C which is connected with the dehydration of zinc(II) compound. When temperature rises, several gaseous products start to liberate. The profiles of CO_2^+ (m/z = 44, 45) exhibit very intensity maximum at 195 °C. At the same temperature is also emitted C^+ with m/z = 12. These ion signals (C^+, CO_2^+) also have the same intensity and similar profiles. The mass spectrometer detected also many fragments containing chlorine with m/z = 35 (Cl⁺), 47 (CCl⁺), 70 (CCl₂⁺), 82 (CCl₂⁺), 117 (CCl₃⁺). The chlorine species appear between 190 and 220 °C. These molecular ions have the main peaks in the temperature close to evolution of carbon and dioxide. This proves a one-step destruction of trichloroacetates. Further small peaks of gaseous products containing chlorine (very low intensities of ion currents) indicate the combustion of organic ligands.



Fig. 6 Selected ion currents detected by the MS spectra for $Zn(CCl_3COO)_2 \cdot 2H_2O$ compound in air, mass sample 16.85 mg: a m/z: 1–35 (Cl⁺), 2–70 (Cl⁺₂), 3–82 (CCl⁺₂), 4–117 (CCl⁺₃) with

sensitivity of ion current: E-13 [A]. **b** m/z: 1–12 (C⁺), 2–44 (CO₂⁺) with sensitivity of ion current: E-11 [A]

The evaluation of all gaseous products finishes at ca 600 °C. Figure 6 presents as an example some ion currents vs temperature.

MS study in argon

In inert atmosphere the ion currents appear in the range 200–240 °C. The peaks of H_2O^+ (m/z = 18) and OH^+ (m/z = 17) are connected with dehydration and occur at about 200 °C. The ion signal intensities of CO^+ (m/z = 28)

and CO_2^+ (*m*/*z* = 44) have centers at 210 °C. The profile of C⁺ (*m*/*z* = 12) with very low intensity has a maximum at ca. 240 °C. These facts suggest decomposition and oxidization of organic ligands and the burning of the organic residues. The major ion signals containing chloride with *m*/*z* = 35, 47, 70 and 82 (Cl⁺, CCl⁺, Cl₂⁺, CCl₂⁺) have centers between 200 and 240 °C. Additionally, the strong peaks of O⁺ and O₂⁺ (*m*/*z* = 16 and 32) were monitored at 200 °C and at 220 °C, respectively. Thermolysis of Zn(CCl₃COO)₂·2H₂O is one-stage in argon atmosphere.



Fig. 7 Selected ion currents detected by the MS spectra for $Zn(CCl_3COO)_2 \cdot 2H_2O$ compound in argon, mass sample 15.15 mg: **a** m/z: 1–28 (CO⁺), 2–44 (CO⁺₂) with sensitivity of ion current:

The process of dehydration is connected with the decomposition of organic ligands. It was confirmed by emission of gaseous products. As an example, Fig. 7 shows some ion currents vs temperature.

Conclusions

From the system: M(II)-RCOOH-H₂O (where M(II) = Zn, Cd, Pb; RCOOH = CClH₂COOH, CCl₂HCOOH and CCl₃COOH) six new compounds with stoichiometry: Zn(CClH₂COO)₂·2H₂O, Zn(CCl₂HCOO)₂·2H₂O, Zn(CCl₃COO)₂·2H₂O, Cd(CCl₂HCOO)₂·H₂O,

E-6 [A]. **b** m/z: 1–35 (Cl⁺), 2–47 (CCl⁺), 3–70 (Cl₂⁺), 4–82 (CCl₂⁺) with sensitivity of ion current: E-7 [A]

 $Cd(CCl_3COO)_2 \cdot 2H_2O$ and $Pb(CCl_3COO)_2 \cdot 2H_2O$ were obtained. Described in [6] compound of zinc with monochloroacetates also contains two water molecules. Most zinc and cadmium acetates were obtained as dihydrated compounds [7–10, 12, 13, 16]. Only Györyovà and Balek [17] synthesized zinc acetate with formulae $Zn(CH_3COO)_2 \cdot 2.5H_2O$.

The IR spectra of the synthesized compounds show, that all carboxylate groups from chloroacetate ligands coordinate with metal(II) atoms. Infrared spectra give us the information about various types of organic ligands bonds.

All obtained compounds are stable at room temperature. During heating they decompose progressively. They start to decompose at 50 °C (except Pb(II), which is stable up to 100 °C). When the temperature rises dehydration and decomposition of organic ligands take place. There are differences in thermal decomposition of zinc and cadmium acetates in comparison to zinc and cadmium chloroacetaes. These differences come from formation of various products containing chlorine. This is reflected in the solid final products of thermolysis [7–10, 12, 13, 16, 17].

In case of zinc(II) and cadmium(II) chloroacetates formation of volatile species containing metal(II) ions take place. A similar phenomenon has been described in the literature [8], where the authors recorded higher than expected final mass loss. It has been attributed the formation of volatile compounds containing metal(II).

Mass study was used to analyze the principal volatile thermal decomposition and fragmentation products in air and in argon of Zn(CCl₃COO)₂·2H₂O. Relative, the most species are detected in temperature ranges 190–220 °C (in air) and 200–240 °C (in argon). In air and argon atmosphere were observed different levels of intensity evolving molecular ions with m/z = 12 and 44 (C⁺ and CO₂⁺). In air was not observed presence of CO⁺. In both atmospheres some fragments containing chlorine (Cl⁺, CCl⁺, Cl₂⁺, CCl₂⁺ and CCl₃⁺) were detected. These molecular ions were not observed by the authors [6, 17].

The results described in this paper complete existing knowledge of metal(II) compounds with halogenoacetates.

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