



Short communications

Research article

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Mass spectrometry of complex compound of bis-thiourea-lead (II) chloride

M. Yu. Krysin¹, V. N. Semenov¹, T. V. Samofalova¹✉, N. M. Ovechkina²

¹Voronezh State University,
1 Universitetskaya pl., Voronezh 394018, Russian Federation

²Voronezh State Medical University named after N. N. Burdenko,
10 Studencheskaya st., Voronezh 394036, Russian Federation

Abstract

Complex compounds of lead salts and thiourea are of interest due to the possibility of their practical application as precursors in the deposition of metal sulphide films. It is relevant to establish the relationship between the composition and structure of the initial complex compounds and the structure of the sulphides formed as a result of their thermal destruction. This paper presents the results of studying the complex compounds formed in an aqueous solution of lead chloride and thiourea.

The structure of the complex compounds was determined by matrix-assisted laser desorption/ionisation mass spectrometry. The mass spectrometry data confirmed the formation of the $[\text{Pb}((\text{NH}_2)_2\text{CS})_2\text{Cl}_2]$ complex in the solution, which is a precursor in the deposition of PbS films. It was demonstrated that mass spectrometry fragmentation of the molecular ion of the $[\text{Pb}((\text{NH}_2)_2\text{CS})_2\text{Cl}_2]$ compound leads to the formation of a lead sulphide ion.

The obtained data confirm the formation of the lead-sulphur bonds in the inner sphere of the complex compound, which are fragments of the crystal structure of the prospective sulphide formed during the thermolysis of the complex.

Keywords: thiourea complex compounds, complexation, lead sulphide, mass spectrometry

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✉ Tatyana V. Samofalova, e-mail: TSamofalova@bk.ru

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1. Introduction

A topical issue of modern materials science is the search, design, and improvement of cost-effective and accessible methods of deposition of semiconductor films of metal sulphides. The solid phase of a sulphide can be formed during the decomposition of thiourea complex compounds (TCCs) in aqueous solutions [1, 2], during the thermal degradation of TCCs during the pyrolysis of their solution aerosol [3–6], or the combustion of solid samples of complexes containing an oxidising anion NO_3^- [7, 8].

Pyrolysis of aerosol solutions of thiourea complex compounds on a heated substrate meets all the requirements for the deposition of metal sulphide films with variable properties [3, 4, 9]. This method is based on the thermal destruction of thiourea complexes formed by the interaction of the metal cation with the sulphur atom of $(\text{NH}_2)_2\text{CS}$ (thiourea). Thus, sulphide fragments (-metal-S-) begin to form already in the solution. The resulting complex compound is a precursor in the process of metal sulphide formation. Therefore, it is important to determine the relationship between the composition and structure of thiourea complexes formed in the initial solution and the structure of sulphides formed by this process.

Previously, complexation in aqueous solutions of various lead salts and thiourea was studied, and the domination regions of lead TCCs used for the deposition of PbS films were determined [10–13]. In studies [14, 15], it was found that, depending on the ratio of components, the interaction of lead nitrate, sodium thiosulphate, and thiourea in aqueous solutions forms $[\text{Pb}(\text{bi-S}_2\text{O}_3)(\text{SC}(\text{NH}_2)_2)(\text{H}_2\text{O})]$ and $[\text{Pb}(\text{mono-S}_2\text{O}_3)(\text{SC}(\text{NH}_2)_2)_2(\text{H}_2\text{O})]$ complexes. Upon the thermolysis of these complexes, lead sulphide is formed. In the paper [16], the geometry of the $[\text{Pb}((\text{NH}_2)_2\text{CS})_2(\text{mono-CH}_3\text{COO})_2]$ complex compound was determined using quantum-chemical modelling. This work presents a mass spectrometric study of the thermolysis of the precursor of bis-thiourea-lead(II) chloride formed in aqueous solution by the interaction of lead chloride and thiourea.

2. Experimental

Lead TCCs were synthesised in aqueous solutions of lead chloride and thiourea $(\text{NH}_2)_2\text{CS}$.

The solid phase complexes were obtained by slow evaporation of the solvent from aqueous solutions of 0.02 mol/L lead salt and thiourea at molar ratios of $C_{\text{Pb}^{2+}}:C_{\text{SC}(\text{NH}_2)_2}$ from 1:1 to 1:4. To obtain the TCCs, pure-grade PbCl_2 and $(\text{NH}_2)_2\text{CS}$ were used.

The structure of the synthesised TCCs was identified by mass spectrometry. The spectra were recorded on a VISION 2000 mass spectrometer (MKS Instruments, Inc.) with matrix-assisted laser desorption ionisation using a pulsed nitrogen laser ($\lambda = 337 \text{ nm}$). In this method, the desorption rate exceeds the degradation rate [17]. Thus, it is possible to capture the primary fragment ions formed during the fragmentation of the molecular ion of the complex. Initially, the samples were prepared in powder form.

3. Results and discussion

Matrix-assisted laser desorption/ionisation mass spectrometry was used to study the directions of fragmentation of the molecular ion of the TCCs of lead. The use of this method to determine the structure of $(\text{NH}_2)_2\text{CS}$ complexes proved to be more representative than electron ionisation mass spectrometry due to rather soft ionisation conditions [17]. Nevertheless, the intensity of the peaks of the molecular ion of the complex and of several fragment ions was low (Table).

It should be noted that the content of aqua complexes in the solution is insignificant, and these compounds mainly have coordination numbers of 1 or 2. Under electron ionisation conditions, these ions were not observed [18].

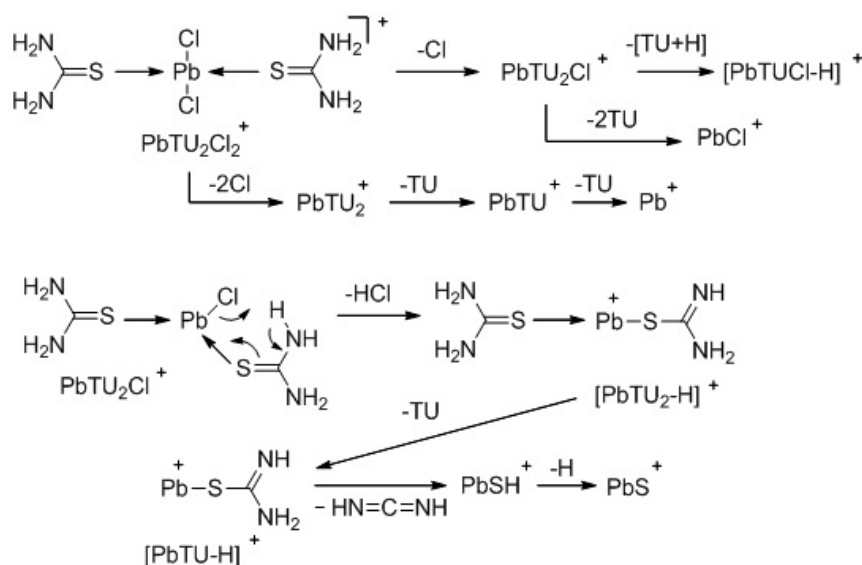
The most probable direction of the fragmentation of the molecular ion of the $[\text{Pb}((\text{NH}_2)_2\text{CS})_2\text{Cl}_2]$ complex is the initial removal of one or two chlorine atoms to form $\text{Pb}((\text{NH}_2)_2\text{CS})_2\text{Cl}^+$ and $\text{Pb}((\text{NH}_2)_2\text{CS})_2^+$ ions. Further decomposition of these ions involves the release of $(\text{NH}_2)_2\text{CS}$ molecules (Figure).

Another fragmentation direction of the $\text{Pb}((\text{NH}_2)_2\text{CS})_2\text{Cl}^+$ fragmentation ion is the rearrangement with the removal of the HCl molecule, resulting in the $[\text{Pb}((\text{NH}_2)_2\text{CS})_2-\text{H}]^+$ ion. The latter is stabilised as a result of diiminomethane release, which leads to PbSH^+ ion and, further, to PbS^+ . Probably, their formation causes the formation of PbS films. The layers

Table. Peak intensity and mass of ions under the conditions of mass spectrometry of matrix-assisted laser desorption/ionization of the complex $[\text{Pb}((\text{NH}_2)_2\text{CS})_2\text{Cl}_2]$

Ion	Molecular formula	Molecular mass (m/z), c.u.		Peak Intensity, %
		Calculated	Found	
$\text{Pb}((\text{NH}_2)_2\text{CS})_2\text{Cl}_2^+$ (molecular ion)	$\text{Pb}(\text{CH}_4\text{N}_2\text{S})_2\text{Cl}_2$	429.933	*	5
$\text{Pb}((\text{NH}_2)_2\text{CS})_2\text{Cl}^+$	$\text{Pb}(\text{CH}_4\text{N}_2\text{S})_2\text{Cl}$	394.946	395.085	20
$[\text{Pb}((\text{NH}_2)_2\text{CS})_2\text{-H}]^+$	$\text{Pb}(\text{CH}_4\text{N}_2\text{S})_2(\text{CH}_3\text{N}_2\text{S})$	358.987	358.954	90
$[\text{Pb}((\text{NH}_2)_2\text{CS})\text{Cl-H}]^+$	$\text{Pb}(\text{CH}_3\text{N}_2\text{S})\text{Cl}$	317.946	317.841	25
$\text{Pb}((\text{NH}_2)_2\text{CS})^+$	$\text{Pb}(\text{CH}_4\text{N}_2\text{S})$	283.955	283.900	10
$[\text{Pb}((\text{NH}_2)_2\text{CS})\text{-H}]^+$	$\text{Pb}(\text{CH}_3\text{N}_2\text{S})$	282.977	282.957	100
$\text{Pb}(\text{H}_2\text{O})_2^+$	$\text{Pb}(\text{H}_2\text{O})$	243.997	*	*
PbCl^+	PbCl	242.944	*	*
PbSH^+	PbSH	240.956	240.594	8
PbS^+	PbS	239.948	*	*
$\text{Pb}(\text{H}_2\text{O})^+$	$\text{Pb}(\text{H}_2\text{O})$	225.986	*	*
Pb^+	Pb	207.976	*	*

* Low intensity

**Figure.** Scheme of mass spectrometric fragmentation under conditions of matrix-assisted laser desorption/ionisation of the molecular ion of the $[\text{Pb}((\text{NH}_2)_2\text{CS})_2\text{Cl}_2]$ complex

are deposited as a result of the layering of these fragments on the surface of the substrate due to the valence electrons in these ions.

Thus, according to the mass spectrometry data, in an aqueous solution of PbCl_2 and $(\text{NH}_2)_2\text{CS}$ a complex compound is formed, with $(\text{NH}_2)_2\text{CS}$ included in its inner sphere. The fragmentation of this compound occurs with the preservation, at least partially, of the Pb-S

covalent bond. So, it can be assumed that during the deposition of sulphide films by aerosol pyrolysis, thiourea acts as a sulphur donor, coordinating to the metal ion already in the initial solution. The formation of the sulphide structure fragments occurs in the inner sphere of the complex compound. During thermal decomposition of this compound, a PbS layer is formed on the heated substrate.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Information about the authors

Mikhail Y. Krysin, Dr. Sci. (Chem.), Associate Professor, Professor of Department of Organic Chemistry, Voronezh State University (Voronezh, Russian Federation).

<https://orcid.org/0000-0002-4336-8935>

kaf261@rambler.ru

Victor N. Semenov, Dr. Sci. (Chem.), Professor, Chair of Department of General and Inorganic Chemistry, Voronezh State University (Voronezh, Russian Federation).

<https://orcid.org/0000-0002-4247-5667>

office@chem.vsu.ru

Tatyana V. Samofalova, Cand. Sci. (Chem.), Associate Professor of the Department of General and Inorganic Chemistry, Voronezh State University (Voronezh, Russian Federation).

<https://orcid.org/0000-0002-4277-4536>

TSamofalova@bk.ru

Nadezhda M. Ovechkina, Assistant of the Department of Chemistry, Voronezh State Medical University named after N. N. Burdenko (Voronezh, Russian Federation).

<https://orcid.org/0000-0002-5841-0403>

nadezhda.ovechkina@rambler.ru

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