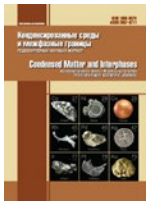


ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

**Original articles**

Research article
https://doi.org/10.17308/kcmf.2021.23/3673

# Complexation processes in "$PbCl_2$-$N_2H_4CS$" aqueous solutions during deposition of lead sulphide films

**V. N. Semenov[1]✉, V. V. Volkov[2], N. V. Pereslytskikh[1]**

[1]*Voronezh State University,*
*1 Universitetskaya pl., Voronezh 394018, Russian Federation*

[2]*Voronezh State Technical University,*
*14 Moskovsky pr., Voronezh 394026, Russian Federation*

**Abstract**

In this study, we proposed a new approach to assessing the processes of complexation in aqueous solutions using the example of the interaction of lead chloride with thiourea. The goal of this study was the investigation of processes of complexation in "$PbCl_2$-$N_2H_4CS$" aqueous solutions and determination of the regions of dominance of thiourea coordination compounds, which are precursors during the deposition of lead sulphide films.

Based on the diagrams and cross section lines of equal fractions constructed in three-dimensional space, the regions of dominance of all complex forms existing in the studied solution were found. Such a graphic image is the most informative, since it allows selection of the concentration ranges of the predominance of certain coordination compounds, especially thiourea complexes, which are precursors during the deposition of lead sulphide films. It was shown that an increase in the concentration of $N_2H_4CS$ led to an increase in the total fraction of thiourea complexes: for a twofold excess of $N_2H_4CS$ its fraction was 0.25, for a threefold excess it was 0.35, for a fourfold excess it was 0.5, for a fivefold excess it was 0.7.

**Keywords**: Distribution diagrams, Complexation, Thiourea, Lead chloride, Coordination compounds

***For citation:*** Semenov V. N., Volkov V. V., Pereslytskikh N. V. Processes of complexation in "$PbCl_2$-$N_2H_4CS$" aqueous solutions during the deposition of lead sulphide films. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2021;23(4): 543–547. https://doi.org/10.17308/kcmf.2021.23/3673

***Для цитирования:*** Семенов В. Н., Волков В. В., Переслыцких Н. В. Процессы комплексообразования в водных растворах «$PbCl_2$–$N_2H_4CS$» при осаждении пленок сульфида свинца. *Конденсированные среды и межфазные границы*. 2021;23(4): 543–547. https://doi.org/10.17308/kcmf.2021.23/3673

✉ Victor N. Semenov, e-mail: semenov@chem.vsu.ru

## 1. Introduction

Traditionally, high-temperature synthesis methods and vacuum technologies, which require complex and expensive equipment are used for obtaining photosensitive PbS layers for the near and mid-IR spectral regions. This determines the high commercial cost of thin-film detectors based on them. Therefore, the development of new cheap technologies for obtaining such photosensitive layers based on lead sulphide with unique properties [1–3] is an important task.

One such method is the method of aerosol spraying of solutions of thiourea coordination compounds (TCC) on a heated substrate [4], based on the thermal destruction of these complexes [5].

In the study [6], all ionic equilibria existing in an aqueous solution of lead chloride and thiourea (TC) were provided, and the equilibrium concentrations of [$Pb^{2+}$], [TC] and [$Cl^-$] for the given initial $C_{Pb^{2+}}$ and $C_{TM}$ were calculated based on them. Further, these data were used for the determination of the equilibrium concentrations of complex ions. Using the data obtained, the fractions of these complex forms were found and distribution diagrams were plotted (about 100 variants of such diagrams were plotted). The process of plotting diagrams is very laborious and inconvenient for comparing and analysing complexation processes in different concentration ranges. For obtaining a more clearly picture, we proposed the construction of three-dimensional distribution diagrams and cross section lines of equal fractions for specific complex forms. The goal of this study was the investigation of processes of complexation in a "$PbCl_2$-$N_2H_4CS$" aqueous solutions and determination of the regions of dominance of TCC, which are precursors during the deposition of lead sulphide films.

## 2. Modelling

The construction of sections of the concentration dependences of the fractions of complex forms present in the solution was carried out using the COMSOL Multiphysics application package by the Newton–Raphson method [7]. Thus, diagrams for all 15 complex forms existing in the "$PbCl_2$-$N_2H_4CS$" aqueous solution were plotted. The use of initial (analytical), rather than equilibrium concentrations allowed realistic assess of the complexation process.

The concentration regions of existence of these complex forms were found by analysis of the diagrams obtained for all coordination compounds in three-dimensional space and the cross-sections plotted on their basis (Table 1).

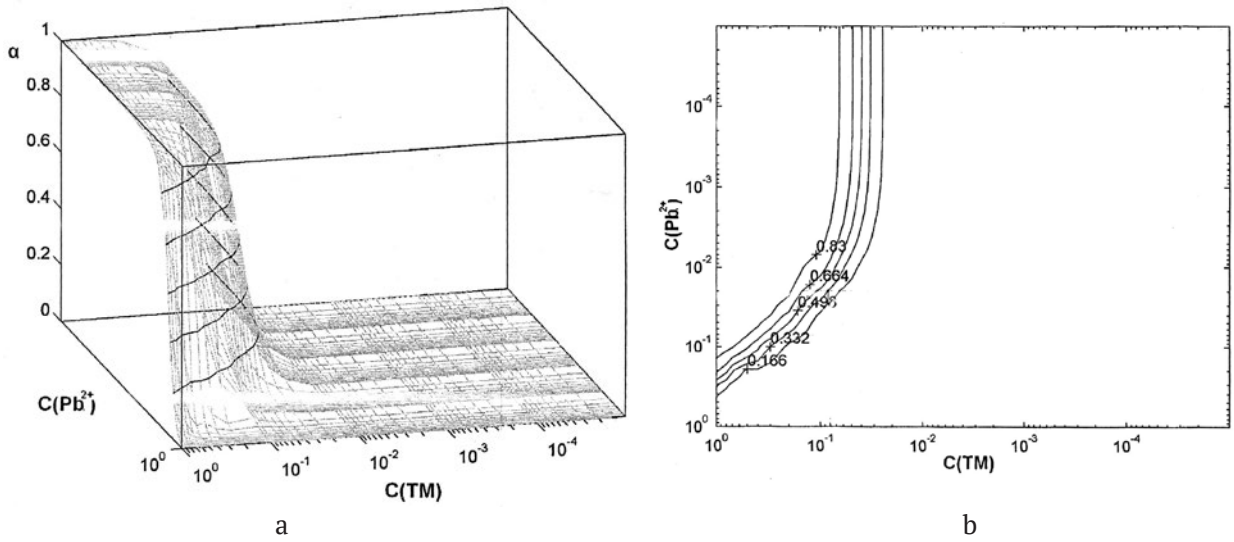
**Table 1.** Fractions of complex forms prevailing in a certain concentration range in the $PbCl_2$-$N_2H_4CS$ system

| Complex form | Maximum fraction of complexes in solution | Intervals of existence for the maximum fractions of complexes, M/l | |
|---|---|---|---|
| | | $C_{TM}$ | $C_{Pb}^{2+}$ |
| $Pb(H_2O)_n^{2+}$ | 1.00 | $1\cdot10^{-5}$–$2\cdot10^{-2}$ | $1\cdot10^{-5}$–$2\cdot10^{-3}$ |
| $PbTM^{2+}$ | 0.08 | $2\cdot10^{-2}$–$4\cdot10^{-2}$ | $1\cdot10^{-5}$–$3\cdot10^{-3}$ |
| $PbTM_2^{2+}$ | 0.025 | $3\cdot10^{-2}$–$5\cdot10^{-2}$ | $1\cdot10^{-5}$–$4\cdot10^{-3}$ |
| $PbTM_3^{2+}$ | 0.06 | $4\cdot10^{-2}$–$8\cdot10^{-2}$ | $1\cdot10^{-5}$–$8\cdot10^{-3}$ |
| $PbTM_4^{2+}$ | 1.00 | $8\cdot10^{-2}$–1 | $1\cdot10^{-5}$–$2\cdot10^{-1}$ |
| $PbCl^+$ | 0.6 | $1\cdot10^{-5}$–$8\cdot10^{-2}$ | $2\cdot10^{-2}$–$3\cdot10^{-1}$ |
| $PbCl_2$ | 0.6 | $1\cdot10^{-5}$–1 | $5\cdot10^{-1}$–1 |
| $PbCl_3^-$ | 0.13 | $7\cdot10^{-1}$–1 | $8\cdot10^{-1}$–1 |
| $PbCl_4^{2-}$ | 0.01 | $9\cdot10^{-1}$–1 | $6\cdot10^{-1}$–$7\cdot10^{-1}$ |
| $PbTMCl^+$ | 0.07 | $6\cdot10^{-2}$–$3\cdot10^{-1}$ | $2\cdot10^{-2}$–$2\cdot10^{-1}$ |
| $PbTMCl_2$ | 0.08 | $7\cdot10^{-1}$–1 | $4\cdot10^{-1}$–1 |
| $PbTMCl_3^-$ | 0.04 | $9\cdot10^{-1}$–1 | $6\cdot10^{-1}$–1 |
| $PbTM_2Cl^+$ | 0.04 | $2\cdot10^{-1}$–$4\cdot10^{-1}$ | $8\cdot10^{-2}$–$2\cdot10^{-1}$ |
| $PbTM_3Cl^+$ | 0.3 | $7\cdot10^{-1}$–1 | $2\cdot10^{-1}$–$4\cdot10^{-1}$ |
| $PbTM_2Cl_2$ | 0.1 | $9\cdot10^{-1}$–1 | $4\cdot10^{-1}$–$7\cdot10^{-1}$ |

As can be seen from these results, in "$PbCl_2$-$N_2H_4CS$" aqueous solution following complexes were dominant: $Pb(H_2O)_n^{2+}$, $PbTM_4^{2+}$, $PbCl^+$, $PbCl_2$ and $PbTM_3Cl^+$. Their fractions (a) were more than 0.3. Out of the homoligand TCC, the most stable is the complex ion $PbTM_4^{2+}$. Out of the thiourea complexes, in addition to those indicated above $PbTM^{2+}$, $PbTM_3^{2+}$, $PbTMCl^+$, $PbTMCl_2$ and $PbTM_2Cl_2$ forms were relatively stable. The fraction of their presence in the solution exceeded 0.05. The maximum fraction of homoligand TCC increased in the following order: $PbTM_2^{2+} < PbTM_3^{2+} < PbTM^{2+} < PbTM_4^{2+}$, for mixed ligands: $PbTMCl_3^- \le PbTM_2Cl^+ < PbTM_2Cl_2 < PbTM_3Cl^+$. As an illustration, diagrams and their cross sections for four TCC are shown (Figs. 1–4).

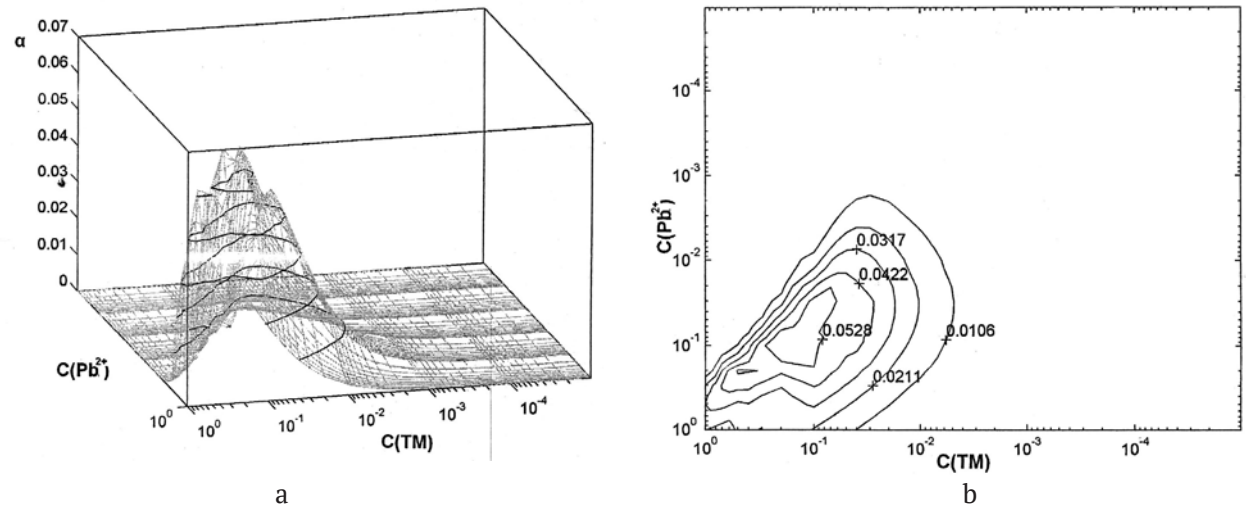
According to the study [8], the solubility of $PbCl_2$ at 25 °C is $4\ 10^{-2}$ M/l. Therefore, considering the cross-section lines of equal fractions in Fig. 1 (b) – 4 (b), it can be noted that in the initial solution the fraction of complexes $[PbTM_2Cl_2]$ is very small (Fig. 4b), while complex forms $PbTM_4^{2+}$, $PbTMCl^+$ and $PbTM_3Cl^+$ actually exist. The dependence of the fraction of formed TCC on the concentration of thiourea at a constant concentration of lead chloride ($2{\cdot}10^{-2}$ M/l) is shown in Table 2. The calculation was carried out based on the constructed distribution diagrams.

Data provided in Table 2 demonstrate that the total fraction of thiourea complexes, which are the supplier of lead sulphide, for a twofold excess of $N_2H_4CS$ is 0.25, for three times excess it was 0.35,



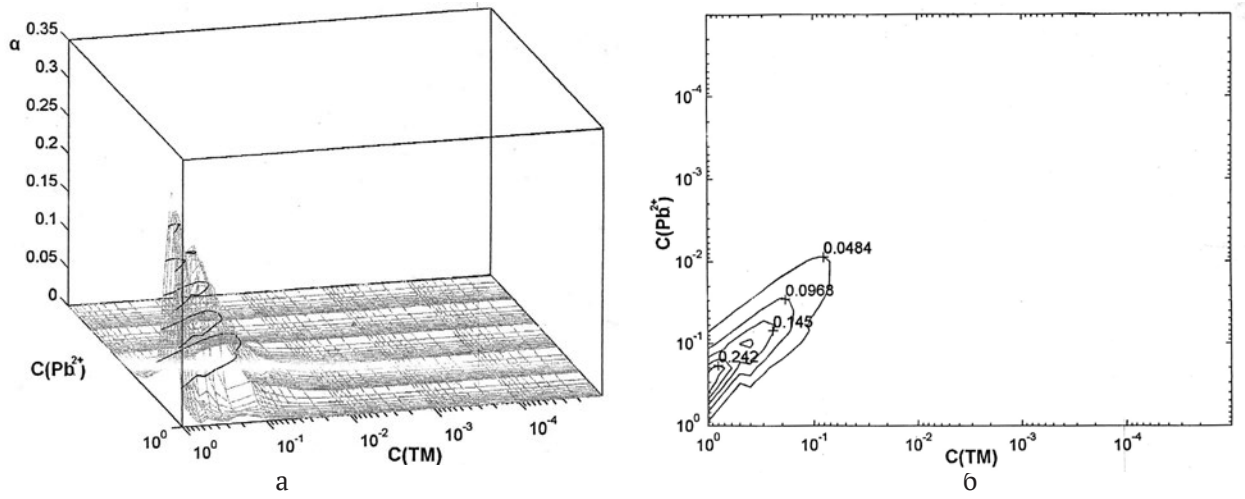

a b

**Fig. 1.** Three-dimensional distribution diagrams (a) and cross section lines of equal fractions (b) for the $PbTM_4^{2+}$ complex



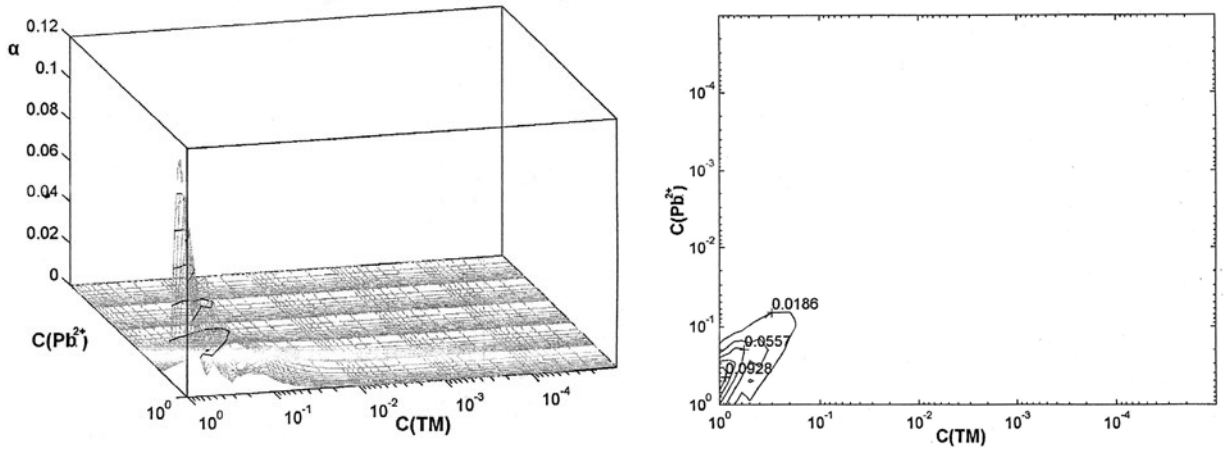

a b

**Fig. 2.** Three-dimensional distribution diagrams (a) and cross section lines of equal fractions (b) for the $PbTMCl^+$ complex




а б

**Fig. 3.** Three-dimensional distribution diagrams (a) and cross section lines of equal fractions (b) for the $PbTM_3Cl^+$ complex




а б

**Fig. 4.** Three-dimensional distribution diagrams (a) and cross section lines of equal fractions (b) for the $PbTM_2Cl_2$ complex

**Table 2.** Formation of thiourea complexes depending on the concentration of thiourea

| $C_{TM}$ | Fractions of complexes | | | | | | | Total fraction of TM complexes |
|---|---|---|---|---|---|---|---|---|
| | $PbTM_4^{2+}$ | $PbTM_3^{2+}$ | $PbTM_2^{2+}$ | $PbTM^{2+}$ | $PbTMCl^+$ | $PbTM_2Cl^+$ | $PbTM_3Cl^+$ | |
| 0.02 | 0.12 | 0.0001 | 0.003 | 0.03 | 0.04 | 0.007 | 0.001 | 0.2 |
| 0.04 | 0.14 | 0.01 | 0.007 | 0.04 | 0.04 | 0.01 | 0.001 | 0.25 |
| 0.06 | 0.17 | 0.02 | 0.01 | 0.04 | 0.045 | 0.02 | 0.04 | 0.35 |
| 0.08 | 0.33 | 0.03 | 0.01 | 0.02 | 0.05 | 0.02 | 0.05 | 0.51 |
| 0.1 | 0.5 | 0.04 | 0.01 | 0.03 | 0.04 | 0.02 | 0.07 | 0.71 |

for four times excess it was 0.5, for five times excess it was 0.7. In the complexation process, thiourea, which is an ambidentate ligand, is coordinated through a sulphur atom. As a result of the thermal destruction of TCC, lead sulphide is the main solid-phase product. Thus, the process of obtaining PbS proceeds through the stage of the formation of the thiourea complex. X-ray phase analysis indicated the precipitation of lead sulphide with a cubic structure [9]. It should be noted that the fraction of aqua and chloride complexes (0.6) was quite high (Table 1); therefore, the concentration intervals $C_{TM} = 1{\cdot}10^{-5}–1{\cdot}10^{-1}$ and $C_{PbCl_2} = 1{\cdot}10^{-5} – 5{\cdot}10^{-2}$ M/l are unsuitable for the deposition of PbS films.

## 3. Conclusions

Based on diagrams and cross section lines of equal fractions for "$PbCl_2$–$N_2H_4CS$" aqueous solutions the areas of dominance of various complex forms formed in the process of complexation were determined. It was shown that the following complex forms dominate in the solution: $Pb(H_2O)_n^{2+}$, $PbTM_4^{2+}$, $PbCl^+$, $PbCl_2$ and $PbTM_3Cl^+$. The maximum fraction of homoligand TCC increases in the series $PbTM_2^{2+}$ < $PbTM_3^{2+}$ < $PbTM^{2+}$ < $PbTM_4^{2+}$, for the mixed ligand $PbTMCl_3^-$ ⩽ $PbTM_2Cl^+$ < $PbTM_2Cl_2$ < $PbTM_3Cl^+$. These thiourea coordination compounds are precursors for the deposition of lead sulphide films, and with an increase in the concentration of $N_2H_4CS$ in the initial solution, their fraction increases sharply.

## Author contributions

Semenov V. N. – scientific leadership, research concept, methodology development, text writing, final conclusions. Volkov V. V. – modelling using Newton – Raphson method. Pereslytskikh N. V. – plotting three-dimensional distribution diagrams, review writing and text editing.

## 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.

## References

1. Sermakasheva N. L., Novikov G. F., Shulga Yu. M., Semenov V. N. Microwave photoconduction and photodielectric effect in thin PbS films prepared from thiocarbamide coordination compounds. *Semiconductors*. 2004;38(4): 380–386. https://doi.org/10.1134/1.1734662

2. Mohsen Cheraghizade, Ramin Yousefi, Farid Jamali-Sheini, Abdolhossein Sa'aedi. Comparative study of Raman properties of various lead sulfide morphologies. *Majlesi Journal of Telecommunication Devices*. 2013;2(1): 163–166. Available at: http://journals.iaumajlesi.ac.ir/td/index/index.php/td/article/view/90

3. Sadovnikov S. I., Gusev A. I., Rempel' A. A. *Poluprovodnikovye nanostruktury sul'fidov svintsa, kadmiya i serebra* [Semiconductor nanostructures of lead, cadmium and silver sulfides]. Moscow: Fizmalit Publ.; 2018. 464 p. (In Russ.)

4. Naumov A. V., Semenov V. N., Averbakh E. M. Tiomochevinnye koordinatsionnye soedineniya v protsessakh sinteza sul'fidov metallov [Thiourea coordination compounds in the synthesis of metal sulfides]. *Khimicheskaya promyshlennost'*. 2003;80(2): 17–26. Available at: https://elibrary.ru/item.asp?id=23712470 (In Russ.)

5. Ugai Ya. A., Semenov V. N., Shamsheeva I. L. Thermal decomposition of dichlorodithioureacadmium (II) *Russian Journal of General Chemistry*. 1986;56(9): 1945–1950. Available at: https://elibrary.ru/item.asp?id=28890314 (In Russ., abstract in Eng.)

6. Semenov V. N., Ovechkina N. M., Volkov V. V. The distributing diagrams of complex form in aqueous solution "$PbCl_2$-$N_2H_4CS$". *Proceedings of Voronezh State University. Series: Chemistry. Biology. Pharmacy*. 2009;2: 59–63. Available at: https://elibrary.ru/item.asp?id=12992204 (In Russ., abstract in Eng.)

7. Malozemov V. N., Tamasyan G. Sh. On the direction of the steepest descent. *Vestnik of St Petersburg University. Applied Mathematics. Computer Science. Control Processes*. 2019;15(4): 489–501. https://doi.org/10.21638/11702/spbu10.2019.406 (In Russ., abstract in Eng.)

8. Volkov A. I., Zharskii I. M. *Bol'shoi khimicheskii spravochnik* [Large chemical reference book]. Moscow: Sovremennaya shkola Publ.; 2005. 608 p.

9. Semenov V. N., Ovechkina N M. Formation of SnS, $SnS_2$, and PbS films from thiourea coordination compounds. *Russian Journal of Applied Chemistry*. 2011;84: 2033–2039. https://doi.org/10.1134/S1070427211120032

## Information about the authors

*Victor N. Semenov*, DSc in Chemistry, Professor, Head of the Department of General and Inorganic Chemistry, Voronezh State University, Voronezh, Russian Federation; e-mail: semenov@chem.vsu.ru. ORCID iD: https://orcid.org/0000-0002-4247-5667.

*Vitaly V. Volkov*, Ph.D. in Physics and Mathematics, Associate Professor, Department of Structural Mechanics, Voronezh State Technical University, Voronezh, Russian Federation; e-mail: kotlac@yandex.ru.

*Natalia V. Pereslytskikh*, Master's degree student, Department of General and Inorganic Chemistry, Voronezh State University, Voronezh, Russian Federation; e-mail: deanery@chem.vsu.ru.

*Received August 22, 2021; approved after reviewing October 15, 2021; accepted for publication November 15, 2021; published online December 25, 2021.*

*Translated by Valentina Mittova*
*Edited and proofread by Simon Cox*