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КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА БИС[(ДИАМИНОМЕТИЛ-1-ЕН)АМИНОТИОМЕТИЛАММОНИЙ] СУЛЬФАТА

В данной работе представлены данные рентгеноструктурного анализа монокристалла бис[(диаминометил-1-ен)аминотиометиламмоний] сульфата, образующегося на промежуточной стадии синтеза 2-имино-4-тиобиурета. Полученный продукт охарактеризован методами ИК спектроскопии и элементного анализа. Кроме того, описаны потенциальные области применения синтезированного соединения. Структурные характеристики соединения находятся в соответствии с таковыми для тиомочевины и ее ранее изученных солей. Известно, что производные тиомочевины существуют в нескольких таутомерных формах, состояние которых в кристаллическом виде часто отличается от состояния в растворе. Так как промежуточный продукт на стадии синтеза 2-имино-4-тиобиурета выделяется в виде кристаллического порошка, а не остается в растворе, предложена измененная схема синтеза. Элементарная ячейка состоит из двух неплоских катионов 1-(диаминометилен)тиомочевины и сульфат-аниона. Полный набор рентгеноструктурных данных депонирован в Кембриджский банк структурных данных (депонент CCDC 1421710) и может быть свободно получен по запросу на сайте www.ccdc.cam.ac.uk/data_request/cif.

Ключевые слова: бис[(диаминометил-1-ен)аминотиометиламмоний] сульфат, тиомочевина, рентгеноструктурный анализ

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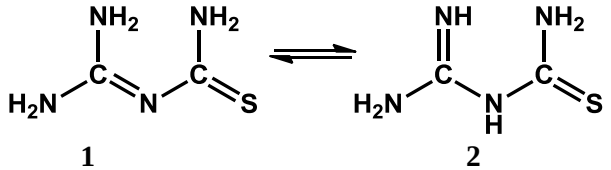
CRYSTAL STRUCTURE OF BIS[1-(DIAMINOMETHYLENE)-THIOURON-1-IUM] SULFATE

In this work crystal data of bis[1-(diaminomethylene)-thiouron-1-ium] sulfate is shown. This compound was characterized by IR spectroscopy and elemental analysis. The monocrystal of this compound was obtained and the structure was confirmed by single X-ray analysis. Moreover, the work describes potential application of synthesized compound. Comparative characteristics of thiourea and its known salts are demonstrated. It is known, that derivatives of thiourea have several tautomeric forms, which can be different in crystalline state or in solution. Therefore, changed scheme of the synthesis of 2-imino-4-thiobiuret is proposed. Elemental cell of crystal consists of two 1-(diaminomethylene)thiouron-1-ium cations and one sulfat anion. A full set of X-ray diffraction data was deposited in the Cambridge Structural Database (deposit CCDC 1421710) and it can be gotten from the site www.ccdc.cam.ac.uk/data_request/cif.

Key words: bis[1-(diaminomethylene)-thiouron-1-ium] sulfate, thiourea, X-ray analysis

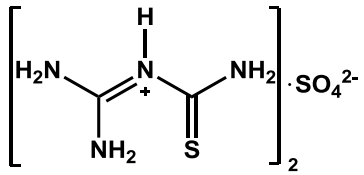
INTRODUCTION

1-(Diaminomethylene)thiourea (**1**) and its imino tautomer, namely 2-imino-4-thiobiuret (**2**) (Scheme 1), have several potential coordination modes and can form complexes with metal ions [1]. Compound **1** is organic ligand with multiple coordination sites, which can be used as building units for formation highly ordered supramolecular compounds with predetermined structure and properties [2].



1 **2**

Scheme 1. Tautomeric forms of 1-(diaminomethylene)thiourea
Схема 1. Таутомерные формы 1-(диаминометилен)тиомочевины



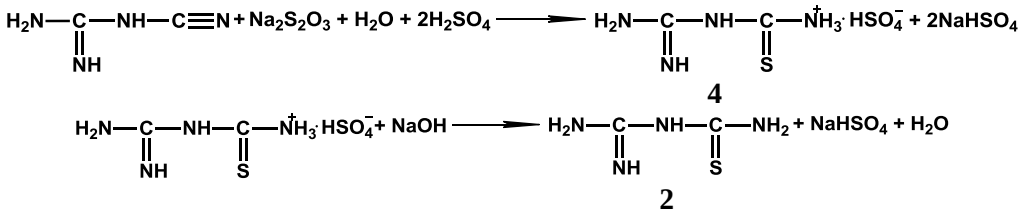
3

Fig. 1. Structure of bis[1-(diaminomethy-lene)thiouron-1-ium] sulfate
Рис. 1. Структура бис[(диаминометил-1-ен)аминотиометиламмоний] сульфата

This property is a result of the presence of donor atoms (N and S) bearing lone pair electrons [3]. It is known, that N,N-coordination is characteristic for basic solution and S,N-coordination was observed in neutral and weakly acid media [4]. 1-(Diaminomethylene)thiourea forms salts both with inorganic and with organic acids. For example, the authors [2] published X-ray data of bis[1-(diaminomethylene)-thiouron-1-

ium] tetrachlorozincate. The crystal structures of several salts of 1-(diaminomethylene)thiourea are known, namely chloride, bromide, iodide [5], perchlorate, hydrogen sulfate, dihydrogen phosphate, dihydrogen arsenate [6], hydrogen difluoride, hexafluorsilicate [7], formate and oxalate dehydrate [8]. In this article, the crystal structure of bis[1-(diaminomethylene)thiouron-1-ium] sulfate (3) is described for the first time (Fig. 1).

The authors [9] proposed new method of synthesis of 2 according to Scheme 2.



Scheme 2. The synthesis of 2-imino-4-thiobiuret
Схема 2. Синтез 2-имино-4-тиобиурета

It is known that substances having tautomeric transformations can have one state in crystalline form and other state in solution, so authors [9] expected that the formation of 2-imino-4-thiobiuret occurs through obtaining of 1-(diaminomethylene)thiourea hydrogen sulfate (**4**). However, we obtained the single crystal of compound formed on intermediate step of synthesis of compound **2**.

EXPERIMENTAL PART

IR spectra were measured with an AVATAR 360 FT-IR spectrometer. X-Ray analysis were carried out with the monocrystal automatic diffractometer Xcalibur R with CCD-detector by standard method.

Crystal of $2C_2H_7N_4S^+ \cdot SO_4^{2-}$ **3** was obtained from dicyandiamide (8.4 g, 0.1 mol) and sodium thiosulfate pentahydrate (27.3 g, 0.11 mol). This mixture was dissolved in water (50 mL) under heating and then 25% sulfuric acid (36.6 mL, 0.11 mol) was added by dropwise. Reaction mixture was heated to 80ºC and stirred at this temperature during 5 hours. Formed sulphur was removed by the method of hot filtration. After several days at room temperature, crystals of **3** were obtained. Yield: 14.14 g (86%). T_{melt} = 190-192 ºC. IR: ν (KBr)/cm^{-1}: 3394 (NH_2, vas), 3309 (NH_2, vs), 3196, 2809, 1700 (C=N), 1631 (NH_2, d), 1601, 1513, 1339, 1199 (C–N, aliph), 1109 (C=S), 1085 (S=O), 835, 750, 663, 636, 612, 545, 511, 445, 427. Found, %: C 14.41, H 4.28, N 31.97, S 28.61. $C_4H_{14}N_8O_4S_3$. Calc., %: C 14.37, H 4.22, N 33.51, S 28.77.

H atoms were located in difference Fourier maps and refined with isotropic displacement parameters. The N–H distances were fixed at 0.86 (2) Å using DFIX restraint. Crystal data was obtained using of computer programs: CrysAlis PRO [10], SHELXS97 [11], SHELXL97 [11], Mercury [12], publCIF [13]. A full set of X-ray diffraction data was deposited in the Cambridge Structural Database (deposit CCDC 1421710).

RESULTS AND DISCUSSION

X-ray analysis of monocrystal **3** shown that the elemental cell contains two nonplanar 1-(diaminomethylene)thiouron-1-ium cations and the sulfate anion linked together *via* N–H···O hydrogen bonds, which were formed by H atom of amino-group **1** and O atom of sulfate anion (Fig. 2).

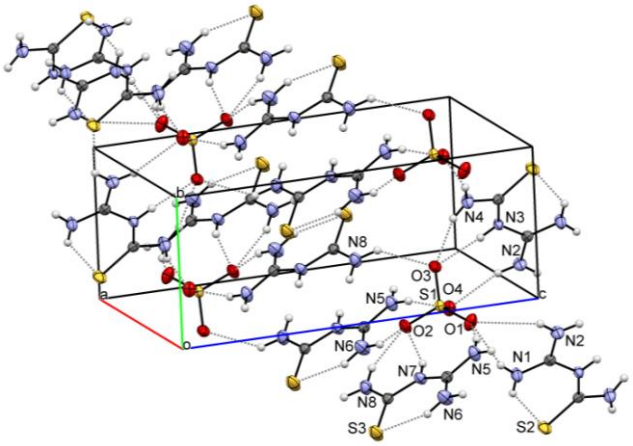


Fig. 2. Fragment of crystal packing of **3**
Рис. 2. Фрагмент кристаллической упаковки **3**

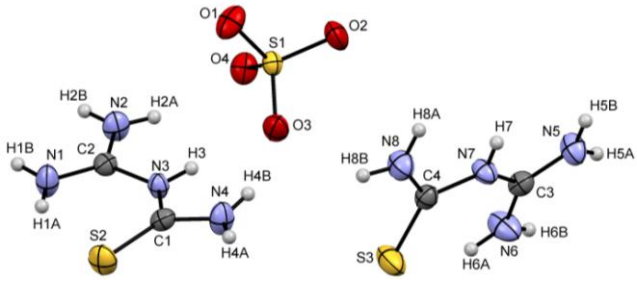


Fig. 3. The molecular structure of the elemental cell of **3**
Рис. 3. Молекулярная структура элементарной ячейки **3**

The compound **3** constructed by two crystallographic independent cations and one anion is crystallized in centrosymmetric space group of triclinic crystal system (Fig. 3).

Sulfate-anion represents slightly distorted tetrahedron, which is typical for structures of this type. As in other salts of 1-(diaminomethylene)thiourea [6], cations consist of two planar parts twisted about each other. The dihedral angle between the mean least-squares planes of fragments N1C2N2N3 and N3C1N4S2 is 12.0º, the angle between fragments N5C3N6N7 and N7C4N8S3 is 10.2º. Double bonds C2=N3 and C3=N7 (Table) are elongated significantly and single bonds C2–N1, C2–N2, C3–N5, C3–N6 are shortened comparing with neutral molecule [1].

The C1=S2, C4=S3 bond lengths in 3 are comparable to those in thiourea (where the C=S distance is 1.683 Å) [14] and in other salts of 1-(diaminomethylene)thiourea, such as the perchlorate and the dihydrogen arsenate [6]. However, these double bonds are shortened significantly comparing with neutral molecule [1]. Such redistribution bond length indicates delocalization of the positive charge of cations between the nitrogen atoms of the amino groups.

Table 1

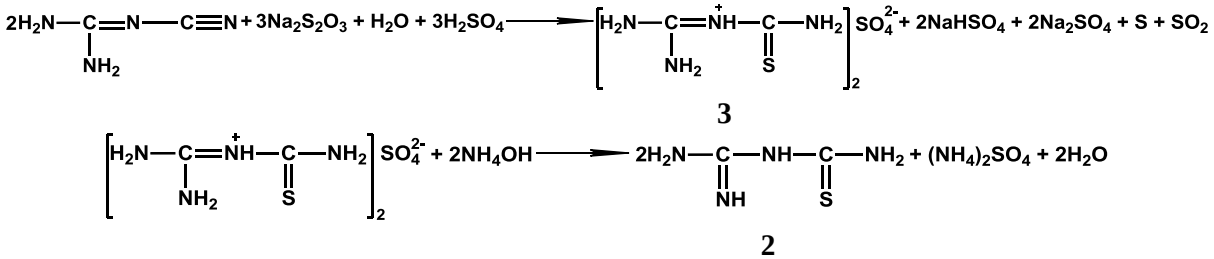
Selected geometric parameters (Å) for 3

***Таблица 1.* Избранные геометрические параметры (Å) 3**

bond	length	bond	length
S2–C1	1.667 (2)	S3–C4	1.662 (2)
C1–N3	1.375 (2)	N7–C3	1.358 (3)
C1–N4	1.326 (2)	N7–C4	1.383 (2)
N3–C2	1.366 (2)	N6–C3	1.305 (2)
C2–N1	1.302 (2)	N5–C3	1.314 (2)
C2–N2	1.305 (3)	N8–C4	1.318 (2)

CONCLUSIONS

Crystal of bis[1-(diaminomethylene)-thiouron-1-ium] sulfate was obtained and characterized by X-ray analysis for the first time. Thus, the synthesis of 2-imino-4-thiobiuret carries out according to Scheme 3.



Scheme 3. The synthesis of 2-imino-4-thiobiuret
Схема 3. Синтез 2-имино-4-тиобиурета

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