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SYNTHESIS AND STRUCTURE OF PLATINUM (II) COMPLEXES WITH DECOMPOSITION PRODUCT OF DITHIODIETHYLAMINE β -MERCAPTOETHYLAMINE**G.I. Ajalova, Kh.I. Hasanov, A.N. Azizova, Sh.Q. Qasimov, K.K. Badalova**

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Abstract: The interaction of dithiodiethylamine (cystamine) (L^1) with Pt(II) in aqueous medium was studied and it showed that in aqueous solutions in an acidic medium, the disulfide bond L^1 was cleaved, followed by coordination of platinum to form β -mercaptoethylamine (mercamine, LH). Depending upon the reaction conditions, binuclear complexes of composition $\mu(S)[Pt_2(LH)_2Cl_4](I)$, $\mu(Cl)[Pt_2(LH)_2Cl_4](II)$ with bridging chlorine or sulfur atoms were formed. At 70°C, a compound with a bridged position of sulfur atoms (complex I), and at lower temperatures (30-50°) with a bridged position of chlorine atoms (complex II) were formed. X-ray structural analysis of the complex $[Pt_2(LH)_2Cl_4](I)$ was carried out. Crystals I are rhombic, with $20^\circ Ca = 17.282(1)$, $b = 9.986(1)$, $c = 8.0188(9)$ Å; $R = 0.029$. Molecule I is a binuclear complex in which platinum atoms are linked by a pair of bridging thiolate ligands ($-SCH_2-CH_2-MH_3^+$). The Pt_2S_2 metallocycle is bent along the sulfur-sulfur line, so that the dihedral angle between the coordination planes of platinum atoms is equal to 138°. The S-S distance, equal to 2.909(1) Å, is noticeably shorter than the doubled van der Waals radius of the sulfur atom (3.60 Å). The structure of the complexes was also confirmed by IR spectroscopy data.

Keywords: platinum, bidentate ligand, cystamine, disulfide bonds, mercamine, cis-, trans-structures, gauche conformation

DOI: 10.32737/2221-8688-2023-1-21-28**Introduction**

As is known, the cystamine has the ability to prevent or facilitate the course of the general radiation reaction of the body, which occurs under the action of large doses of x-rays and gamma rays. In this case, the disulfide bond is cleaved with the formation of β -mercaptoethylamine (mercamine) at the first stage [1,2].

The research into the interaction of cystamine $NH_2CH_2CH_2S-SCH_2CH_2NH_2$ (L^1) with palladium, mercury, silver, and copper compounds revealed that this also leads to the cleavage of the disulfide bond with the metal coordinating the formed deprotonated molecules of β -mercaptoethylamine $HSCH_2CH_2NH_2$ [3].

Information about complex compounds of platinum with cystamine was not found in the literature prior to our study. However, it is of particular interest to consider the data available in the literature on the complexes of palladium with β -mercaptoethylamine (LH).

It follows from the literature data that LH forms two types of compounds with palladium (II): the mononuclear complex PdL_2 and the trinuclear complex $[Pd_3L_4]Cl_2$. The PdL_2 compound was first synthesized by reacting stoichiometric amounts of $K_2[PdCl_4]$ with an alkaline solution $LH \cdot HCl$ [4]. The authors [5] studied the structure of this complex by IR spectroscopy using metal isotope substitution

($^{104}\text{Pd}/^{110}\text{Pd}$) and amino-groups (NH_2/ND_2) and proved that in the PdL_2 complex the PdN_2S_2 skeleton has a *cis*-configuration, as evidenced by the presence of two bands of stretching vibrations $\text{asv}(\text{PdN})$ (421, 309 cm^{-1}), such $\text{asv}(\text{PdS})$ (368 and 337 cm^{-1}).

Changing the ratio of the initial reagents leads to the formation of trinuclear palladium complexes: both homometallic $[\text{Pd}_3\text{L}_4]\text{C}_{12}$ [4] and heterometallic: $[\text{PdNi}_2\text{L}_4]\text{C}_{12}$ or $[\text{Pd}_2\text{NiL}_4]\text{C}_{12}$. During the interaction of the $[\text{Pd}_2\text{NiL}_4]\text{C}_{12}$ complex with the tetrachloromercurate anion in an aqueous solution, Ni is replaced by Hg to form the complex $[\text{Pd}_2\text{HgL}_4][\text{HgCl}_4]$ [6].

Our earlier studies [7] of the interaction of platinum salts with $\text{L1} \cdot 2\text{HCl}$ in alkaline medium (pH 10) showed that a compound is formed with the ratio $\text{Pt} : \text{L1} : \text{C1} = 3 : 4 : 2$, similar in composition to the compound obtained by interaction with β -mercaptoethylamine - $[\text{Pt}_3\text{L}_4]\text{C}_{12}$ [6]. However, as a result of X-ray diffraction studies, it was found that not a trinuclear, but a hexanuclear complex of the noncluster type is formed $[\text{Pt}_6\text{L}_8\text{C}_{14}]$ [7,8].

This work deals with the study of the interaction of platinum (II) with cystaminedihydrohalide in aqueous medium in the pH range 1 -7.

Experimental part

We used cystaminedihydrochloride (Fluka) without additional purification. $\text{H}_2[\text{PtCl}_4]$ was obtained by the method [9].

Synthesis of the $[\text{Pt}_2(\text{LH})_2\text{C}_{14}]$ complex (bridging sulfur atoms, I). To a filtered solution of 1.17 g (0.65 mmol) of $\text{H}_2[\text{PtCl}_4]$ in a mixture of 5 mL of water with 5 mL of concentrated HCl was added with stirring 0.78 g (0.65 mmol) of $\text{L1} \cdot 2\text{HCl}$ dissolved in 10 mL of water, while the color of the solution became pale red. When this solution was evaporated in a water bath at a temperature of 70-75°C, a precipitate was formed of a small volume, containing yellowish-red crystals, which were taken under a microscope and analyzed. The substance was slightly soluble in water and insoluble in alcohol, acetone, chloroform,

carbon tetrachloride, benzene, ether.

Synthesis of the complex $[\text{Pt}_2(\text{LH})_2\text{C}_{14}]$ (bridging chlorine atoms, II). A solution of 0.46 g (0.38 mmol) $\text{L1} \cdot 2\text{HCl}$ in 10 ml water with stirring was added to a filtered solution of 0.67 g (0.38 mmol) $\text{H}_2[\text{PtCl}_4]$ in a mixture of 5 ml H_2O with 5 ml concentrated HCl. The color of the solution changed from light red to yellow. After 5 min. at a temperature of 35 – 40 °C, a dark yellow precipitate precipitated from the solution. The precipitate was filtered off and dried first in air and then in vacuum to constant weight. Yield 0.93 g (48%). The substance is slightly soluble in water and insoluble in alcohol, acetone, chloroform, carbon tetrachloride, benzene, ether. Analytical data for complexes I and II are given in Table 1.

Table 1. Results of elemental analysis of the complexes I, II

Complex	Brutto-formula	Content (calculated/found), %			
		Pt	C1	S	N
I	$\text{C}_4\text{H}_{14}\text{N}_2\text{S}_2\text{Pt}_2\text{C}_{14}$	56.86/56.41	20.66/20.87	9.34/9.60	4.08/4.20
II	$\text{C}_4\text{H}_{14}\text{N}_2\text{S}_2\text{Pt}_2\text{C}_{14}$	56.86/56.63	20.66/20.57	9.34/9.51	4.08/4.31

The IR spectra of the starting substances and complexes were measured on Thermo-scientific, Nicoletis 10 and Bruker IFS-113V spectrometers in vaseline or suspension of fluorinated oils, as well as in the form of tablets with KBr in the range of 100-4000 cm^{-1} , in the solid state (suspension in vaseline or fluorinated oils, tablets with KBr and CsI).

X-ray photoelectron spectra (XES) (obtained on a Varian VIEE-15 spectrometer. The Cl_{2s} - 285.0 eV line was used as a standard. The reproducibility of the electron detachment energies was ± 0.1 eV.

X-ray diffraction data - unit cell parameters and intensities of 1619 reflections with $I > 2\sigma$ - were obtained on a Bruker X8

APEX automatic four-circle diffractometer equipped with a two-coordinate SDS detector at 273(2)K using molybdenum radiation and a graphite monochromator according to the standard method ($\lambda\text{MoK}\alpha$, graphite monochromator, $\theta/2\theta$ -scanning, 2θ max = 56°). The structure was solved by the heavy atom method and refined by the least squares method (LSM), first in the isotropic and then in the anisotropic approximation. In the difference

synthesis, all hydrogen atoms calculated geometrically were revealed. The final refinement of the least squares in the full-matrix anisotropic approximation for non-hydrogen atoms and in the isotropic approximation for hydrogen atoms was brought to $R=0.029$; $RW=0.044$ over 1551 reflections with $F_2 > 3\sigma$. The atomic coordinates are given in Table 1, 2, bond lengths and bond angles are given in Table 3.

Results and discussions

The study of the interaction of cystamine dihydrochloride with platinum showed that the

nature of the products formed depends on the reaction conditions.

Table 2. Coordinates of non-hydrogen atoms ($\times 10^5$) in complex I

Atoms	x	y	z
Pt(1)	16492(2)	17828(3)	15691(4)
C1(1)	0.12306	0.00451	0.01324
C1(2)	0.04669	0.24053	0.05361
S(1)	21332(5)	38109(10)	23615(14)
N(1)	5649(30)	53159(60)	26109(70)
C(1)	17819(30)	51079(50)	9429(70)
C(2)	12209(3)	60409(50)	18149(90)

Table 3. Bond lengths and bond angles in complex I

Bonds	d, Å	Angle	ω , grad
Pt(1)-C1(1)	2.353(1)	S(1)Pt(1)Cl(2))C1(2)	96.50(4)
Pt(1)-C1(2)	2.369(1)	S(1)Pt(1)S(1A)	79.31(4)
Pt(1)-S(1)	2.280(1)	S(1A)Pt(1)Cl(1)	93.45(4)
Pt(1)-S(1)	2.275(1)	C1(1)Pt(1)C1(2)	91.55(4)
S(1)-C(1)	1.826(5)	Pt(1)S(1)Pt(1A)	91.72(3)
C(1)-C(2)	1.515(8)	Pt(1)S(1)C(1)	109.4(2)
C(2)-N(1)	1.491(8)	Pt(1A)S(1)C(1)	108.4(2)
		S(1)C(1)C(2)	111.1(4)
		C(1)C(2)N(1)	112.6(4)

The structure of complex I was established by X-ray diffraction analysis (XRD). Crystals of I are rhombic, at 200 C $a = 17.282(1)$ Å, $b = 9.986(1)$, $c = 8.0188(9)$ Å; $V = 1383.0(3)$ Å³, $Z = 4$ sp. gr. Rsp. The molecule is located in a particular position on axis 2.

Molecule 1 (Fig.1) is a binuclear complex in which platinum atoms, each having two terminal chlorine atoms, are linked by a pair of bridging thiolate ligands $-\text{SCH}_2\text{CH}_2\text{NH}_3^+$. Axis 2 passes through the middle of the metal cycle, perpendicular to its root-mean-square plane.

Platinum atoms have square-planar coordination. The Pt_2S_2 metallocycle is bent along the sulfur-sulfur line, so that the dihedral angle between the coordination planes of platinum atoms is 138° . The angle Pt(1)S(1)Pt(1A) is 91.720° and the angle S(1)Pt(1)S(1A) is 79.310° . The Pt-Pt distance in the cycle ($3.270(1)$ Å) actually coincides with the sum of the van der Waals radii (3.26 Å), while the S-S distance ($2.909(1)$ Å) is noticeably shorter than twice the van der Waals radius of the atom sulfur (3.60 Å) [10].

However, this last distance is significantly [11]. longer than in the cystamine molecule. (2.06 Å)

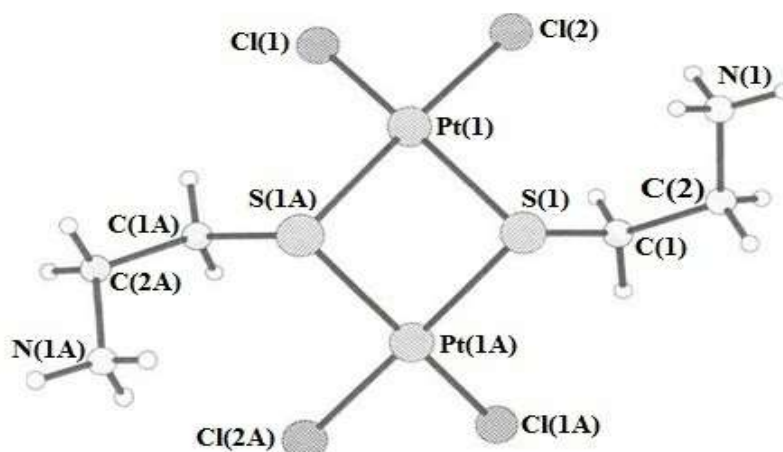
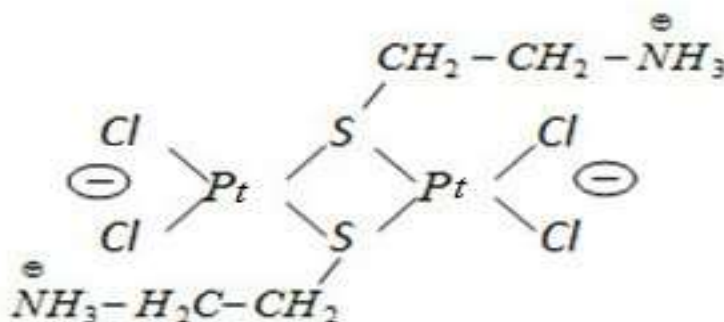


Fig.1. Molecular structure and numbering of atoms of the complex 1.

Thus, X-ray diffraction studies revealed that under the conditions of a chemical reaction, the sulfur-sulfur bond of the initial cystamine molecule is broken, followed by coordination of the resulting β -mercaptoethylamine protonated

at the amino group and deprotonated at the sulfhydryl group.

Schematically, the structure of complex I can be represented as follows:



Positive charges are localized on nitrogen atoms and negative charges on chlorine atoms. Both Pt-S bonds (2.280 and 2.275 Å) are aligned but noticeably shorter than in other platinum complexes, in which the metal atoms are linked by a pair of bridging thiolate ligands (2.282–2.454 Å, the average value is 2.359 Å [11–13]). Such a shortening of the Pt-S distances in complex I is apparently due to its zwitterionic nature.

The length of the Pt-Cl bond in various platinum complexes can vary within fairly wide limits, in particular, depending on the nature of the *trans* ligand. For those complexes in which a ligand with a weak π -acceptor ability is located in the *trans* position to the Pt-Cl bond, the length of the Pt-Cl bond is 2.30–2.34 Å [14,15]. If the ligand is capable of exhibiting a

significant *trans* effect (σ -bonded carbon atom, carbene ligand), then the Pt-Cl bond lengthens to 2.35–2.45 Å [16, 17]. In complex I, the Pt-Cl(1) and Pt-Cl(2) bond lengths (2.353 and 2.369 Å) are close to the lower limit of values characteristic of the second group of complexes with the Pt-Cl bond. At the same time, in the binuclear $[\text{Pt}_2\text{Cl}_6]^{2-}$ dianion, the bond lengths of platinum with terminal chlorine atoms are 2.25–2.27 Å [18,19], i.e. shorter than in the complex I studied by us than in the platinum complexes discussed above and belonging to the first group. A small but significant (16σ) difference in the Pt-Cl(1) and Pt-Cl(2) bond lengths in complex I should be emphasized. Apparently, the proposed above color-ion scheme of the structure of the complex does not fully reflect the nature of the delocalization of the negative

charge in it and the degree of participation of two chlorine atoms in this delocalization.

Comparison of the interatomic distances in coordinated mercamine and mercamine hydrochloride [20] shows that, upon platinum coordination, the lengths of the C–C and C–N bonds in the ligand practically do not change; however, the C–S bond shortens from 1.86 Å in free mercamine hydrochloride to 1.826 Å in complex I, while the SC(1)C(2) angle also decreases from 112.6° in the free ligand to 111.1° in complex I. As in the free ligand, β -mercaptoethylamine in complex I has a gauche conformation with an angle rotation of 55° (the angle between the SCC and CCN planes) around the C–C bond.

And, finally, in the crystal, I molecules form a three-dimensional network of intermolecular hydrogen bonds Cl(1)⋯H(N¹)-

N¹, C1(2)⋯H(N¹)-N¹ (distances C1⋯H 2.41, 2.46 Å; C1⋯N 3.196, 3.238 Å, respectively, transformation i [(-x)(-0.5 + y)(0.5 - z)]; transformation j [(x)(0.5 - y)(-0.5 - z)]). The third hydrogen atom does not participate in the system of hydrogen bonds. There are no grounds to conclude about the existence of an intramolecular interaction MH₃⁺⋯S in complex I.

The IR spectral data (Table 4) are in good agreement with the XRD results, according to which the central Pt₂S₂ metallocycle in complex I is non-planar (bent along the sulfur-sulfur line) and has local C_{2v} symmetry. The most characteristic in the spectra of Pt chloride complexes are the frequencies of stretching vibrations ν (PtCl), which give intense bands in the region of 300–380 cm⁻¹ for vibrations of Pt–Cl bonds (types A1 + B1 + B2).

Table 4. Main vibrational frequencies (cm⁻¹) in the IR spectra of the complexes I, II

Assignment	I	II
	Cl	Cl
$\nu(\text{NH}_3^+)$ $\nu(\text{NH}_2)$	3200-2000	3200-2000
$\delta(\text{NH}_3^+)$	1582	1570
$\delta(\text{NH}_2)$	1559	1561
ν (PtX _K)	376	359
	364	
	330	
ν (PtX _M)		308
		287
ν (PtS _K)		380
ν (PtS _M)	285	
	271	

Indeed, in the IR spectrum of complex I, three ν (PtCl) bands with frequencies of 376, 364, and 330 cm⁻¹ are observed, which is consistent with the nonplanar structure of the metallocycle in this complex. Stretching vibrations ν (PtS) correspond to bands at 285 and 271 cm⁻¹. The protonated amino group is characterized by broad absorption in the region of 2000–3200 cm⁻¹ and bands of bending vibrations ν (NH₃⁺) near 1582 and 1559 cm⁻¹.

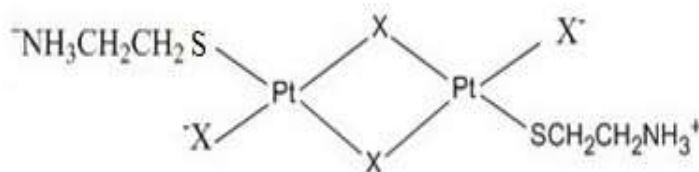
XPS data are also consistent with the presence in complex I of a protonated NH₃⁺ group ($E_b(\text{N}_{1s}) = 401.4$ eV), the same as in the

initial cystamine hydrochloride ($E_b(\text{N}_{1s}) = 401.4$ eV), and a sulfur atom, platinum coordinated ($E_b(\text{S}_{2p}) = 163.4$ eV).

The IR spectrum of complex II differs significantly from the spectrum of complex I. Besides, it contains three bands ν (PtCl) at 359, 308 and 287 cm⁻¹. The reduced values of the last two frequencies in the spectra of II suggest that they refer to stretching vibrations ν (PtClM) with the participation of bridging rather than terminal halogen atoms. The frequency 359 cm⁻¹ lies in the region characteristic of vibrations of the terminal bonds ν (PtClK). The presence of

two bands ν (PtXM) and one band ν (PtClK) is characteristic of binuclear complexes of the $[\text{Pt}_2\text{L}_2\text{Cl}_4]$ type with halide bridges and trans

position L [20,21]. This suggests the following structure of complex II:



The stretching vibrations of the Pt-S bonds in the IR spectra of complex II have a frequency of 390 cm^{-1} . The presence of one ν (PtS) band is consistent with the trans structure of these complexes. The ν (PtS) vibrations in the case of complex II have higher frequencies as compared to ν (PtS) in the spectrum of I, which is defined by the terminal rather than bridging nature of these bonds. The protonated amino group in complex II has the same frequencies as in complex I.

Thus, the study of the interaction of cystamine dihydrochloride with platinum in aqueous solutions in an acidic medium showed that in all cases the formation of complexes with

the product of cystamine cleavage at the disulfide bond - (β -mercaptoethylamine (mercamine) (LH)) occurs.

In acidic medium, $[\text{Pt}_2(\text{LH})_2\text{Cl}_4]$ complexes are formed with a protonated amino group and the ligand is coordinated by a platinum atom through a sulfur atom. In this case, depending upon the reaction temperature, it is possible to synthesize complexes of the same composition but different structures: at 70°C , a compound with a bridging position of sulfur atoms is formed (complex I) at lower (500) with bridging position of chlorine atoms (complex II).

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DİTİODİETİLAMİNİN PARÇALANMA MƏHSULU - β -MERKAPTOETİLAMİNİLƏ PLATİNİN (II) KOMPLEKSLƏRİNİN SİNTEZİ VƏ QURULUŞU

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Xülasə: Ditioldietilaminin (sistamin) (L^1) su mühitində platinin birləşmələri ilə qarşılıqlı təsiri öyrənilmiş və turş mühitdə sulu məhlullarda L^1 –in disulfid rabitəsinin qırılması nəticəsində yaranan β -merkaptotetilaminin (merkamin, LH) platinlə koordinasiyasının baş verdiyi göstərilmişdir. Reaksiyanın getmə şəraitindən asılı olaraq xlor və ya kükürd atomlarının körpü rolunu oynadığı $\mu(S)[Pt_2(LH)_2Cl_4](I)$, $\mu(Cl)[Pt_2(LH)_2Cl_4](II)$ tərkibli iki nüvəli komplekslər əmələ gəlir. Reaksiya $70^\circ C$ aparıldıqda kükürd körpülü (kompleks I), nisbətən aşağı $30-50^\circ C$ temperaturda isə xlor körpülü (kompleks II) birləşmə alınır. Kompleksin $[Pt_2(LH)_2Cl_4](I)$ quruluşu rentgen-quruluş analizi üsulu ilə öyrənilmişdir. Kompleksin I kristalları $20^\circ C$ -də rombikdir, $a = 17.282(1)$, $b = 9.986(1)$, $c = 8.0188(9)$; $R = 0.029$. İkinüvəli kompleksdə (I) platin atomları biri-birilə bir cüt körpü tiolat ($-SH_2-CH_2-NH_3^+$) ligandları ilə birləşdirilir. Kompleksdə Pt_2S_2 metal tsikli kükürd-kükürd xətti boyunca əyilir, platin atomlarının koordinasiya müstəviləri arasındakı ikiüzlü bucaq 138° -yə bərabərdir. S-S məsafəsi $2.909(1)$ Å bərabər olub, kükürd atomunun (3.60 Å) van-der-Vaals radiusunun iki qatından xeyli qısadır. Komplekslərin quruluşu İQ spektroskopiyasının məlumatları ilə də təsdiqlənmişdir.

Açar sözlər: platin, sistamin, merkamin, disulfid rabitəsi, ligand, iki nüvəli komplekslər

СИНТЕЗ И СТРУКТУРА КОМПЛЕКСОВ ПЛАТИНЫ(II) С ПРОДУКТОМ РАСЩЕПЛЕНИЯ ДИТИОДИЭТИЛАМИНА- β -МЕРКАПТОЭТИЛАМИНОМ

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Аннотация: Изучено взаимодействие дитиодиэтиламина (цистамина) (L^1) с Pt(II) в водных средах и показано, что в водных растворах в кислой среде происходит расщепление дисульфидной связи L^1 с последующей координацией платины образующегося β -merkaptotetilamina (merkamina, LH). В зависимости от условий реакции образуются биядерные комплексы состава $\mu(S)[Pt_2(LH)_2Cl_4](I)$, $\mu(Cl)[Pt_2(LH)_2Cl_4](II)$ с мостиковыми атомами хлора или серы. При $70^\circ C$ образуется соединение с мостиковым положением атомов серы (комплекс I), а при более низких температурах ($30-50^\circ$) - с мостиковым положением атомов хлора (комплекс II). Проведен рентгеноструктурный анализ комплекса $[Pt_2(LH)_2Cl_4](I)$. Кристаллы I ромбические, при $20^\circ C$ $a = 17.282(1)$, $b = 9.986(1)$, $c = 8.0188(9)$ Å; $R = 0.029$. Молекула I представляет собой биядерный комплекс, в котором атомы платина объединены парой мостиковых тиолатных лигандов ($-SCH_2-CH_2-NH_3^+$). Металлоцикл Pt_2S_2 перегнут по линии сера-сера, так что двугранный угол между координационными плоскостями атомов платины равен 138° . Расстояние S-S, равное $2.909(1)$ Å, заметно короче удвоенного ван-дер-ваальсова радиуса атома серы (3.60 Å). Строение комплексов также подтверждено данными ИК-спектроскопии.

Ключевые слова: платина, бидентатный лиганд, цистамин, дисульфидная связь, меркамин, цис-, транс- строение