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Synthesis and structure of platinum (II) complexes with dithiodiethylamine

Seljan Nurullayeva, Ziya Babayev
Azerbaijan Medical University, Bakikhanov st., 23, Baku, Azerbaijan

Abstract— **The interaction of dithiodiethylamine (cystamine) (L1) with platinum compounds in non-aqueous and aqueous media has been studied. It was shown that in aqueous solutions the disulfide bond L1 cleaves with the subsequent coordination of platinum of the resulting β-mercaptoethylamine (mercamine, LH). Depending on the reaction conditions, binuclear complexes of the composition [Pt2(LH)2C14] with bridging chlorine or sulfur atoms or [Pt2L2C12] with bridging chlorine atoms are formed. An X-ray structural analysis of the complex [Pt2(LH)2C14] (I) was carried out. Crystals of I are rhombic, at 20°C** a **= 17.283(1),** b **= 9.987(1),** c **= 8.0187(9)** Å; **R = 0.030. Molecule I is a binuclear complex in which platinum atoms are linked by a pair of bridging thiolate ligands (-SCH2-CH2-MH3+). The Pt2S2 metal cycle is bent along the sulfur-sulfur line, so that the dihedral angle between the coordination planes of platinum atoms is 138 °. The S-S distance, equal to 2.909 (1) Å, is noticeably shorter than the double van der Waals radius of the sulfur atom (3.60 Å). Carrying out the reaction in benzene makes it possible to obtain the complex (L1H2)[PtX4] (X = C1, Br) with the retention of the sulfur-sulfur bond in the ligand. The structure of the complexes is confirmed by the data of IR spectroscopy.**

Keywords— dithiodiethylamine, platinum compounds, cystamine, Synthesis and structure.

I. Introduction

IT is known that cystamine has the ability to prevent or facilitate the course of the general radiation reaction of the body, which occurs when exposed to high doses of X-rays and gamma rays. In this case, the cleavage of the disulfide bond occurs with the formation of β-mercaptoethylamine (mercamine) at the first stage [1,2].

The study of the interaction of cystamine NH2CH2CH2S-SCH2CH2NH2 (L1) with compounds of palladium, mercury, silver, copper showed that cleavage of the disulfide bond with the metal coordination of the formed deprotonated β-mercaptoethylamine HSCH2CH2NH2 molecules also occurs [3, 4]. No information on the complex compounds of platinum with cystamine has been found in the literature before our study. However, it is of some interest to consider the literature data on palladium complexes with (β-mercaptoethylamine (LH)).

It follows from the literature data that LH forms two types of compounds with palladium (II): the mononuclear complex PdL2 and the tricyclic complex [Pd3L4]Cl2. The PdL2 compound was first synthesized by the interaction of stoichiometric amounts of K2[PdCl4] with an alkaline solution of LH • HC1 [5]. The authors of [6] investigated the structure of this complex by IR spectroscopy using isotopic substitution for the metal (104Pd/1I0Pd) and for the amino group (NH2/ND2) and proved that the PdN2S2 skeleton in the PdL2 complex has a cis-configuration, as evidenced by the presence of two stretching vibration bands of both ν(PdN) (421, 309 см -1), and ν (PdS) (368 и 337 см -1).

A change in the ratio of the starting reagents leads to the formation of trinuclear palladium complexes: both homometallic [Pd3L4]C12 [5] and heterometallic: [Pd2NiL4]C12 or [Pd2NiL4]C12. When the [PdNi2L4|C12 complex interacts with the tetrachloromercurate anion in an aqueous solution, Ni is replaced by Hg with the formation of the [Pd2HgL4][HgC14] complex [7].

Our earlier studies of the interaction of platinum salts with L1 • 2HC1 in alkaline media (pH 10) showed that a compound is formed with the ratio Pt : L1 : C1 = 3 : 4 : 2, similar in composition to the compound, obtained by interaction with β-mercaptoethylamine - [Pt3L4]C12 [6]. However, as a result of an X-ray structural study, it was found

that not a trinuclear, but a hexanuclear complex of the non-cluster type [Pt6 L8C14] is formed [8, 9].

This work is devoted to the study of the interaction of platinum (II) salts with cystamine dihydrohalide in non-aqueous and aqueous media in the pH range 1-7.

II. Units

We used cystamine dihydrochloride (Fluka) without additional purification. K2[PtC14] , H2 [PtCl4] , K2[PtBr4], H2[PtBr4] ,(C6H5CN) 2PtX2 (X = C1, Br) were obtained by the method of [10].

Synthesis of the complex [Pt2(LH)2C14] (bridging sulfur atoms, I). To a filtered solution of 1.17 g (0.65 mmol) H2[PtCl4] in a mixture of 5 ml of water with 5 ml of concentrated HCl was added with stirring 1.48 g (0.65 mmol) of L1 • 2HC1, dissolved in 10 ml of water, the color of the solution became pale red. Evaporation of this solution in a water bath at a temperature of 70-75 ° C to a small volume resulted in a precipitate containing yellowish-red crystals, which were selected under a microscope and analyzed. The substance is slightly soluble in water and insoluble in alcohol, acetone, chloroform, carbon tetrachloride, benzene, ether.

Synthesis of the complex [Pt2(LH) 2C14] (bridging chlorine atoms, II). To a filtered solution of 0.67 g (0.38 mmol) H2[PtCl4] in a mixture of 5 ml of H2O with 5 ml of concentrated HCl, a solution of 0.86 g (0.38 mmol) of L1•2HC1 in 10 ml of water was added with stirring. In this case, 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 formed from the solution. The precipitate was filtered off and dried, first in air, then in vacuum until constant weight. Yield 0.93 g (48%). The substance is slightly soluble in water and insoluble in alcohol, acetone, chloroform, carbon tetrachloride, benzene, ether.

Synthesis of the complex [Pt2(LH)2Br4] (IIa). To a solution of 0.37 g (1.40 mmol) H2[PtBr4] in a mixture of 5 ml of H2O with 10 ml of concentrated HBr, a solution of 0.32 g (1.40 mmol) of L1 • 2HBr in 10 ml of water was added with stirring. After 10-15 minutes at a temperature of 45-50 ° C, a light cherry-colored precipitate formed from the solution. The precipitate was filtered off and dried first in air, then in vacuum until constant weight. Yield 0.36 g (44%). The substance is insoluble in alcohol, chloroform, carbon tetrachloride, benzene, ether.

Synthesis of the [Pt2L2C12] complex (III). Method 1. A solution of 0.39 g (1.74 mmol) L1• 2HC1 in 10 ml of water was added to a filtered solution of 0.57 g (1.74 mmol) K2[PtC14] in 10 ml of water. While stirring the solution, a greenish-yellow precipitate formed. The reaction mixture was heated to 50-60 ° C and cooled to room temperature. Then the precipitate was filtered off, washed with water, alcohol and ether. They were dried first in air, then in vacuum to constant weight. Yield 0.33 g (45%).

Method 2. Compound II, when washed with water on a filter, changed its color and turned from dark yellow to greenish yellow. The solid product thus obtained was washed with alcohol, ether, and dried to constant weight.

Method 3. Complex V (see below) was heated in water for 40 minutes at a temperature of 50-55 ° C. This precipitated a greenish-yellow precipitate. The precipitate was filtered off and dried to constant weight.

Method 4. Stirring a solution of 0.58 g (1.74 mmol) K2[PtC14] in 10 ml of water and 0.39 g (3.48 mmol) of mercamine gives a greenish-yellow precipitate. The precipitate was filtered off and dried to constant weight, first in air and then in vacuum.

The identity of the structure of the complexes obtained by methods 1-4 was proved using IR spectroscopy. The substance is insoluble in water, alcohol, acetone, chloroform, carbon tetrachloride, benzene, ether.

[PtL2Br2] was obtained according to a procedure similar to that used for the synthesis of [Pt2L2Cl2] (method 1). The yield is 43%.

Synthesis of the complex

[Pt2(LH)2{S(CH2CH2COOH)2}2C12]C12 (IV).

A suspension in 20 ml of benzene was prepared from 0.62 g (1.21 mmol) of complex I. 0.37 g (2.42 mmol) of thiodipropionic acid S(CH2CH2 COOH)2 in the form of a powder was added to the suspension with stirring on a magnetic stirrer. The reaction mixture was stirred for an hour and a half at room temperature and then heated at 40–45 ° C for 10 min. In this case, a yellowish precipitate formed, which was filtered off, washed first with benzene and then with ether. Dry in air, then in vacuum to constant weight. Yield 0.87 g (89%). The substance is slightly soluble in alcohol, insoluble in chloroform, carbon tetrachloride, benzene, ether, acetone. When the complex is dissolved in water, a yellow-orange precipitate is formed, which, after drying to constant weight, is identical in composition and IR spectrum to III.

Synthesis of the complex (L1H2)[PtX4] (V). To a filtered solution of 0.22 g (0.58 mmol) (C6H5CN)2PtC12 in 20 ml of benzene, 0.13 g (0.58 mmol) of solid L1• 2HC1 powder was added with stirring. The solution was stirred first at room temperature for 2 h, then at 40–45 ° C for about 30 min. When the solution was cooled to room temperature, a precipitate formed, which was filtered off, washed with benzene, and then with ether. They were dried first in air, then in vacuum to constant weight. Yield 0.19 g (81%). The substance is insoluble in acetone, benzene, chloroform, carbon tetrachloride, ether. It dissolves in water with decomposition.

Synthesis of the complex (L1H2)[PtCl2Br2] (VI). To a filtered solution of 0.29 g (0.62 mmol) (C6H5CN)2PtBr2 in 20 ml of benzene was added 0.12 g (0.62 mmol) of L1 • 2HC1 powder. The reaction mixture was stirred for 3 h at room temperature, heated for 45 min to 45-50 ° C, then heating was stopped and stirring was continued for 12 h until a precipitate formed, which was filtered off, washed with benzene, then with ether, and dried in sleep. Started in air, then in vacuum until constant weight. Yield 0.23 g (78%). The substance is insoluble in acetone, alcohol, benzene, chloroform, carbon tetrachloride, ether. It dissolves in water with decomposition. Analytical data of complexes I-VI are given in table. 1.

Complex	Gross formula	Content (calculated / found), %			
		Pt	C1(Br)	S	N
I	$C_4H_{14}N_2S_2Pt_2C1_4$	56.86/56.41	20.66/20.87	9.34/9.60	4.08/4.20
II	$C_4H_{14}N_2S_2Pt_2C1_4$	56.86/56.63	20.66/20.57	9.34/9.51	4.08/4.31
IIa	$C_4H_{14}N_2S_2Pt_2Br_4$	45.16/45.39	36.99/36.58	7.42/7.30	3.24/3.17
III method 1	$C_4H_{12}N_2S_2Pt_2C1_2$	63.62/63.84	12.91/12.77	10.45/10.26	4.56/4.42
method 2		63.62/63.92	12.91/12.81	10.45/10.36	4.56/4.61
method 3		63.62/63.86	12.91/12.69	10.45/10.66	4.56/4.48
method 4		63.62/63.72	12.91/12.76	10.45/10.71	4.56/4.63
IV	$C_{16}H_{34}N_2S_4O_8Pt_2C1_4$	37.44/37.30	13.54/13.85	12.30/12.52	2.68/2.46
V	$C_4H_{14}N_2S_2PtC1_4$	39.77/39.44	28.78/28.54	13.07/13.39	5.70/5.95
VI	$C_4H,_4N_2S_2PtC1_2Br_2$	33.63/33.65	12.22/12.53	11.05/13.25	4.82/4.50

IR spectra of the starting materials and complexes were measured on Thetmoscientific, Nicoletis 10 and Bruker IFS-113V spectrometers in vaseline or in a suspension of fluorinated oils, as well as in the form of tablets with KBr in the range of 50-4000 cm-1, in the solid state (suspensions in vaseline or fluorinated oils, tablets with KBr and CsI).

X-ray photoelectron spectra (XPS) (obtained on a Varian VIEE-15 spectrometer. The ClS line - 285.0 eV was used as a standard; the reproducibility of the electron detachment energies was ± 0.1 eV.

X-ray structural data - unit cell parameters and intensities of 1619 reflections with $I > 2\sigma$ - were obtained on an automatic four-circle diffractometer Bruker X8 APEX, equipped with a two-axis SSD - detector, at 273 (2) K using molybdenum radiation and a graphite monochromator according to the standard technique (λMoKα, graphite monochromator, θ / 2θ-scanning, 2θ max = 56°). The structure was solved by the heavy atom method, refined by the least squares method (LSM), first in the isotropic and then in the anisotropic approximation. In difference synthesis, all hydrogen atoms calculated geometrically are revealed. The final refinement of least squares in the full-matrix anisotropic approximation for non-hydrogen atoms and in the isotropic approximation for hydrogen atoms was brought to R= 0.030; RW= 0.045 по 1550 отражениям с $F2 > 3\sigma$. The coordinates of the atoms are given in table. 2, bond lengths and bond angles are given in table 3.

III. RESULTS AND ITS DISCUSSION

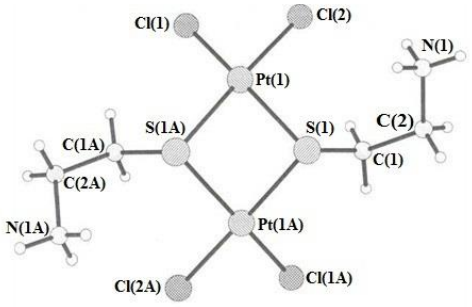
The study of the interaction of cystamine dihydrochloride with various platinum compounds showed that the nature of the resulting products depends on the reaction conditions

Table 2. Coordinates of non-hydrogen atoms (x105) in complex

Atoms	x	y	z
Pt(1)	16493(2)	17829(3)	15692(4)
C1(1)	0.12307	0.00452	0.01325
C1(2)	0.04670	0.24054	0.05362
S(1)	21333(5)	38110(10)	23616(14)
N(1)	5650(30)	53160(60)	26110(70)
C(1)	17820(30)	51080(50)	9430(70)
C(2)	12210(3)	60410(50)	18150(90)

Table 3. Bond lengths and bond angles in complex I

Connection	d ,Å	angle	ω, degree
Pt(1)-C1(1)	2.354(1)	S(1)Pt(1)Cl(2))C1(2)	96.51(4)
Pt(1)-C1(2)	2.370(1)	S(1)Pt(1)S (1A)	79.32(4)
Pt(1)-S(1)	2.281(1)	S(1A)Pt(1)Cl(1) A)Pc1(1)C1(1)	93.46(4)
Pt(1)-S(1 A)	2.276(1)	C1(1)Pt(1)C1 (2)	91.56(4)
S(1)-C(1)	1.827(5)	Pt(1)S(1)Pd (1A)	91.73(3)
C(1)-C(2)	1.516(8)	Pt(1)S(1)C (1)	109.5(2)
C(2)-N(1)	1.490(8)	Pt(1A)S(1)C (1)	108.5(2)
		S(1)C(1)C(2)	111.2(4) 11.2(4)
		C(1)C(2)N(1)	112.7(4)



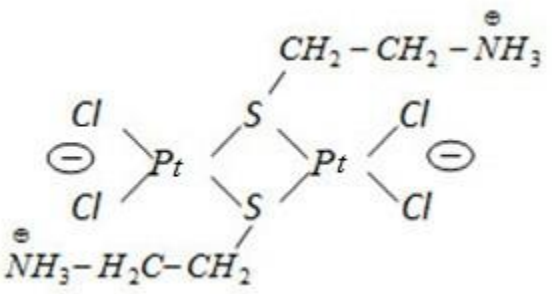
Molecular structure and numbering of atoms of complex 1.

The structure of complex I was established by X-ray structural analysis (XRD). Crystals of I are rhombic, at 200 C a =17.283(1) ,b= 9. 987(1), c = 8.0187(9) Å; V = 1384.0(3) Å3, Z= 4 sp.gr. Rssp. The molecule is located in a particular position on axis 2.

Molecule 1 (figure) is a binuclear complex in which platinum atoms, each having two terminal chlorine atoms, are united by a pair of bridging thiolate ligands – SCH2CH2NH+3.. Axis 2 passes through the middle of the metal cycle, perpendicular to its rms plane. Platinum atoms have a square-planar coordination. The Pt2S2 metal cycle is bent along the sulfur-sulfur line, so that the dihedral the angle between the coordination planes of platinum atoms is 1380; the Pt(1)S(1)Pt(1A) coal is 91.730, and the S(1)Pt(1)S(1A) angle is 79.320. The Pt-Pt distance in the cycle (3.271 (1) Å) actually coincides with the sum of van der Waals radii (3.26 Å), while the S-S distance (2.909 (1) Å) is noticeably shorter than the doubled van der Waals radius of the sulfur atom (3.60 Å) [11] ... However, this last distance is significantly longer than in the cystamine molecule (2.06 Å) [12]. Thus, X-ray

diffraction studies have established that, under the conditions of a chemical reaction, the sulfur-sulfur bond of the initial cystamine molecule is broken, followed by coordination of the formed β-mercaptoethylamine protonated at the amino group and deprotonated at the sulfhydryl group.

The structure of complex I can be schematically represented as follows:



Positive charges are localized on nitrogen atoms and negative charges on chlorine atoms. Both Pt-S bonds (2.281 and 2.276 Å) are aligned but noticeably shorter than in other platinum complexes, in which metal atoms are linked by a pair of bridging thiolate ligands (2.282-2.454 Å, average value 2.359 Å [12-15]). Such a reduction in the Pt-S distances in complex I, apparently, is due to its zwitterionic nature.

The Pt-C1 bond length in various platinum complexes can vary over a fairly wide range, 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-C1 bond, the Pt-Cl bond length is 2.30-2.34 Å [16-19]. If the ligand is capable of exhibiting a significant trans effect (σ-bonded carbon atom, carbene ligand), then the Pt-Cl bond is extended to 2.35-2.45 Å [20-23]. In complex I, the lengths of Pt-C1 (1) and Pt-C1 (2) bonds (2.354 and 2.370 Å) are close to the lower limit of values characteristic of the second group of complexes with a Pt-C1 bond. At the same time, in the [Pt2C16]2- binuclear dianion, the bond lengths of platinum with terminal chlorine atoms are 2. 25–2.27 Å [24–25]; shorter than in the studied complex I and than in the platinum complexes discussed above and belonging to the first group. A small but significant (16σ) difference in the lengths of the Pt-Cl (l) and Pt-Cl (2) bonds in complex I. A comparison of the bond lengths of Pt-Cl in the studied complex I with the data available in the literature [16-26] indicates , that, apparently, the above-proposed zwitterion 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 interatomic distances in coordinated mercamine and mercamine hydrochloride [27] shows that, upon coordination of platinum, the C – C and C – N bond lengths in the ligand practically do not change, but the C – S bond shortens from 1.86 Å in free mercamine hydrochloride to 1.827 Å in complex 1, while the SC (1) C (2) angle also decreases from 113.4 ° in the free ligand to 111.2 ° in complex I. As in the free ligand, in complex I, β-mercaptoethylamine has a gauche conformation with an angle rotation of 55 ° (angle between the planes SCC and CCN) around the C-C link.

And, finally, in the crystal molecules I form a three-dimensional network of intermolecular hydrogen bonds Cl(1)···H(Ni1)-Ni1 , C1(2) ···H(Ni1)- Ni1 (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 for the conclusion about the existence of intramolecular interaction MH+3··· S in complex I.

The IR spectral data (Table 4) are in good agreement with the results of X-ray diffraction analysis, according to which the central metallocycle Pt2S2 in complex I is non-planar (bent along the sulfur-sulfur line) and has a local C2v symmetry. The most characteristic in the spectra of chloride complexes Pt are the frequencies of stretching vibrations ν (PtC1), which give intense bands in the region of 300-380 cm-1. For vibrations of bonds Pt-C1 (types A1+B1+B2).

Table 4. Basic vibrational frequencies (cm-1) in the IR spectra of complexes I-V

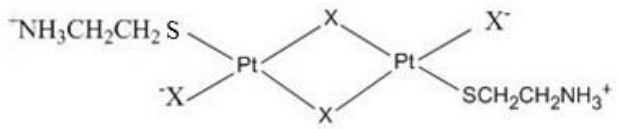
Assignment	I	II		III		IV	V	
	Cl	Cl	Br	Cl	Br	Cl	Cl	Cl,Br
ν (NH_3^+)	} 3200-	3200-	3200-	3296	3282	3200-	3200-	3200-
ν (NH_2)	} 2000	2000	2000	3191	3184	2000	2000	2000
ν (C=O)				3118	3114	1695		
δ(NH_3^+)	1583	1570	1567	1569	1564	1582	1603	1603
δ(NH_2)	1561	1561				1565	1592	1592
ν (PtX_K)	378						327	301
	366	361	250					252
	332							
ν (PtX_M)		310	205	268	202	286		
		289	188	260	197 .	270		
ν (PtS_K)		382	392	386	385	395		
				381	379	379		
						353		
						336		
ν (PtS_M)	287							
	273							
ν (PtN)				338	332			
				327	324			

Indeed, the IR spectrum of complex 1 exhibits three ν (PtCl) bands at frequencies of 378, 366, and 332 cm-1, which is consistent with the nonplanar structure of the metal cycle in this complex. Stretching vibrations ν (PtS) correspond to

bands at 287 and 273 cm-1. The protonated amino group is characterized by broad absorption in the range of 2000-3200 cm-1 and bands of bending vibrations ν (NH +3) at about 1583 and 1561 cm-1.

The XPS data also agree with the presence of a protonated NH+3 group in complex I (Есв(N1s) = 401.4 eV), the same as in the initial cystamine hydrochloride (Есв(N1s) = 401.4 eV), and a sulfur atom, coordinated by platinum (Есв (S2p) = 163.4 eV).

The IR spectrum of complex II differs significantly from the spectrum of complex I. It also exhibits three ν (PtCl) bands at 361, 310, and 289 cm -1, which are shifted when Cl is replaced by Br to 250, 205, and 188 cm-1 in the spectrum of complex IIa. The reduced values of the last two frequencies in the spectra II and IIa suggest that they refer to stretching vibrations ν (PtXM) with the participation of not terminal, but bridging halogen atoms. The frequency of 361 cm-1 lies in the region characteristic of the vibrations of terminal bonds ν (PtClK). The presence of two ν (PtXM) bands and one ν (PtClK) band is characteristic of binuclear complexes of the [Pt2L2X4] (X = C1, Br) type with halide bridges and the trans arrangement of L [28, 29]. This suggests the following structure of complex II:



Stretching vibrations of Pt-S bonds in the IR spectra of complexes II and IIa have frequencies of 392 and 382 cm -1, respectively. The presence of one ν (PtS) band is consistent with the trans structure of these complexes. Vibrations ν (PtS) in the case of complexes II and IIa have higher frequencies compared to ν (PtS) in spectrum I, which is determined by the terminal rather than bridging character of these bonds. The protonated amino group in complex II has the same frequencies as in complex I.

When complexes II and IIa are treated with water, the amino group is deprotonated and the chelate ring is closed with the formation of a Pt-N bond and the displacement of the terminal chlorine atom from the platinum coordination sphere. In this case, complexes III of the composition [Pt2L2X2] are formed.

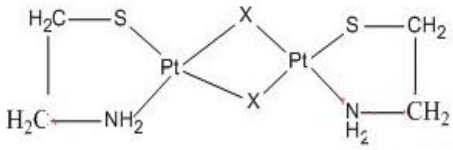
In the low-frequency IR spectrum of complex III (X = C1), a strong broad doublet band with maxima at 268 and 260 cm-1 is observed. In the spectrum of complex III (X = Br), a band similar in contour and intensity appears instead with maxima at 202 and 197 cm-1. The frequency shift upon replacing the halogen indicates that these bands are due to stretching vibrations ν (PtX), and the lower value of these frequencies compared to the usual values of ν (PtXK) allows us to attribute them to the vibrations of the bridging PtXPt groups. Based on this, it can be assumed that complex III has a binuclear structure with bridging halogen atoms and a flat central Pt2X2 fragment.

Indeed, in the case of a planar structure of the central site of the complex (local symmetry D2h), two ν (PtX) bands of B2u and B3u symmetry types should be observed in the IR spectrum. It was shown earlier [30] that the splitting between them depends on the intracyclic angle and for Pt complexes usually does not exceed 10–15 cm – 1. For example, in the π-allyl complex [(η3-Allyl)PtCl]2, these frequencies are 254 and 243 cm-1 [30].

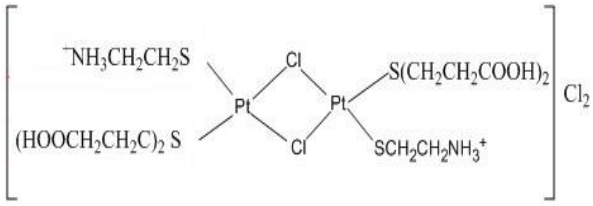
The bands at 386 and 381 cm - 1 in the IR spectrum of III (X = C1) are assigned to ν (PtS), since they do not shift when C1 is replaced by Br and are close to the frequencies ν (PtS) of the terminal PtS bonds in complex II. The bands at 338 and 327 cm-1 can be attributed to the ν (PtN) vibrations. The presence of two ν (PtS) and two ν (PtN) bands in the spectrum is consistent with the cis arrangement of donor ligand atoms (C2v symmetry). Thus, during the hydrolysis of complex II, a change in the trans-configuration of its skeleton occurs, and the resulting complex III has a cis-structure of the coordination unit:

The amino group coordinated with platinum has frequencies ν (NH2) 3296, 3191, and 3118 cm-1. These XPS are consistent with the presence of nitrogen atoms (Eb (N1s) = 400.1 eV) and sulfur (Eb (S2p = 163.5 eV) coordinated with platinum in complex III.

In addition to the above method, complex III was obtained in other ways: by the interaction of cystamine with an aqueous solution of K2 [PtCl4], as a result of the disintegration of the "onium" palladium complex with cystamine (V) in water, and as a result of the interaction of K2 [PtCl4] with mercamine (see experimental part).



The protonated amino group of coordinated mercamine can be preserved only in a non-aqueous medium (benzene). When complex II is acted upon by thiodipropionic acid (TDPA), two of its molecules enter the coordination sphere of platinum instead of two terminal chlorine atoms and are coordinated by the platinum atom monodentately at the sulfur atom to form the complex [Pt2(LH)2(ТДПК)2C12]C12 (IV). According to the IR spectra, complex IV has a binuclear structure and contains bridging chlorine atoms (ν (PtCl) = 286 and 270 cm-1). The ν (PtS) (mercamine) and ν (PtS) (TDPC) vibrations include the bands at 395, 379, 353, and 336 cm-1. Carboxyl groups of TDPK are not ionized (ν (C = O) = 1695 cm-1). The protonated amino group is characterized by a wide diffuse ν (NH+3) band with a maximum at about 3100 cm-1. Thus, complex IV can be attributed to the structure:



When complex IV is treated with water at a temperature of 70 ° C, two molecules of thiodipropionic acid are displaced from the coordination sphere of platinum and the cycle is closed with the formation of a complex, the IR spectrum of which is identical to that of complex III, which is also an argument in favor of structure IV with bridging chlorine atoms.

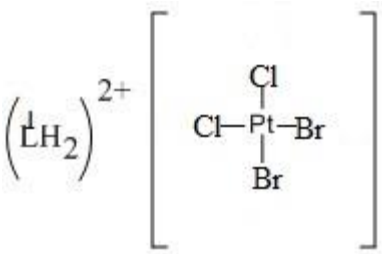
When platinum salts interact with cystamine dihydrochloride in benzene, it is possible not only to preserve the protonated amino group, but also to prevent the cleavage of the S-S bond. To implement this reaction, a method was developed for the formation of a complex tetracidoanion platinum in the absence of hydrohalic acids, which consists in supplementing the coordination sphere of platinum with two halide atoms L1 • 2HX in accordance with the following reaction [31]:

[(C6H5CN)2PtX2] + L1 • 2HC1 → [L1H2] [PtC12X2], X = C1 (complex V), Br (complex VI).

The structure of complex V is confirmed by the IR spectrum, in which there is an intense band at 327 cm – 1, which is characteristic of the planar anion [PtC14]2 with the D4h symmetry. The protonated NH + 3 group of cystamine is characterized by a number of ν (NH + 3) bands in the range of 2000-3150 cm -1 and two δ (NH + 3) bands at 1603 and 1592 cm-1.

This method was also used to synthesize the cation-anionic complex of platinum VI with a mixed chloride-bromide anion, which cannot be obtained by the acid method. In the long-wave IR spectrum of complex VI, the ν (PtC1) band of the [PtC14]2- anion (327 cm-1), observed in the V spectrum, disappears, and two new bands appear at about 301 and 252 cm-1, which refer to the vibrations ν (PtC1) and ν (PtBr) in the anion [PtC12Br2]2-.

To determine the relative positions of chlorine and bromine atoms in the anion, a model calculation of the vibrations of the [PtC14]2- , [PtBr4]2-, cis- and trans- [PtC12Br2]2- ions was carried out. It follows from the calculation that in a flat-square complex, the vibrations of two XPtX fragments located at an angle of 90 ° are not cinematically connected and have little effect on each other. Therefore, in the trans-decomposition of two identical halogen atoms (symmetry D2h), the frequencies ν (PtX) of the linear fragments C1PtC1 and BrPtBr should be close to the frequencies ν (PtX) of the [PtC14] 2- ions (327 cm-1) and [PtBr4] 2- (243 cm -1). In the case of the cis arrangement of two identical halogen atoms (C2v symmetry), according to the selection rules, the presence of four valence vibrations ν (PtX) can be expected in the IR spectrum, however, due to the weak vibrational interaction of the frequencies of two linear fragments the C1PtBr bonds will be close and in the spectrum one can expect the appearance of only two ν (PtX) bands (in phase and antiphase vibrations of PtC1 and PtBr bonds). Since both the PtC1 bond and the PtBr bond contribute to each of these vibrations, their frequencies should differ from the frequencies ν (PtX) in the [PtX4]2- - ions. The presence in the spectrum of VI of two new bands (301 and 252 cm – 1) in comparison with [PtC14]2– allows us to conclude that the same halogen atoms and the [PtCl2Br2] anion are also in the cis position to each other; complex VI has a structure:



When complexes V and VI are treated with water at a temperature of 50 ° C, binuclear platinum complexes are formed, the structure of which is similar to the structure of complex III.

Thus, the study of the interaction of cystamine dihydrochloride with various platinum compounds in aqueous solutions at pH 1-7 showed that in all cases the formation of complexes with the product of the cleavage of cystamine at the disulfide bond - (β-mercaptoethylamine (mercamine) (LH).

In acidic media (at pH <1), complexes of the composition [Pt2(LH)2C14] with a protonated amino group and coordination of the ligand by a platinum atom through a sulfur atom are formed. In this case, depending on the reaction temperature, it is possible to synthesize complexes of the same composition, but different structures: at 70 ° C, a compound is formed with the bridging position of sulfur atoms (complex I), and at lower temperatures (30- 500) with the bridging position of chlorine atoms (complex II).

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