

Synthesis and Structure of $[\text{Pd}(\text{NH}_3)_4][\text{cis-Pd}(\text{NH}_3)_2(\text{SO}_3)_2][\text{Pd}(\text{NH}_3)_3(\text{SO}_3)] \cdot \text{H}_2\text{O}$

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Received January 24, 2002

Abstract—A new palladium compound $[\text{Pd}(\text{NH}_3)_4][\text{cis-Pd}(\text{NH}_3)_2(\text{SO}_3)_2][\text{Pd}(\text{NH}_3)_3(\text{SO}_3)] \cdot \text{H}_2\text{O}$ (**I**) was synthesized and its structure was studied by X-ray powder diffraction method. In the course of the synthesis, the initial *trans*-diamminesulfite anionic complex is transformed into the *cis*-configuration. Further heating in aqueous solution results in isomerization of a substance into a neutral complex $[\text{Pd}(\text{NH}_3)_3(\text{SO}_3)]$. Crystals **I** are triclinic: $a = 10.3297(2) \text{ \AA}$, $b = 14.1062(3) \text{ \AA}$, $c = 6.8531(1) \text{ \AA}$, $\alpha = 101.36(0)^\circ$, $\beta = 92.74(0)^\circ$, $\gamma = 92.71(0)^\circ$, space group $P\bar{1}$. Structure **I** consists of the columns with alternating *cis*- $[\text{Pd}(\text{NH}_3)_2(\text{SO}_3)_2]^{2-}$ and $[\text{Pd}(\text{NH}_3)_3(\text{SO}_3)]$ complexes and $[\text{Pd}(\text{NH}_3)_4]^{2+}$ ions between the columns.

The syntheses of two-complex platinum and palladium aminosulfite compounds by means of sulfitation of the respective tetraammine chlorides $[\text{M}(\text{NH}_3)_4]\text{Cl}_2$ with sodium sulfite were described in [1–4]. The reactions were carried out in aqueous solutions and, depending on the temperature and stoichiometric ratio of the initial reagents, different reaction products were obtained. In particular, for platinum, $[\text{Pt}(\text{NH}_3)_4][\text{trans-Pt}(\text{NH}_3)_2(\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$ was isolated at room temperature. The formation of this *trans*-configuration is explained in [1–4] as a characteristic manifestation of a strong *trans*-effect of a sulfite group. In the case of palladium, the two-complex compound is stable at the lowered temperature, whereas at room temperature, $[\text{Pd}(\text{NH}_3)_3(\text{SO}_3)]$ is formed. The synthesis of $[\text{Pt}(\text{NH}_3)_4][\text{trans-Pt}(\text{NH}_3)_2(\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$ via the ion exchange between $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ and *trans*- $\text{Na}_2[\text{Pt}(\text{NH}_3)_2(\text{SO}_3)_2]$ is described in [5]. With the aim to obtain adequate crystals for $[\text{Pd}(\text{NH}_3)_4][\text{trans-Pd}(\text{NH}_3)_2(\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$, we used the method described in [5], since it is most suitable for monitoring the crystallization conditions. The resulting compound with the expected composition $\text{Pd}(\text{NH}_3)_3(\text{SO}_3)$ had an unusual structure that corresponded to the formula $[\text{Pd}(\text{NH}_3)_4][\text{cis-Pd}(\text{NH}_3)_2(\text{SO}_3)_2][\text{Pd}(\text{NH}_3)_3(\text{SO}_3)] \cdot \text{H}_2\text{O}$ (**I**). It is likely that the author of [4] isolated the same compound but assigned different structure to it. This work was undertaken with the aim to synthesize complex **I** and to study it by X-ray powder diffraction method.

EXPERIMENTAL

Complex **I** was synthesized by the procedure similar to that in [4]. All initial compounds were prepared using procedures described in [6]. The reagent grade chemicals were used in the synthesis. Two samples of

the *trans*-diamminedichloride palladium(II) (1 g) were each suspended in 20 ml of distilled water in two beakers. Ammonium hydroxide was added by drops to one beaker to dissolve the suspension, such that excess ammonium hydroxide would be avoided. The obtained $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ solution was cooled with ice to 5°C . Na_2SO_3 crystals (1.2 g) were added to the second beaker until the suspension was dissolved. The *trans*- $\text{Na}_2[\text{Pd}(\text{NH}_3)_2(\text{SO}_3)_2]$ solution was also cooled to 5°C . When these two cooled solutions were mixed, a white precipitate formed almost immediately. It was filtered off and washed with cold water. After the mother liquor was allowed to stand at room temperature, the molecular complex $[\text{Pd}(\text{NH}_3)_3(\text{SO}_3)]$ precipitated [7]. The compound under study was dried in air at room temperature. When the synthesis was carried out with cooling to a lower temperature, the crystallization time increased and the compound formed in the lower yield.

Compound **I** forms white finely crystalline powder poorly soluble in water. When dry, the compound is stable at room temperature. When the powder or its aqueous solution is heated, $[\text{Pd}(\text{NH}_3)_3(\text{SO}_3)]$ is formed.

The crystal structure of **I** was solved and refined by X-ray powder diffraction method. The experimental data were obtained on a DRON-4-07 diffractometer at 20°C ($\text{CuK}\alpha$ radiation, graphite monochromator). In order to minimize the effect of the preferred orientation, the sample was prepared by spreading the powder on the plane of a single-crystal silicon plate cut in the nonreflecting direction. Scanning was carried out in the range of 2θ from 6° to 80° at a step of 0.02° and record time 10 s. The unit cell parameters were found from X-ray powder diffraction pattern using the program [8]. The structure was solved and refined with the program package based on the modified and supplemented version of the DBWC-9006PC program [9]. Positions of

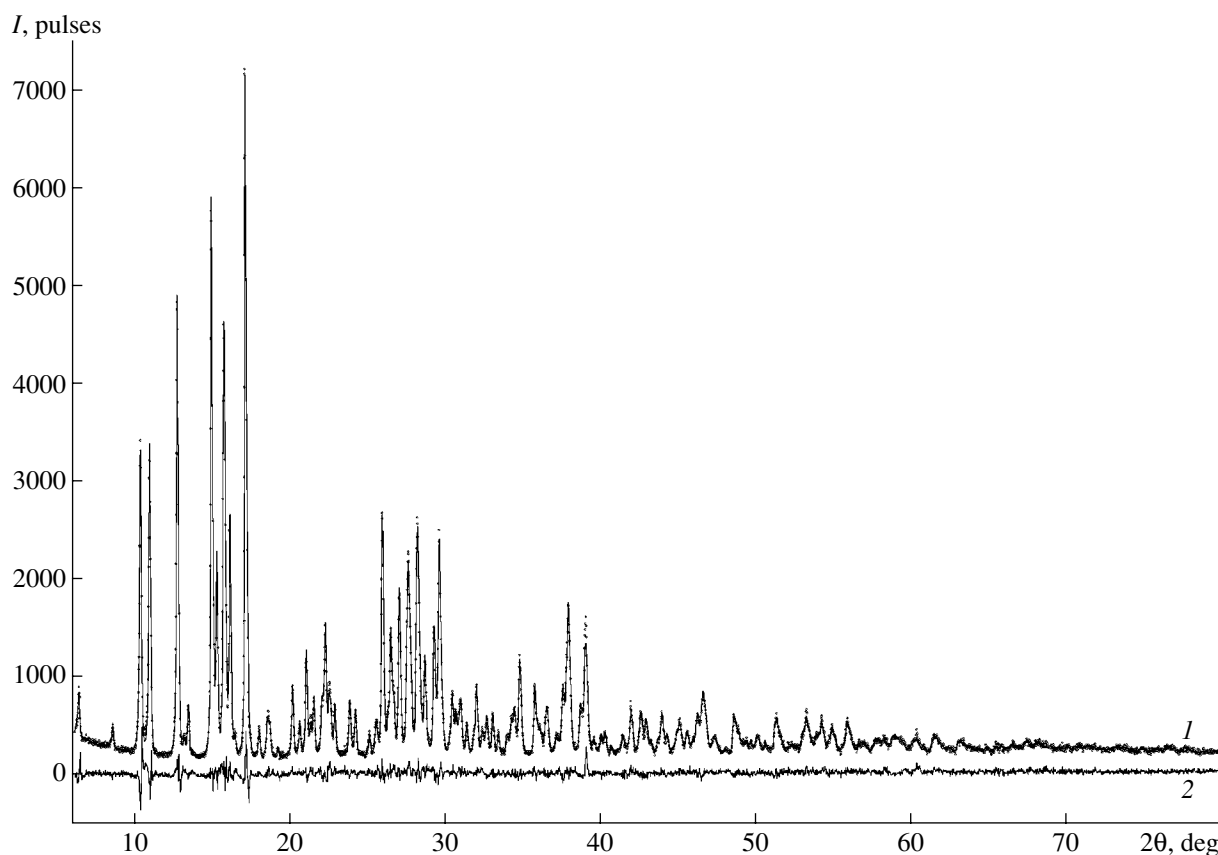


Fig. 1. Experimental and calculated X-ray powder diffraction patterns after refinement of structure I.

the metal atoms and orientations of ligands were located from the Patterson synthesis. The remaining non-hydrogen atoms were located from the Fourier synthesis. The Rietveld method [10] was used for refining the crystal structure. Hydrogen atoms were located geometrically with account of the structures of ammonia and water molecules and of the analysis of the most probable hydrogen bonding system. Hydrogen atoms were rigidly fixed at the respective N and O atoms.

The refined experimental and calculated X-ray patterns are shown in Fig. 1. Data on the crystal structure of I are presented in Table 1. Atomic coordinates and thermal parameters are listed in Table 2, while the bond lengths and angles are given in Table 3.

RESULTS AND DISCUSSION

Crystals I (Fig. 2) consist of the complex anions *cis*-[Pd(NH₃)₂(SO₃)₂]²⁻, neutral complexes [Pd(NH₃)₃(SO₃)], complex cations [Pd(NH₃)₄]²⁺, and water molecules. A fragment of structure I is shown in Fig. 3.

No data are available in the literature on the geometry of the *cis*-[Pd(NH₃)₂(SO₃)₂]²⁻ complexes. The Pd atom in this anion has almost planar coordination environment of two S atoms of two sulfite groups, and two N atoms of two ammonia molecules. The angles

between the coordination bonds deviate by no more than 5° from the standard value of 90°, the SPdS angle being the largest, which is explained by mutual steric effect of two sulfite groups. An average Pd–S bond length (2.291(6) Å) in the known *trans*-diamminedisulfite palladium complexes [11, 12] coincides within the limits of the standard deviations with that in compound I (2.28(2) Å). However, the Pd–N bonds in the

Table 1. Crystal data and *R* factors for structure I

Space group	P $\bar{1}$
<i>a</i> , Å	10.3297(2)
<i>b</i> , Å	14.1062(3)
<i>c</i> , Å	6.8531(1)
α , deg	101.36(0)
β , deg	92.74(0)
γ , deg	92.71(0)
<i>V</i> , Å ³	976.3(4)
<i>Z</i>	2
ρ (calcd), g/cm ³	2.486
<i>R</i> _{wp}	0.0697
<i>R</i> _b	0.0330

Table 2. Atomic coordinates and thermal parameters for structure **I**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Pd(1)	0.2374(5)	0.8373(3)	0.9799(8)	3.8(2)
Pd(2)	0.2377(5)	0.3480(4)	0.1521(8)	4.5(2)
Pd(3)	0.2354(5)	0.8093(3)	0.4628(7)	2.8(2)
S(1)	0.251(2)	1.003(1)	1.068(3)	4.7(4)
O(11)	0.130(3)	1.027(2)	1.174(5)	4.6(4)
O(12)	0.368(3)	1.040(2)	1.176(4)	4.6(4)
O(13)	0.246(3)	1.047(2)	0.882(5)	4.6(4)
S(2)	0.393(2)	0.700(1)	0.396(2)	4.7(4)
O(21)	0.433(3)	0.685(2)	0.597(5)	4.6(4)
O(22)	0.506(3)	0.747(2)	0.330(5)	4.6(4)
O(23)	0.341(3)	0.607(2)	0.294(4)	4.6(4)
S(3)	0.068(2)	0.697(1)	0.399(2)	4.7(4)
O(31)	-0.057(3)	0.753(2)	0.412(5)	4.6(4)
O(32)	0.057(3)	0.641(2)	0.552(5)	4.6(4)
O(33)	0.064(3)	0.630(2)	0.196(5)	4.6(4)
N(1)	0.037(3)	0.817(2)	0.973(4)	4.2(5)
N(2)	0.428(3)	0.833(2)	0.999(4)	4.2(5)
N(3)	0.233(3)	0.684(2)	0.907(4)	4.2(5)
N(4)	0.095(3)	0.917(2)	0.526(4)	4.2(5)
N(5)	0.375(3)	0.924(2)	0.535(4)	4.2(5)
N(6)	0.270(3)	0.244(2)	-0.105(4)	5.0(6)
N(7)	0.213(3)	0.437(2)	0.409(5)	5.0(6)
N(8)	0.274(3)	0.255(2)	0.317(4)	5.0(6)
N(9)	0.191(3)	0.447(2)	0.010(4)	5.0(6)
O(w)	0.580(3)	0.497(2)	0.267(3)	4(1)

trans-complexes [11, 12] (average length 2.069(9) Å) are somewhat shorter than similar bonds in **I** (2.11(2) Å). Although this difference only slightly exceeds the standard deviation, one can suggest that an increase in the Pd–N distance is caused by the *trans*-labilizing effect of the sulfite group. Geometrical parameters of the sulfite groups in *cis*-[Pd(NH₃)₂(SO₃)₂]²⁻ are almost the same as those in *trans*-diamminedisulfite palladium [11, 12].

In the [Pd(NH₃)₄]²⁺ complex cation of structure **I**, the Pd–N distances are close to those in [Pd(NH₃)₄]C₂O₄ [13] and in [Pd(NH₃)₄]Cl₂ · H₂O [7]. At the same time, the NPdN angles substantially devi-

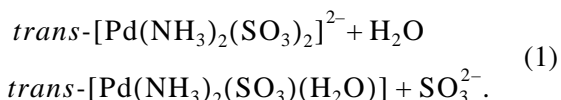
ate from 90°, probably, due to the effect of hydrogen bonds.

On the whole, geometrical parameters of a neutral [Pd(NH₃)₃(SO₃)] molecule are close to those for [Pd(NH₃)₃(SO₃)] [14]. Some deviations include an increase in the Pd–S distance by 0.05 Å and a decrease in the average Pd–N distance (2.05(3) Å) as compared to analogous data (2.11(2) Å) [14].

A peculiar feature of compound **I** is that its structure consists of columns of alternating *cis*-[Pd(NH₃)₂(SO₃)₂]²⁻ anions and neutral [Pd(NH₃)₃(SO₃)] molecules. The columns are directed along the *c* axis and have zigzag elements with the Pd(1)···Pd(3) distances being 3.410(8) and 3.486(7) Å and Pd(1)···Pd(3)···Pd(1) angle being 167.1(2)°. The [Pd(NH₃)₃(SO₃)] complexes occupy the space-saving *anti*-position with respect to the *cis*-[Pd(NH₃)₂(SO₃)₂]²⁻ anions; the torsion S–Pd···Pd–S angle is close to 130°. One can notice that the columns form corrugated planes parallel to the *xOz* axis, such that each column is surrounded by two closest columns.

The most probable hydrogen bonding system was established by analyzing the N···O and O···O distances (Table 3) and the Pd–N···O, O···N···O, and O···O···O angles. In the cationic complex, each nitrogen atom, except for N(7), forms three hydrogen bonds linking a cation with the remaining complexes and water molecules. Hydrogen bonds of the anionic and neutral complexes are realized between the neighboring columns and inside the column. Hydrogen bonds inside the column are likely to favor stabilization of the *cis*-configuration of the anion in the course of crystallization. Water molecules are also connected to the columns by the O(1)···O(21) and O(1)···O(23) hydrogen bonds.

Proceeding from the synthesis and analysis of the crystal structure of **I**, one can suggest the mechanism of transformation of the initial *trans*-diamminedisulfite complex into the *cis*-configuration, taking into account that the *trans*-diamminedisulfitepalladate(II) anion undergoes dissociation and hydration in aqueous solution:



It is obvious that equilibrium (1) should be significantly shifted to the left due to a high affinity of Pd(II) toward sulfite group. However, the particles that can interact with the sulfite ions (in particular, the [Pd(NH₃)₄]²⁺ complex cations) can shift equilibrium (1) toward the aqua complex. As a result of an increased *trans*-effect of its sulfite group, this complex is rearranged into the *cis*-configuration or adds ammonia. Ammonia is obtained due to the interaction of [Pd(NH₃)₄]²⁺ and SO₃²⁻ with the formation of a stable triamminesulfite complex. The final reaction products are in fact the result of this activity. Evidently, the fixation of *cis*-com-

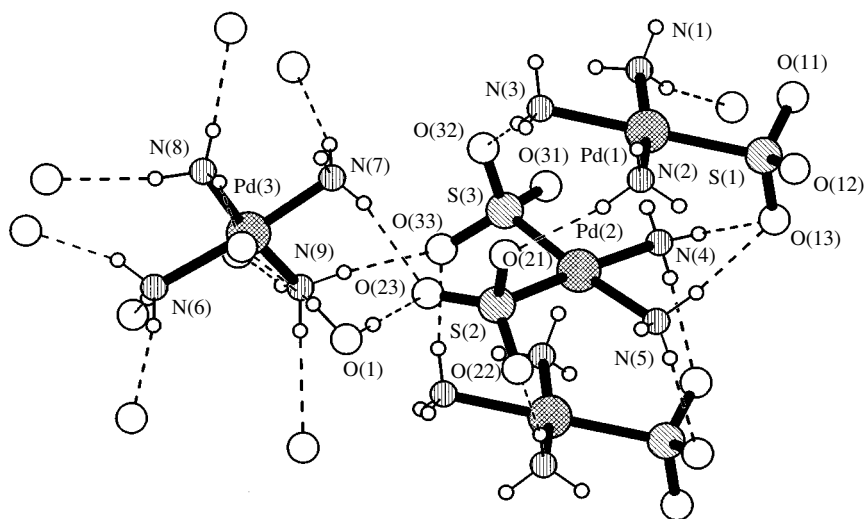
Table 3. Selected bond lengths and angles in structure **I***

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Angle	ω, deg	Angle	ω, deg
Pd(1)–N(1)	2.07(3)	N(2)···O(22) ^{#2}	2.87(5)	S(1)Pd(1)N(1)	98(1)	O(11)S(1)O(12)	115(2)
Pd(1)–N(2)	1.97(3)	N(2)···O(21)	3.12(4)	S(1)Pd(1)N(2)	91(1)	O(12)S(1)O(13)	106(2)
Pd(1)–N(3)	2.12(3)	N(3)···O(32)	2.91(4)	N(1)Pd(1)N(3)	84(1)	O(13)S(1)O(11)	108(2)
Pd(2)–N(4)	2.15(3)	N(3)···O(33) ^{#2}	2.89(5)	N(3)Pd(1)N(2)	86(1)	O(21)S(2)O(22)	105(2)
Pd(2)–N(5)	2.08(3)	N(4)···O(13)	3.06(4)	S(1)Pd(1)N(3)	177.3(9)	O(22)S(2)O(23)	122(2)
Pd(3)–N(6)	2.11(3)	N(4)···O(11) ^{#3}	3.14(5)	N(1)Pd(1)N(2)	169(1)	O(23)S(2)O(21)	104(2)
Pd(3)–N(7)	1.99(3)	N(5)···O(13)	3.06(4)	S(2)Pd(2)S(3)	95.1(7)	O(31)S(3)O(32)	103(2)
Pd(3)–N(8)	1.93(3)	N(5)···O(12) ^{#3}	3.21(4)	N(4)Pd(2)N(5)	86(1)	O(32)S(3)O(33)	110(2)
Pd(3)–N(9)	1.92(3)	N(6)···O(22) ^{#4}	2.85(5)	S(2)Pd(2)N(5)	91.2(9)	O(33)S(3)O(31)	108(2)
Pd(1)–S(1)	2.29(1)	N(6)···O(13) ^{#5}	2.76(4)	S(3)Pd(2)N(4)	87.7(9)	Pd(1)S(1)O(11)	104(1)
Pd(2)–S(2)	2.30(2)	N(6)···O(31) ^{#6}	2.98(4)	S(2)Pd(2)N(4)	177.3(9)	Pd(1)S(1)O(12)	113(1)
Pd(2)–S(3)	2.26(2)	N(7)···O(23)	2.94(4)	S(3)Pd(2)N(5)	174(1)	Pd(1)S(1)O(13)	110(1)
S(1)–O(11)	1.50(4)	N(7)···O(32) ^{#7}	2.99(4)	N(6)Pd(3)N(8)	90(1)	Pd(2)S(2)O(21)	102(1)
S(1)–O(12)	1.41(3)	N(8)···O(31) ^{#7}	2.99(5)	N(6)Pd(3)N(9)	95(1)	Pd(2)S(2)O(22)	109(2)
S(1)–O(13)	1.52(4)	N(8)···O(12) ^{#5}	3.21(4)	N(7)Pd(3)N(8)	84(1)	Pd(2)S(2)O(23)	112(1)
S(2)–O(21)	1.48(4)	N(9)···O(33)	3.03(4)	N(7)Pd(3)N(9)	90(1)	Pd(2)S(3)O(31)	106(2)
S(2)–O(22)	1.45(4)	N(9)···O(1) ^{#4}	3.27(4)	N(6)Pd(3)N(7)	175(1)	Pd(2)S(3)O(32)	113(1)
S(2)–O(23)	1.43(3)	N(9)···O(33) ^{#6}	2.98(4)	N(8)Pd(3)N(9)	174(1)	Pd(2)S(3)O(33)	115(1)
S(3)–O(31)	1.54(4)	N(8)···O(21) ^{#8}	3.10(4)				
S(3)–O(32)	1.44(4)	O(1)···O(23)	2.97(4)				
S(3)–O(33)	1.52(3)	O(1)···O(21) ^{#8}	2.90(4)				
N(1)–O(11) ^{#1}	3.15(4)						

* Symmetry operations: ^{#1} $-x, 2-y, 2-z$; ^{#2} $x, y, 1+z$; ^{#3} $x, y, -1+z$; ^{#4} $1-x, 1-y, -z$; ^{#5} $x, -1+y, -1+z$; ^{#6} $-x, 1-y, -z$; ^{#7} $-x, 1-y, 1-z$; ^{#8} $1-x, 1-y, 1-z$.

plex is realized due to hydrogen bonding with [Pd(NH₃)₃(SO₃)] resulting in the formation of poorly soluble groups. The formation of crystals **I** is likely to

be the most advantageous process due to a specific packing of complexes that provides the energy gain as a result of the higher structural compatibility of the

**Fig. 2.** Crystal structure **I**.

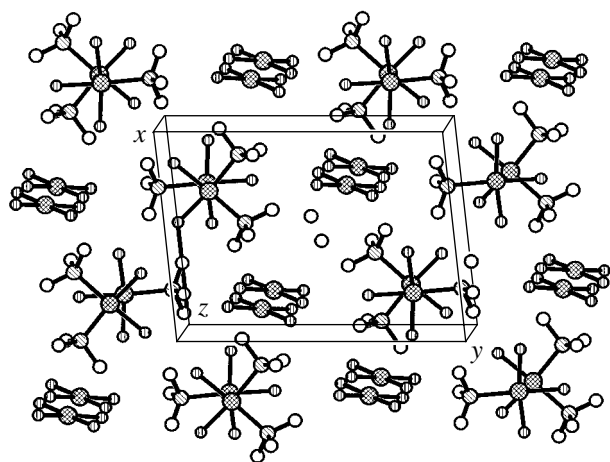


Fig. 3. Packing of structural units in crystal I.

$[\text{Pd}(\text{NH}_3)_3(\text{SO}_3)]$ and *cis*- $[\text{Pd}(\text{NH}_3)_2(\text{SO}_3)_2]^{2-}$ complexes as compared to the $[\text{Pd}(\text{NH}_3)_4]^{2+}$ and *trans*- $[\text{Pd}(\text{NH}_3)_2(\text{SO}_3)_2]^{2-}$ complexes.

The interpretation based on the hydrolysis of the Pd(II) *trans*-diamminedisulfite complex agrees with the data on the hydrolysis of the Pt(II) *trans*- and *cis*-diamminedihalides [15, 16]. The estimation of the instability constants of the Pt(II) *trans*- and *cis*-diamminedihalides shows that the *trans*-compounds are hydrolyzed to a greater extent than the *cis*-complexes. The amminesulfite complexes are likely to exhibit the same tendencies. However, unlike the halide complexes, the *trans*-*cis* and the *cis*-*trans* transformations are accompanied here by the formation of a stable non-electrolytic $[\text{Pd}(\text{NH}_3)_3(\text{SO}_3)]$ complex.

Thus, with a view to the above-said, one can conclude that the course of a chemical reaction affording $[\text{Pd}(\text{NH}_3)_4][\text{cis-Pd}(\text{NH}_3)_2(\text{SO}_3)_2][\text{Pd}(\text{NH}_3)_3(\text{SO}_3)] \cdot \text{H}_2\text{O}$ or $[\text{Pd}(\text{NH}_3)_4][\text{trans-Pd}(\text{NH}_3)_2(\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$ depends on whether the hydrolysis (1) is an essential or inessential process. In the presence of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and reactive Na_2SO_3 sulfite agent, the *trans*- $[\text{Pd}(\text{NH}_3)_2(\text{SO}_3)_2]^{2-}$ anion is rapidly formed and is

bound into a weakly soluble $[\text{Pd}(\text{NH}_3)_4][\text{trans-Pd}(\text{NH}_3)_2(\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$ compound. In this case, the concentration of a free *trans*- $[\text{Pd}(\text{NH}_3)_2(\text{SO}_3)_2]^{2-}$ anion is low and equilibrium (1) is thus inessential. When the *trans*- $\text{Na}_2[\text{Pd}(\text{NH}_3)_2(\text{SO}_3)_2]$ solution is used as the initial carrier of the sulfite group, the concentration of $[\text{Pd}(\text{NH}_3)_2(\text{SO}_3)(\text{H}_2\text{O})]$ attains the value at which the transformations proceed further and give compound I.

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