# COORDINATION COMPOUNDS

# Reaction of Chlorine with Platinum(IV) Triamine Containing N,N- Dimethylethylenediamine. The Crystal Structure of [Pt{(CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>}PyCl<sub>3</sub>]Cl· H<sub>2</sub>O[Pt{(CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NCl}PyCl<sub>3</sub>], and [Pt{(CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>}PyCl<sub>4</sub>]

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Abstract—The Platinum(II) diamine *N*,*N*-dimethylethylenediamine (N,N-dimeEn) with  $Pt\{(CH_3)_2N(CH_2)_2NH_2\}Cl_2\}$  (I) was synthesized. The reaction of the diamine with pyridine gave Pt(II) tetramine  $[Pt{(CH_3)_2N(CH_2)_2NH_2}Py_2]Cl_2$  (II), which was oxidized with chlorine to give Pt(IV) triamine  $Pt{[(CH_3)_2N(CH_2)_2]PyCl_3]Cl \cdot H_2O$  (III). The reaction of III with chlorine (chloroamidation) yielded chloroimide [Pt{(CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NCl}PyCl<sub>3</sub>] (IV). The IR spectra of complexes I–IV and UV/Vis spectra of III and IV were studied. X-Ray diffraction analysis was performed for III (monoclinic crystals, space group  $P2_1/c$ ,  $a = 7.7437(6), b = 8.1100(7), c = 28.52992(2) \text{ Å}, \beta = 93.7280(10)^{\circ}, Z = 4, R_{hkl} = 0.0420)$  and IV (orthorhombic crystals, space group  $Pna2_1$ , a = 15.7825(12), b = 7.4447(6), c = 12.3099(6) Å, Z = 4,  $R_{hkl} = 0.0539$ ). During oxidation of Pt(II) tetramine with chlorine, the pyridine molecule is removed from the *cis* position relative to the  $(CH_3)_2N$  group (*trans* position relative to the NH<sub>2</sub> group) of *N*,*N*-dimethylethylenediamine. The reaction of chloroimide complex IV with concentrated HCl (dechloroamidation) at 20°C afforded the initial complex III; that at 100°C, gave triamine III together with Pt(IV) diamine [Pt(N,N-dimeEn)Cl<sub>4</sub>] (V) (monoclinic crystals, space group  $P2_1/n$ , a = 7.1278(5), b = 11.5384(8), c = 12.7501(9) Å,  $\beta = 93.23(10)^\circ$ , Z = 4,  $R_{hkl} = 0.0239$ ).

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The <sup>195</sup>Pt and <sup>14</sup>N NMR studies of the reactions of mixed platinum(IV) amine complexes containing both ethylenediamine and ammonia molecules with chlorine have shown that only ammonia molecules are involved in the reaction [1]. Aliphatic ring-forming diamines, in particular, ethylenediamine, propylenediamine, trimethylenediamine (En, Pn, Tn), being incorporated in platinum(IV) triamines and tetramines are involved into reactions with chlorine only in those cases where the complexes contain aromatic amine ligands with  $\pi$ -acceptor properties (Py, bipy) [2-7]. The inner-sphere En and Pn, which form five-membered metal rings with platinum, are converted into N- and N,N'-chloroimides in these reactions. In these aliphatic diamines, both NH<sub>2</sub> groups are equivalent and equally reactive. Therefore, the reactions with chlorine give several products difficult to identify rather than a single complex. In Pt(IV) triamines, the NH<sub>2</sub> group located in the trans-position to an anionic ligand was found to be most reactive. However, chlorination of triamines, too, gave a mixture of several compounds rather than one complex. For example, the reaction of Pt(IV) triamine [PtEn PyCl<sub>3</sub>]Cl with chlorine was reported [3] to yield a bright-red chloroimide

[8]) orange complex [Pt(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCl)PyCl<sub>3</sub>]Cl. In our experiment, red chloroimide was formed during the first 2–5 min of chlorination of this triamine, while after ~10–15 min a lighter compound started to appear, and subsequently a dark yellow complex was produced. We were unable to separate sufficient amounts of these complexes by consecutive filtration and recrystallization; therefore, we studied chloroamidation for Pt(IV) complexes with one reactive NH<sub>2</sub> group in a ring-forming diamine and attempted to obtain the product of reaction of this Pt(IV) complex with chlorine in a high yield and study it by X-ray diffraction. No structural data for chloroamidation products of platinum complexes containing a chelating diamine were available so far. Only the crystal structure of the product of chloroamidation Pt(IV) ammonia of complex  $[Pt(NH_3)_3(NCl_2)_2Cl]Cl$  is known [9]. In this work, we prepared platinum(II) diamine with N.N-dimethylethylenediamine (N,N-dimeEn), made this compound to react with pyridine to obtain platinum(II) tetramine, and carried out oxidation with chlorine, which gave platinum(IV) triamine  $[{Pt[CH_3)_2N(CH_2)_2NH_2}PyCl_3]Cl \cdot H_2O$  instead

[Pt(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NCl)PyCl<sub>3</sub>] or (in another publication

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of Pt(IV) tetramine. The reaction of the obtained product with chlorine afforded chloroimide derivative of Pt(IV) triamine, namely  $[Pt\{(CH_3)_2N(CH_2)_2NCl\}PyCl_3]$ . Dechloroamidation at 20°C and at 100°C was also studied.

### **EXPERIMENTAL**

Synthesis of  $[Pt{(CH_3)_2N(CH_2)_2NH_2}Cl_2]$  (I).  $K_2$ PtCl<sub>4</sub> (5 g) was dissolved in boiling water (15 ml). After cooling with magnetic stirring, N,N-dimethylethylenediamine ( $d^{20} = 0.803$ ) (1.5 ml, 10% excess) was added to the suspension. K<sub>2</sub>PtCl<sub>4</sub> gradually dissolved, and a pale precipitate started to form. After 1 h, the gray-yellow precipitate was filtered off and, as precipitation progressed, the product was collected several more times on the same filter. The product was recrystallized from hot water containing some HCl (~10% solution). This gave finely crystalline (needles) light green-colored compound, fraction 1, 0.7 g (~16.5%). After separation of fraction 1, a mixture of yellowgreen and red (probably  $[Pt(N,N-dimeEn)_2][PtCl_4])$ compounds was isolated from the filtrate. This mixture was not separated by two recrystallizations. The filtrate obtained after the second recrystallization (together with wash water) was concentrated on a rotary evaporator and combined with the mixture. The complex  $[Pt(NH_3)_4]Cl_2$  (0.6 g) was added, and the mixture was heated with continuous stirring. After 15 min, green Magnus salt [Pt(NH<sub>3</sub>)<sub>4</sub>][PtCl<sub>4</sub>] precipitated from the hot green solution and was collected on a filter. Light green finely crystalline Pt(II) diamine gradually precipitated from the filtrate. The product was washed with dilute HCl ( $\sim 10\%$ ) and ethanol to give fraction 2, 1.43 g. The overall yield was 2.13 g ( $\sim 50\%$ ).

For C<sub>4</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>Pt anal. calcd. (%): Pt, 55.08.

Found (%): Pt, 54.79 (fraction 1).

Found (%): Pt, 54.91 (fraction 2).

Synthesis of  $[Pt{(CH_3)_2N(CH_2)_2NH_2}Py_2]Cl_2 \cdot H_2O$ (II). A mixture of diamine I, pyridine (0.2 mL), and water (10 mL) was heated on a water bath until the diamine dissolved (~1 h). After cooling, the colorless solution was filtered, evaporated almost to dryness, and left overnight in a vacuum dessicator over P<sub>2</sub>O<sub>5</sub> to give 0.5 g of a snow-white finely crystalline tetramine II in ~85% yield.

For  $C_{14}H_{24}Cl_2N_4OPt$  ([Pt(*N*,*N*-dimeEn)Py<sub>2</sub>)] $Cl_2 \cdot H_2O$ ) anal. calcd. (%): Pt, 36.79; Cl, 13.37; N, 10.56; C, 31.70.

Found (%): Pt, 37.92; Cl, 13.71; 13.65.

After storage in a dessicator for 5 days, found (%): Pt, 39.16; N, 9.95; 9.89; C, 28.16; 28.63.

After 1.5 months, found (%): Pt, 43.45; Cl, 15.60; N, 9.27; 9.01; C, 24.01; 24.49.

For  $C_9H_{19}Cl_2N_3OPt$  ([Pt(*N*,*N*-dimeEn)PyCl)]Cl · H<sub>2</sub>O) anal. calcd. (%): Pt, 43.23; Cl, 15.71; N, 9.31; C, 23.96.

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The IR spectrum of complex II (cm<sup>-1</sup>): 3438 s, 3358 s v(OH); 3210 w v(NH); 1630 s  $\delta(H_2O)$ ; 1581 m  $\delta(NH_2)$  and narrow strong bands at 1611, 770, and 699 cm<sup>-1</sup> corresponding to pyridine ring vibrations.

Synthesis of  $[Pt{(CH_3)_2N(CH_2)_2NH_2}PyCl_3]Cl \cdot H_2O$  (III). Chlorine was slowly passed for 10 min through a solution of freshly prepared platinum(II) tetramine (0.45 g) in water (3 mL) containing several drops of HCl (1 : 1) (to prevent the formation of chloroamides). The solution turned yellow and a solid started to precipitate almost immediately. After 1 h, the precipitate was collected on a filter and, without any washing, kept in a dessicator over fused KOH for 48 h to give 0.31 g of finely crystalline pale yellow powder (~67%).

For C<sub>9</sub>H<sub>19</sub>Cl<sub>4</sub>N<sub>3</sub>OPt anal. calcd. (%): Pt, 37.36; N, 8.04; C, 20.75; H, 3.60; Cl, 27.10; H<sub>2</sub>O, 3.44.

Found (%): Pt, 37.58; N, 7.46; C, 22.31; H, 2.86; Cl, 25.31; H<sub>2</sub>O, 3.42.

The IR spectrum of III exhibits bands (cm<sup>-1</sup>): 3450 m, ~3129 w, 1630 vw, and 1572 m assigned to v(OH), v(NH),  $\delta$ (H<sub>2</sub>O), and  $\delta$ (NH<sub>2</sub>), respectively, and narrow strong bands at 1602, 761, and 687 cm<sup>-1</sup> caused by pyridine ring vibrations.

Recrystallization from water gave crystals of III suitable for X-ray diffraction.

The IR spectrum of the crystals of III was identical to the spectrum of non-recrystallized sample except for stronger  $\delta(H_2O)$  band (1630 cm<sup>-1</sup>), which is due to higher content of crystallization water after recrystallization (three H<sub>2</sub>O molecules instead of one molecule according to X-ray diffraction data).

Synthesis of  $[Pt{(CH_3)_2N(CH_2)_2NCl}PyCl_3]$  (IV). Chlorine was slowly passed for 5–7 min through a solution of complex I (0.136 g) in water (5 mL). A bright orange solid started to precipitate almost immediately. After 30 min, the red precipitate was collected on a filter; at the end of filtration, several drops of water were added to the precipitate. The filtrate was yellowish. The precipitate was kept in air for 1 h and then in a dessicator over fused KOH for 24 h to give 0.122 g (~89.5%) of finely crystalline homogeneous (under a microscope) dark cherry-colored compound insoluble in water.

For C<sub>9</sub>H<sub>15</sub>Cl<sub>4</sub>N<sub>3</sub>Pt anal. calcd. (%): Pt, 38.85; C, 21.53; N, 8.36; H, 3.01; Cl<sub>tot</sub>, 28.24; Cl<sub>outer</sub>, 0.0.

Found (%): Pt, 38.40; C, 22.01; N, 8.07; H, 2.67; Cl<sub>tot</sub>, 28.55; Cl<sub>outer</sub>, 0.0.

Found (%): Pt, 38.56; C, 22.18; N, 8.08; H, 2.60; Cl<sub>tot</sub>, 28.33; Cl<sub>outer</sub>, 0.0

The compound is readily soluble in acetonitrile and dimethylformamide (DMF) to form bright red solutions from which bright red crystals suitable for X-ray diffraction were obtained.



**Fig. 1.** Complex  $[Pt{(CH_3)_2N(CH_2)_2NH_2}PyCl_3]^+$  in compound III.



Fig. 2. Complex  $[Pt{(CH_3)_2N(CH_2)_2NCl}PyCl_3]$  in compound IV.



Fig. 3. Complex  $[Pt{(CH_3)_2N(CH_2)_2NH_2}Cl_4]$  in compound V.

The IR spectrum of complex IV contains no v(NH) or  $v(NH_2)$  bands; the strong bands at 1602, 768, and 691 cm<sup>-1</sup> due to pyridine ring vibrations are retained; the band at 662 cm<sup>-1</sup> becomes much more intense than in the initial complex I and may probably be assigned to v(N-CI).

**Reaction of complex IV with concentrated HCl** (dechloroamidation). Concentrated HCl (2 ml) was added to complex IV (25 mg). The bright red color disappeared immediately but the yellow complex was not completely dissolved. After addition of hot water (1 ml), the solution was filtered and left to evaporate in air. This gave pale yellow crystals, which were studied by X-ray diffraction (complex VI).

A mixture of complex IV (25 mg) and concentrated HCl (3 mL) was heated on a boiling water bath; this was accompanied by vigorous evolution of bubbles an chlorine smell. After 15 min, the precipitate dissolved and during slow cooling on the hot switched-off bath, very fine crystals separated from the solution. The solution was concentrated almost to dryness to give a mixture of very thin pale yellow plate crystals and a number of yellow crystals of a different habit. This mixture was recrystallized from hot water with addition of HCl. This gave two kinds of crystals, which were studied by X-ray diffraction (complexes VII and V).

**IR absorption spectra** in the 4000–400 cm<sup>-1</sup> range were recorded on a Specord M-82 spectrophotometer for mineral oil mulls.

**UV/Vis spectra** of an aqueous solution of III and a DMF solution of IV were recorded on a Varian/Cary 50 spectrophotometer.

**X-Ray diffraction.** The experimental data for structure solution for III, IV, and V were collected from  $0.33 \times 0.23 \times 0.15$ ,  $0.45 \times 0.24 \times 0.03$ , and  $0.32 \times 0.18 \times 0.09$  mm single crystals, respectively, using Bruker Smart CCD Apex II automated diffractometer (293 K,  $\lambda MoK_{\alpha}$ ,  $\lambda 0.71073$  Å, graphite monochromator,  $\omega$  scan mode). The absorption correction was applied semiempirically. The structures of III, IV, and VII were solved by the direct method and refined by the least-squares method using SHELXS-97 [10] and SHELXL-97 [11] software in the anisotropic full-matrix approximation for non-hydrogen atoms. The positions of H atoms were calculated geometrically and refined isotropically in the riding model.

The key crystal data and X-ray experiment details for compounds III– V are summarized in Table 1, atom coordinates and thermal factors are in Table 2, and interatomic distances and bond angles are in Table 3.

#### **RESULTS AND DISCUSSION**

For investigating chloroamidation of platinum(IV) complexes containing an aliphatic diamine with one reactive NH<sub>2</sub> group, Pt(II) diamine I was prepared by the reaction of  $K_2$ PtCl<sub>4</sub> with *N*,*N*-dimethylethylenedi-

	III	IV	V
Formula weight	C <sub>9</sub> H <sub>23</sub> C <sub>14</sub> N <sub>3</sub> O <sub>3</sub> Pt	C <sub>9</sub> H <sub>15</sub> C <sub>14</sub> N <sub>3</sub> Pt	$C_4H_{12}C_{14}N_2Pt$
Molecular formula	558.19	502.13	425.05
System	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pna2_1$	$P2_1/n$
<i>a</i> , Å	7.7437(6)	15.7825(12)	7.1278(5)
b, Å	8.1100(7)	7.4447(6)	11.5384(8)
<i>c</i> , Å	28.529(2)	12.3099(10)	12.7501(9)
β, deg	93.7280(10)	90	93.2300(10)
<i>V</i> , Å <sup>3</sup>	1787.9(3)	1446.4(2)	1046.95(13)
Ζ	4	4	4
$\rho_{calcd}$ , g/cm <sup>3</sup>	2.074	2.306	2.697
$\mu$ , cm <sup>-1</sup>	8.454	10.422	14.367
<i>F</i> (000)	1072	944	784
θ, deg	3.30-30.34	2.58-31.49	2.38-31.74
Index range	-10 < h < 10, -11 < k < 11, -22 < l < 39	-23 < h < 18, -10 < k < 10, -17 < l < 17	-9 < h < 10, -16 < k < 15, -18 < l < 18
The total number of measured reflec- tions	9910	13720	9682
The number of independent reflections	4841 [ <i>R</i> (int) = 0.0463]	4589 [ <i>R</i> (int) = 0.0387]	3320 [R(int) = 0.0280]
The number of refined parameters	207	143	100
GOOF on $F^2$ $R [I > 2\sigma(I)]$	$\begin{array}{c} 1.002\\ R1 = 0.0420, \ wR2 = 0.0943 \end{array}$	$\begin{array}{c} 1.013\\ R1 = 0.0539,  wR2 = 0.1361 \end{array}$	$\begin{array}{c} 1.002\\ R1 = 0.0239, \ wR2 = 0.0484 \end{array}$
<i>R</i> (for all reflections)	R1 = 0.0514, wR2 = 0.0974	R1 = 0.1123, wR2 = 0.1896	R1 = 0.0381, wR2 = 0.0536
$\Delta \rho_{max}$ and $\Delta \rho_{min} e/Å$	2.463 and -2.408	2.711 and -1.698	1.387 and -0.754

Table 1. Crystal data and X-ray experiment details for III, IV, and V

amine. Dissolution of the resulting platinum diamine in a small excess of pyridine (1:5) with heating followed by evaporation yielded a snow-white finely crystalline powder. According to elemental analysis, the complex was Pt(II) tetramine (II). Analysis of this sample after 5 days showed higher contents of Pt and Cl and lower contents of C and N. One month later, the compound corresponded, according to elemental analysis, to platinum(II) triamine [Pt(*N*,*N*-dimeEn)PyCl]Cl  $\cdot$  H<sub>2</sub>O (see Experimental).

Chlorine oxidation of an aqueous solution of the freshly prepared Pt(II) tetramine II at room temperature afforded a light yellow complex, which was identified as platinum(IV) triamine III according to elemental analysis.

The UV/Vis spectrum of a solution of III exhibited the following bands in the visible region: 410 nm (24390 cm<sup>-1</sup>,  $\varepsilon = 51.8$  L/(mol cm)) and 352 nm (28410 cm<sup>-1</sup>,  $\varepsilon = 216.5$  L/(mol cm)). The positions and intensities of these bands corresponded to Pt(IV) triamines (compare 25000 cm<sup>-1</sup> and  $\varepsilon = 55.8$  L/(mol cm) for [PtEnPyCl<sub>3</sub>]Cl).

X-Ray diffraction data supported the assumption that complex III is Pt(IV) triamine,  $[Pt{(CH_3)_2N(CH_2)_2NH_2}PyCl_3]Cl 3H_2O$  (Fig. 1). Thus, upon chlorine oxidation of the tetramine  $[Pt(N,N-dimeEn)Py_2]Cl_2$ , one pyridine molecule is replaced by Cl<sup>-</sup>. However, as noted above, this platinum(II) tetramine loses a Py molecule also during long-term storage, being converted spontaneously into Pt(II) triamine.

It is noteworthy that the tetramine  $[PtEnPy_2]Cl_2$  does not lose pyridine even on long-term storage or on chlorination of Pt(IV) tetramine  $[PtEnPy_2Cl_2]Cl_2$  [4]. This difference in the behaviors of platinum tetramines with En and *N*,*N*-dimeEn is due to the presence of two CH<sub>3</sub> groups at one nitrogen atom of ethylenediamine, resulting in specific steric features that dictate the chemical behavior of the complex. As a consequence, triamine III is formed instead of platinum(IV) tetramine.

The addition of several drops of HCl (1 : 1) to the reaction solution (to prevent the chloroimide formation) accelerates the removal of the pyridine molecule with replacement by Cl<sup>-</sup>. Chlorine oxidation of platinum(II) tetramine without addition of HCl yielded an orange-colored mixture, recrystallization of which from warm water gave a yellow compound and insoluble bright red finely crystalline chloroimide precipitate.

**Table 2.** Atom coordinates (×10<sup>4</sup>) and equivalent isotropic thermal factors (×10<sup>3</sup>) for **III**, **IV**, **V** ( $U_{eq}$  is 1/3 of the sum of orthogonalized anisotropic  $U_{ij}$ )

Atom	x	у	z	$U_{\rm eq},{\rm \AA}^2$			
III							
Pt(1)	-3033(1)	-2698(1)	935(1)	25(1)			
Cl(1)	-464(2)	-1260(2)	930(1)	38(1)			
Cl(2)	-5438(2)	-4383(2)	947(1)	39(1)			
Cl(3)	-3848(2)	-1869(2)	176(1)	40(1)			
Cl(4)	1492(2)	-3309(2)	2109(1)	52(1)			
N(1)	-2448(7)	-3303(6)	1624(2)	32(1)			
N(2)	-4287(6)	-632(5)	1216(2)	31(1)			
N(3)	-1742(6)	-4712(5)	690(2)	30(1)			
C(1)	-3589(12)	-2286(8)	1917(3)	52(2)			
C(2)	-3702(10)	-609(8)	1724(2)	49(2)			
C(3)	-6224(8)	-735(8)	1160(3)	49(2)			
C(4)	-3806(9)	985(7)	1006(3)	52(2)			
C(5)	-2371(8)	-5545(7)	314(2)	38(1)			
C(6)	-1536(9)	-6871(8)	138(2)	43(2)			
C(7)	-6(9)	-7405(7)	362(3)	42(2)			
C(8)	633(8)	-6559(7)	754(2)	42(2)			
C(9)	-248(8)	-5223(7)	909(2)	37(1)			
O(1W)	6661(10)	3602(8)	1963(3)	79(2)			
O(2W)	3108(9)	3129(9)	1830(3)	69(2)			
O(3W)	884(11)	693(9)	2075(3)	91(2)			
		IV					
Pt(1)	1056(1)	8443(1)	5000	54(1)			
Cl(1)	1796(6)	10055(13)	6351(9)	123(5)			
Cl(2)	1770(7)	10093(14)	3655(11)	148(6)			
Cl(3)	153(6)	6972(11)	3732(6)	94(3)			
Cl(4)	-407(7)	6816(10)	6341(7)	105(3)			
N(2)	1975(8)	6424(16)	5062(24)	96(7)			
N(3)	684(10)	7088(24)	6289(16)	152(18)			
N(1)	154(4)	10389(9)	5008(13)	43(2)			
C(1)	-214(11)	11035(19)	4059(10)	53(6)			
C(2)	-863(10)	12293(19)	4114(16)	75(8)			
C(3)	-1145(6)	12906(14)	5118(20)	92(8)			
C(4)	-777(12)	12260(24)	6067(15)	110(11)			
C(5)	-128(11)	11001(22)	6012(11)	70(8)			
C(6)	1904(13)	5141(32)	5992(21)	83(8)			
C(7)	961(13)	5193(23)	6074(17)	79(6)			
C(8)	2866(9)	7176(30)	5079(55)	253(25)			
C(9)	1915(17)	5472(45)	3997(25)	142(18)			
V							
Pl(1)	1129(1)	7922(1)	0155(1)	21(1) 26(1)			
CI(1)	2997(2)	92/0(1)	5555(1) 5072(1)	30(1)			
CI(2)	2338(2)	0.00000000000000000000000000000000000	$\frac{50}{5(1)}$	40(1) 42(1)			
CI(3)	-02(2) 2452(2)	9433(1) 7612(1)	7081(1) 7466(1)	43(1) 20(1)			
$\mathbf{U}(4)$	000(5)	7012(1) 8160(2)	7400(1) 5028(2)	39(1) 32(1)			
N(2)	709(5)	0109(3) 6676(2)	5028(3) 6770(3)	$\frac{32(1)}{28(1)}$			
$\Gamma(2)$	-708(3)	7614(5)	5282(4)	20(1) 46(1)			
C(1)	-2724(7) -2713(7)	6403(4)	5000(4) 5000(4)	40(1) 45(1)			
C(2)	-2213(7) 100(7)	5530(4)	7006(4)	53(1)			
C(3)	-1575(8)	7067(5)	7748(4)	51(1)			
$\sim$	10,0(0)	,007(0)	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	~ 1(1)			

According to X-ray diffraction data, the yellow product was triamine III.

The reaction of an aqueous solution of complex III with chlorine gave a bright red-colored, water-insoluble, finely crystalline homogeneous compound. According to elemental analysis, this was the expected chloroimide  $[Pt{(CH_3)_2N(CH_2)_2NCl}PyCl_3]$  (IV) (Fig. 2). The IR spectrum of complex IV contained no v(OH), v(NH),  $\delta(H_2O)$ , or  $\delta(NH_2)$  absorption bands observed in the IR spectrum of initial complex III (see Experimental). The visible region of the UV/Vis spectrum of a DMF solution of IV exhibited absorption bands at 447 nm (22370 cm<sup>-1</sup>,  $\epsilon = 762.7$  L/(mol cm)), 394 nm (25380 cm<sup>-1</sup>,  $\epsilon =$ 1627 L/(mol cm), 345 nm (28985 cm<sup>-1</sup>,  $\varepsilon$  = 1822 L/(mol cm)), their intensity being much higher than that of the d-d absorption bands in the spectrum of initial triamine III. These spectral changes are always observed in chloroamidation of Pt(IV) amine complexes and are due to the presence of complexes with chloroimide groups  $R-NCl^{-}$  and  $NCl_{2}^{-}$  in the solution [4].

As noted above, we carried out the reaction of triamine [PtEnPyCl<sub>3</sub>]Cl with chlorine several times and obtained three compounds of different colors (red, yellow, and dark yellow) depending on the chlorination time and solution concentration. The compositions of these complexes and the initial triamine are the same according to elemental analysis (Pt : Cl : C : N = 1 : 4 : 9 : 3). Red chloroimide is always contaminated by some yellow compound. The intensity of UV/Vis absorption bands of this chloroimide in a DMF solution (at 22500, 27000, and 30000 cm<sup>-1</sup>,  $\varepsilon = 315$ , 529, and 975 L/(mol cm), respectively) is approximately half that of chloroimide IV, although the intensities of UV/Vis bands of initial triamines are the same. This is explained by the fact that chloroamidation of [PtEnPyCl<sub>3</sub>]Cl yields not only bright red chloroimide [Pt{NCl(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>}PyCl<sub>3</sub>] but also products formed apparently upon oxidative dehy-([Pt(HN=CHCH<sub>2</sub>NH<sub>2</sub>)PyCl<sub>4</sub>] dration of or  $[Pt(N=CHCH_2NH_2)PyCl_4])$ , which are yellow- rather than red-colored [6, 12].

In this work, the reaction of chlorine with platinum(IV) triamine containing N,N-dimethylethylenediamine with one reactive NH<sub>2</sub> group gave a single bright red complex identified as chloroimide [Pt{(CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NCl}PyCl<sub>3</sub>] (IV). From chloroimide solutions in CH<sub>3</sub>CN and DMF, bright red crystals were isolated; the former were studied by X-ray diffraction (see below).

Previously, it was considered that chloroamidation is a reversible reaction if it does not involve cleavage of the metal ring. The reactions of chloroamides with HCl (dechloroamidation) give rise to the initial complexes [13]. However, currently irreversible chloroamidation of [PtEnPy<sub>2</sub>Cl<sub>2</sub>]Cl<sub>2</sub> [14] is known in addition to the reversible chloroamidation of tetramine

Bond	<i>d</i> , Å	Angle	ω, deg	Angle	ω, deg	Bond	<i>d</i> , Å
III		Cl(2)Pt(1)Cl(3)	90.83(6)	N(3)Pt(1)N(2)	79.0(8)	Pt(1)-Cl(1)	2.3191(11)
Pt(1)–N(1)	2.047(4)	C(1)N(1)Pt(1)	107.5(4)	N(1)Pt(1)N(2)	177.6(8)	Pt(1)-Cl(2)	2.3216(11)
Pt(1)–N(3)	2.060(4)	C(2)N(2)C(4)	108.1(5)	N(3)Pt(1)Cl(2)	168.1(6)	N(1)–C(1)	1.480(6)
Pt(1)–N(2)	2.119(4)	C(2)N(2)C(3)	110.0(5)	N(1)Pt(1)Cl(2)	88.1(4)	N(2)–C(4)	1.492(6)
Pt(1)–Cl(1)	2.3071(14)	C(4)N(2)C(3)	106.2(5)	N(2)Pt(1)Cl(2)	94.0(6)	N(2)–C(3)	1.492(6)
Pt(1)–Cl(2)	2.3121(14)	C(2)N(2)Pt(1)	105.1(4)	N(3)Pt(1)Cl(1)	80.8(7)	N(2)–C(2)	1.506(5)
Pt(1)–Cl(3)	2.317(2)	C(4)N(2)Pt(1)	114.2(4)	N(1)Pt(1)Cl(1)	88.9(4)	C(1)–C(2)	1.493(7)
N(1)-C(1)	1.501(9)	C(3)N(2)Pt(1)	113.3(4)	N(2)Pt(1)Cl(1)	89.8(7)	Angle	ω, deg
N(2)–C(2)	1.490(8)	C(5)N(3)C(9)	118.4(5)	Cl(2)Pt(1)Cl(1)	89.6(3)	N(1)Pt(1)N(2)	84.59(13)
N(2)–C(4)	1.498(7)	C(5)N(3)Pt(1)	121.0(4)	N(3)Pt(1)Cl(3)	96.5(6)	N(1)Pt(1)Cl(3)	88.49(11)
N(2)–C(3)	1.500(7)	C(9)N(3)Pt(1)	120.7(4)	N(1)Pt(1)Cl(3)	84.9(4)	N(2)Pt(1)Cl(3)	94.37(11)
N(3)–C(5)	1.334(7)	C(2)C(1)N(1)	108.9(6)	N(2)Pt(1)Cl(3)	96.2(6)	N(1)Pt(1)Cl(4)	177.80(10)
N(3)–C(9)	1.344(7)	C(1)C(2)N(2)	111.1(6)	Cl(2)Pt(1)Cl(3)	93.8(4)	N(2)Pt(1)Cl(4)	93.34(9)
C(1)–C(2)	1.467(9)	N(3)C(5)C(6)	122.5(6)	Cl(1)Pt(1)Cl(3)	172.9(4)	Cl(3)Pt(1)Cl(4)	90.95(5)
C(5)–C(6)	1.367(8)	C(5)C(6)ë(7)	119.3(6)	C(6)N(2)C(9)	111.4(14)	N(1)Pt(1)Cl(1)	91.16(11)
C(6)–C(7)	1.379(10)	C(6)C(7)C(8)	118.2(6)	C(6)N(2)C(8)	107(2)	N(2)Pt(1)Cl(1)	175.47(9)
C(7)–C(8)	1.378(10)	C(9)C(8)C(7)	119.7(6)	C(9)N(2)C(8)	104(3)	Cl(3)Pt(1)Cl(1)	87.06(5)
C(8)–C(9)	1.368(8)	N(3)C(9)C(8)	121.9(6)	C(6)N(2)Pt(1)	115.8(13)	Cl(4)Pt(1)Cl(1)	90.93(4)
Angle	ω, deg	IV	IV		105(2)	N(1)Pt(1)Cl(2)	88.27(11)
N(1)Pt(1)N(3)	93.1(2)	Bond	<i>d</i> , Å	C(8)N(2)Pt(1)	112.3(11)	N(2)Pt(1)Cl(2)	90.65(10)
N(1)Pt(1)N(2)	84.5(2)	Pt(1)–N(3)	1.97(2)	C(7)N(3)Cl(4)	100.7(13)	Cl(3)Pt(1)Cl(2)	173.74(4)
N(3)Pt(1)N(2)	177.4(2)	Pt(1)–N(1)	2.031(6)	C(7)N(3)Pt(1)	104.7(11)	Cl(4)Pt(1)Cl(2)	92.49(5)
N(1)Pt(1)Cl(1)	89.5(2)	Pt(1)–N(2)	2.090(13)	Cl(4)N(3)Pt(1)	112.6(10)	Cl(1)Pt(1)Cl(2)	87.66(4)
N(3)Pt(1)Cl(1)	87.76(13)	Pt(1)–Cl(2)	2.349(8)	C(1)N(1)Pt(1)	122.4(10)	C(1)N(1)Pt(1)	108.7(3)
N(2)Pt(1)Cl(1)	91.09(13)	Pt(1)–Cl(1)	2.360(6)	C(5)N(1)Pt(1)	117.5(10)	C(4)N(2)C(3)	107.0(4)
N(1)Pt(1)Cl(2)	88.4(2)	Pt(1)–Cl(3)	2.381(7)	N(2)C(6)C(7)	96.3(13)	C(4)N(2)C(2)	109.9(4)
N(3)Pt(1)Cl(2)	86.88(13)	Cl(4)–N(3)	1.736(10)	N(3)C(7)C(6)	109(2)	C(3)N(2)C(2)	107.6(4)
N(2)Pt(1)Cl(2)	94.16(13)	N(2)–C(6)	1.495(10)	V		C(4)N(2)Pt(1)	113.4(3)
Cl(1)Pt(1)Cl(2)	174.13(5)	N(2)–C(9)	1.493(10)	Bond	<i>d</i> , Å	C(3)N(2)Pt(1)	114.1(3)
N(1)Pt(1)Cl(3)	175.57(14)	N(2)–C(8)	1.513(9)	Pt(1)–N(1)	2.048(3)	C(2)N(2)Pt(1)	104.7(2)
N(3)Pt(1)Cl(3)	91.25(14)	N(3)–C(7)	1.500(10)	Pt(1)–N(2)	2.126(3)	N(1)C(1)C(2)	109.1(4)
N(2)Pt(1)Cl(3)	91.16(13)	Angle	ω, deg	Pt(1)–Cl(3)	2.3138(11)	C(1)C(2)N(2)	110.6(4)
Cl(1)Pt(1)Cl(3)	91.68(6)	N(3)Pt(1)N(1)	98.8(6)	Pt(1)-Cl(4)	2.3157(10)		
[PtPnPy <sub>2</sub> Cl <sub>2</sub> ]Cl <sub>2</sub> five-membered	$_2$ [5]. No data metal ring a	for Pt(IV) triar re available. We	nines with a studied the	chloroimide l yielded compl	V with co ex VII (~809	ncentrated HC 6) and V (~20%	l at 100°0 ). Accordin

Table 3. Bond lengths (d) and bond angles ( $\omega$ ) in structures II–V

*d*, Å

reaction of chloroimide IV with concentrated HCl at room temperature and obtained compound VI. According to X-ray diffraction data, this was the initial triamine III (unit cell parameters a = 7.92, b = 8.32,c = 29.28 Å,  $\beta = 93.67^{\circ}$ , V = 1927 Å<sup>3</sup>). The reaction of

C ıg to X-ray diffraction data, these were the initial triamine III  $[Pt(N,N-dimeEn)PyCl_3]Cl$  and Pt(IV) diamine [Pt(*N*,*N*-dimtEn)PyCl<sub>4</sub>)], respectively.

X-Ray diffraction studies of complexes III-V gave the following results. The structure of III is ionic and

D−H…, Å	d, Å		DHA angle deg	Coordinates of A stom		
	D–H	Н…А	D…A	DIA aligie, deg	Coordinates of A atom	
III						
N1-H1C…O(1x)	0.90	1.93	2.793(7)	160	x - 1, y - 1, z	
N1-H1DCl(4)	0.90	2.41	3.267(5)	159		
$O(1w)-H(2w)\cdots Cl(4)$	0.76	2.84	3.311(5)	122	-x + 1, y + 1/2, -z + 1/2	
$O(2w)-H(3w)\cdots Cl(4)$	0.76	2.51	3.267(5)	174	x, y + 1, z	
$O(2w)-H(4w)\cdots O(3w)$	0.76	1.99	2.741(8)	172		
$O(3w)-H(5w)\cdots Cl(4)$	0.76	2.43	3.166(5)	164	-x, y + 1/2, -z + 1/2	
O(3w)- $H(6w)$ ··· $Cl(4)$	0.76	2.56	3.280(5)	160		
· · · · · · · · · · · · · · · · · · ·						
N(1)-H(1A)····Cl(1)	0.90	2.45	3.305(4)	158	-x, -y + 2, -z + 1	
N(1)–H(1B)····Cl(4)	0.96	2.58	3.390(4)	149	x - 1/2, -y + 3/2, z - 1/2	

Table 4. Geometric parameters of hydrogen bonds in structures III and V

consists of  $[Pt{(CH_3)_2N(CH_2)_2NH_2}PyCl_3]^+$  complex cations, Cl-anions, and solvation water molecules combined by hydrogen bonds (Table 4). Complexes IV and V are neutral; complex V also contains hydrogen bonds (Table 4). All three structures are octahedral complexes with chelating N,N-dimethylethylenediamine ligands typical of tetravalent platinum. Correspondingly, they have roughly the same bond angles at Pt atoms (Table 3). The Pt-Cl bonds in these three complexes are similar irrespective of the trans-partner. However, note that the Pt-N distances to the chelating ligand are substantially dissimilar. The Pt(1)–N(1) bonds are usually somewhat shorter than Pt(1)-N(2), which is evidently due to the steric overcrowding of the N(1) atom caused by the presence of two methyl groups. Thus, in complex III, Pt–N(1), 2.047(4) Å; Pt–N(2), 2.119(4) Å; in complex V, Pt-N(1), 2.048(3) Å; Pt-N(2), 2.126(3) Å. In the triamine structure with unsubstituted ethylenediamine [PtEnPyCl<sub>3</sub>]Cl, the Pt–N(1) and Pt–N(2) bond lengths are equal (2.05 Å) [8]. The presence of Cl substituent at N(3) in the chelating ligand N,N-dimeEn in complex IV results in insignificant shortening of the Pt-N(3) bond (to 1.97(2) Å). However, to within  $3\sigma$ , this bond length is equal to the corresponding  $Pt-N(H_2)$  bond lengths in complexes III and V. The N(3)-Cl(4) bond length in the  $((CH_3)_2N(CH_2)_2NCI)^-$  ligand in complex IV (1.736(10) Å)

coincides with the N–Cl bond length in the  $NCl_2^-$  ligand of the dichloroimide [Pt(NH<sub>3</sub>)<sub>3</sub>(NCl<sub>2</sub>)<sub>2</sub>Cl]Cl [9]. The Pt– N(Py) bonds in complexes III and IV have similar lengths (2.060(4) and 2.031(6) Å, respectively). The planes of the pyridine rings in these complexes form dihedral angles of 142.6° and 137.2° with the corresponding equatorial planes. The conformation of the dimethylethylenediamine-platinum metal rings in III and V is gauche (the corresponding carbon atoms deviate from the PtN(2) planes to different sides by 0.37 and 1.30 Å in III and 0.33 and 0.34 Å in V) and that in complex IV is envelope with the C(7) atom shifted from the plane through the other atoms by 0.75 Å. The NPtN angles in the ring in III and V are equal (84.5° and 84.6(1)°) and that in IV is somewhat smaller (79.0(8)°).

The structures of VI and VII are identical to that of III.

Thus, X-ray diffraction study of complex III has shown that the reaction of chlorine with platinum(II) tetramine  $[Pt{(CH_3)_2N(CH_2)_2NH_2}Py_2]Cl_2$ (II) results in removal of a pyridine molecule located in the *trans*position to the *N*,*N*-dimethylethylenediamine NH<sub>2</sub> group. The chlorine oxidation of tetramine II does not give platinum(IV) tetramine but gives the triamine  $[Pt(N,N-dimeEn)PyCl_3]Cl(III)$  with a Cl<sup>-</sup> ion in the *trans*-position to the NH<sub>2</sub> group (or in the *cis*-position to the (CH<sub>3</sub>)<sub>2</sub>N group) (Fig. 1).

The reaction of III with chlorine gave the bright redcolored chloroimide  $[Pt\{(CH_3)_2N(CH_2)_2NCl]PyCl_3\}$  (IV) whose structure was confirmed by X-ray diffraction.

Chloroamidation of complex III is a reversible reaction. The reaction of chloroimide IV with HCl at 20°C afforded the initial triamine III (complex VI). At 100°C, the reaction gave ~80% of the initial triamine III and ~20% of platinum(IV) diamine [Pt(N,N-dimeEn)Cl<sub>4</sub>] (V). Somewhat unexpectedly, under these rigorous conditions of dechloroamidation of complex IV containing the ligand (CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>)NCl)<sup>-</sup> (refluxing at 100°C), the five-membered ring was retained but pyridine molecules were partly removed. The reaction of HCl with the dichloroimide  $[Pt\{(NCl(CH_2)_2NCl\}Py_2Cl_2]$  at 100°C resulted in complete chelate destruction but the pyridine molecules were retained (the reaction gave *trans*<sup>\*</sup>- $[Pt(NH_3Py)_2^*Cl_2^*]$  [14]). Thus, the outcome of dechloroamidation of Pt(IV) chloroimides depends on the type of

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the chloroimide ligand and the metal ring geometry.

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