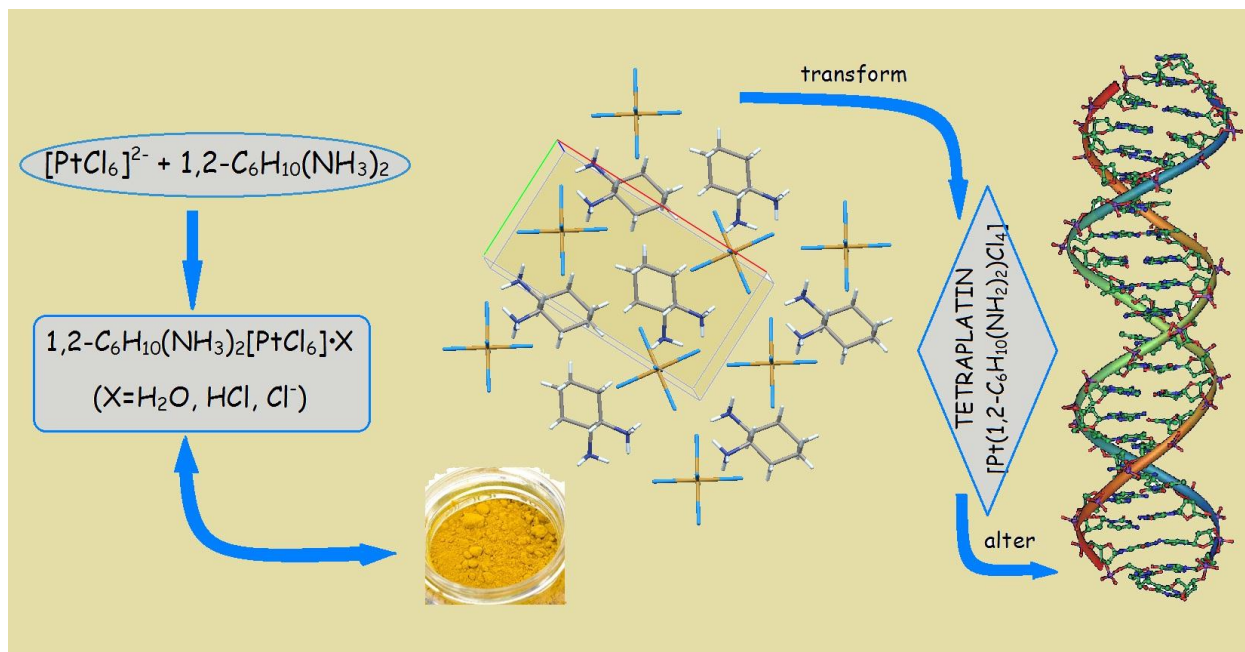


## Supplementary materials

### Graphical abstracts

#### Multivariant crystallization of tetraplatin precursors from solutions containing $1,2\text{-C}_6\text{H}_{10}(\text{NH}_3)_2^{2+}$ and $[\text{PtCl}_6]^{2-}$ ions.

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#### Highlights

1. The crystallization of the solution contained  $[\text{PtCl}_6]^{2-}$  and  $1,2\text{-C}_6\text{H}_{10}(\text{NH}_3)_2^{2+}$  ions was investigated.
2. Seven new phases were obtained at mildly varied crystallization conditions.
3. The phases can be used as precursors for the synthesis of the anticancer drug tetraplatin.
4. The crystal structures of five phases were determined using X-ray powder diffraction technique.
5. The phase diversity is due to specific ion sizes, shapes, symmetry, charges and configurations.

## Synthesis

### (I) 1,2-dachH<sub>2</sub>[PtCl<sub>6</sub>]·H<sub>2</sub>O

1 g ( $1.8 \cdot 10^{-3}$  mol) Na<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was dissolved in 10 ml of water. The solution was stirred at 20-25°C and was added 0.34 g ( $1.8 \cdot 10^{-3}$  mol) to 1,2-dachH<sub>2</sub>Cl<sub>2</sub> in 2 ml of water. The yellow crystalline powder precipitated within a few minutes. The precipitate was filtered off and washed with cold water and acetone and then dried in air. Yield: 45 % respectively to Pt. The substance is well soluble in water, slightly soluble in acetone.

Anal. calc. for C<sub>6</sub>Cl<sub>6</sub>H<sub>18</sub>N<sub>2</sub>OPt (%) : C, 13.296(1); H, 3.3473(3); N, 5.1684(3); Pt, 35.991(6). Found: C, 13.07; H, 3.35; N, 5.10; Pt, 35.42 %.

IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3551, 3474, 3126, 3079, 2944, 2928, 2863, 2601, 2576, 1581, 1513, 1481, 1399, 1372, 1337, 1319, 1281, 1239, 1192, 1137, 1081, 1063, 1027, 1018, 1001, 930, 898, 843, 769, 646, 557, 507, 485, 432.

### (II) 1,2-dachH<sub>2</sub> [PtCl<sub>6</sub>]·2HCl

1 g ( $1.9 \cdot 10^{-3}$  mol) H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was dissolved in a mixture of 5 ml of water, 1 ml of hydrochloric acid and 40 ml of acetone. 0.41 g ( $2.2 \cdot 10^{-3}$  mol) of 1,2-dachH<sub>2</sub>Cl<sub>2</sub> in 5 ml of water was added to the solution. Then it was slowly evaporated at 20-25°C. The resulting pale-yellow precipitate was filtered, washed with acetone and dried in air. Yield: 45 % . The substance is highly soluble in water and acetone.

Anal. calc. for C<sub>6</sub>Cl<sub>8</sub>H<sub>18</sub>N<sub>2</sub>Pt (%): C, 12.073(1); H, 3.0394(3); N, 4.6930(2); Pt, 32.681(5). Found: C, 11.98; H, 3.01; N, 4.54; Pt, 32.55 %.

IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3472, 3331, 3221, 3139, 3018, 2942, 2913, 2861, 1671, 1519, 1450, 1426, 1366, 1321, 1290, 1264, 1230, 1131, 1058, 1003, 958, 878, 822, 804, 609, 559, 512, 497, 450.

### (III) 1,2-dachH<sub>2</sub>[PtCl<sub>6</sub>] (the first modification)

a) Fine powder of 1,2-dachH<sub>2</sub>[PtCl<sub>6</sub>]·H<sub>2</sub>O (I) was dipped into acetic anhydride, heated with stirring up to 110°C and kept for 20 min. The precipitate was filtered off from the hot solution at 90-100°C, and washed with hot acetic acid at 100°C. The substance was dried in the desiccator over fused alkali. Yield: 97 %. The substance is a yellow powder. It gradually adsorbs water and transform into (I) in the air.

b) Phase (III) may be obtained by heating (I), (II), (VI) or (VII) at 120-140°C for an hour, however, the product has a low crystallinity.

Anal. calc. for C<sub>6</sub>Cl<sub>6</sub>H<sub>16</sub>N<sub>2</sub>Pt (%): C, 13.753(1); H, 3.0777(3); N, 5.3461(3); Pt, 37.229(6). Found: C, 13.58; H, 3.04; N, 5.29; Pt, 37.21 %.

IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 3488, 3149, 3127, 2947, 2864, 2550, 1800, 1580, 1481, 1449, 1417, 1400, 1372, 1281, 1238, 1192, 1129, 1076, 1059, 1019, 1000, 970, 928, 898, 852, 772, 646, 554, 508, 431.

**(IV) 1,2-dachH<sub>2</sub>[PtCl<sub>6</sub>] (the second modification)**

Fine powder **1,2-dachH<sub>2</sub>[PtCl<sub>6</sub>]·H<sub>2</sub>O (I)** or **(III)** was dissolved in a minimal amount of concentrated hydrochloric acid at 90-100°C. Acetyl chloride (CH<sub>3</sub>COCl) was added by small portions to the stirred solution until end of precipitation. The separated precipitate was filtered off and washed with hot acetic acid at 100°C. Then it was dried in a desiccator over fused alkali. Yield: 95 % respectively to **(I)** or **(III)**. The substance is a yellow-orange powder. In the air it gradually adsorbs water and transforms to phase **(I)**.

Anal. calc. for C<sub>6</sub>Cl<sub>6</sub>H<sub>16</sub>N<sub>2</sub>Pt (%): C, 13.753 (1); H, 3.0777 (3); N, 5.3461 (3); Pt, 37.229 (6). Found: C, 13.67; H, 3.05; N, 5.44; Pt, 37.16%.

IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 3125, 2946, 2863, 1581, 1481, 1447, 1400, 1371, 1281, 1237, 1191, 1075, 1002, 928, 898, 506, 430.

**(V) (1,2-dachH<sub>2</sub>)<sub>2</sub>[PtCl<sub>6</sub>]Cl<sub>2</sub>**

1 g ( $1.9 \cdot 10^{-3}$  mol) H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was dissolved in 5 ml of water. 0.80 g ( $4.2 \cdot 10^{-3}$  mol) 1,2-dachH<sub>2</sub>Cl<sub>2</sub> in 5 ml of water and 0.05 ml of concentrated hydrochloric acid was added to the resulting solution under stirring at 20-25°C. The solution was left to evaporate slowly at 25-35°C. The resulting orange powder was filtered, washed with glacial acetic acid and then was dried in air. Yield: 60 %. The substance is soluble in water, hardly soluble in glacial acetic acid.

Anal. calc. for C<sub>12</sub>Cl<sub>8</sub>H<sub>32</sub>N<sub>4</sub>Pt (%): C, 20.268 (2); H, 4.5357 (4); N, 7.8788 (3); Pt, 27.433 (4). Found: C, 20.13; H, 4.47; N, 7.34; Pt, 26.96%.

IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 3178, 3124, 3000, 2928, 2866, 2576, 2515, 2008, 1622, 1587, 1569, 1510, 1495, 1462, 1449, 1400, 1374, 1244, 1135, 1076, 1004, 515, 437.

**(VI) 1,2-dachH<sub>2</sub>[PtCl<sub>6</sub>]·HCl (the first modification)**

1 g ( $1.9 \cdot 10^{-3}$  mol) H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was dissolved in 5 ml of water. A solution of 0.80 g ( $4.2 \cdot 10^{-3}$  mol) 1,2-dachH<sub>2</sub>Cl<sub>2</sub> in 5 ml of water and 0.05 ml of concentrated hydrochloric acid was added to the resultant solution at 20-25°C. The glass with solution was placed in the desiccator with concentrated hydrochloric acid for slow saturation of HCl vapor at 20-25°C. The formed yellow precipitate was filtered, washed with glacial acetic acid and dried in air. Yield: 60 %. The powder is soluble in water, slightly soluble in acetic acid.

Anal. calc. for  $C_6Cl_7H_{17}N_2Pt$  (%): C, 12.858 (1); H, 3.0573 (3); N, 4.9983 (3); Pt, 34.807 (6). Found: C, 12.43; H, 3.10; N, 4.74; Pt, 34.56%.

IR spectrum ( $\nu$ ,  $cm^{-1}$ ): 3120, 2928, 2866, 2774, 2575, 2511, 1869, 1585, 1500, 1487, 1454, 1399, 1367, 1315, 1265, 1244, 1197, 1132, 1082, 1005, 934, 903, 845, 650, 560, 509, 439.

### (VII) 1,2-dach $H_2[PtCl_6] \cdot HCl$ (the second modification)

1 g ( $1.9 \cdot 10^{-3}$  mol)  $H_2PtCl_6 \cdot 6H_2O$  was dissolved in 5 ml of water. 0.80 g ( $4.2 \cdot 10^{-3}$  mol) 1,2-dach $H_2Cl_2$  in 5 ml of water and 0.05 ml of concentrated hydrochloric acid was added to the resultant solution at 20-25°C. The solution was heated up to 70°C and equal amount of glacial acetic acid heated at the same temperature was slowly added. The fine crystalline yellow precipitate was filtered off, washed with glacial acetic acid and dried in air. Yield: 75%. The substance gradually transforms into (III) in the air. It is soluble in water, slightly soluble in acetic acid.

Anal. calc. for  $C_6Cl_7H_{17}N_2Pt$  (%): C, 12.858 (1); H, 3.0573 (3); N, 4.9983 (3); Pt, 34.807 (6). Found: C, 12.57; H, 3.03; N, 4.81; Pt, 34.67%.

IR spectrum ( $\nu$ ,  $cm^{-1}$ ): 3117, 2928, 2866, 2809, 2773, 2573, 2510, 1883, 1578, 1500, 1485, 1453, 1399, 1366, 1265, 1243, 1196, 1132, 1082, 1005, 933, 902, 844, 650, 560, 508, 440.

Table 1 - Thermal stability of the synthesized compounds

Tetraplatin $[Pt(1,2\text{-dach})Cl_4] \cdot 1/3H_2O$	Beginning of decomposition 60-90 °C; formation $[Pt(1,2\text{-dach})Cl_2]$ at 320-330 °C, $\Delta m = -17,7$ % (calc.: -16,83 %); complete decomposition, residual weight 42,8 % (calculation on the formation of metal Pt: 42,68 %).
1,2-dach $H_2^{2+} \cdot [PtCl_6]^{2-} \cdot H_2O$ (I)	Cleavage $H_2O$ at 90-140 °C, $\Delta m = -3,3$ % (calc.: -3,32 %); formation $[Pt(1,2\text{-dach})Cl_2]$ at 320-330 °C, $\Delta m = -27,4$ % (calc.: -26,54 %); complete decomposition, residual weight 35,2 % (calculation on Pt: 35,99 %).
1,2-dach $H_2^{2+} [PtCl_6]^{2-} \cdot 2HCl$ (II)	Cleavage $HCl$ at 210 °C; formation $[Pt(1,2\text{-dach})Cl_2]$ at 290-300 °C, $\Delta m = -33,0$ % (calc.: -36,31 %); complete decomposition, residual weight 31,6 % (calc. on Pt: 32,68 %).
$(1,2\text{-dach}H_2^{2+})_2 [PtCl_6]^{2-} \cdot 2Cl^-$ (V)	Beginning of decomposition 150 °C, отщепление $HCl$ и 1,2-dach $H_2Cl_2$ at 270-280 °C, $\Delta m = 29,6$ % (calc.: -26,31 %); formation $[Pt(1,2\text{-dach})Cl_2]$ (340-350 °C), $\Delta m = -16,2$ % (calc.: -20,23 %); complete decomposition, residual weight 26.4% (calc. on Pt: 27,43 %).
1,2-dach $H_2^{2+} [PtCl_6]^{2-} \cdot HCl$ (VI)	Beginning of decomposition: отщепление $HCl$ at 210 °C; formation $[Pt(1,2\text{-dach})Cl_2]$ at 290-300 °C $\Delta m = -29,7$ % (calc.: -32,17 %); complete decomposition, residual weight 30,7 % (calc. on Pt: 34,81 %).

