

## Electronic Supporting Information

### The first representatives of tetranuclear gold (I) complexes of P,N-containing cyclophanes.

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## 1. Experimental

### General

All the reactions and manipulations with phosphines **2** and **3** were carried out under a dry argon atmosphere using standard vacuum-line techniques. All manipulations with complexes **4** and **5** were carried out under normal conditions without inert atmosphere. Solvents were purified, dried, deoxygenated, and distilled before use. EI-MS (70 eV) were recorded with a DFS Thermo Electron Corporation (Germany) spectrometer with direct sample admission into the ion source (ion-source temperature = 2808°C; vaporizer temperature programmed from 50-3508 °C). The XCalibur program was used to process the mass spectrometry data. The mass spectra are reported as *m/z* values with relative intensities (*I<sub>rel</sub>*) [%]. <sup>1</sup>H NMR (400 MHz and 600 MHz) and <sup>31</sup>P NMR (162 and 242 MHz) spectra were obtained with Bruker Avance-DRX 400 and Bruker Avance-600 spectrometers. The chemical shifts are reported in ppm relative to SiMe<sub>4</sub> (<sup>1</sup>H, internal standard), and 85% H<sub>3</sub>PO<sub>4</sub> (aq) (<sup>31</sup>P; external standard). The coupling constants (*J*) are reported in Hz. Determination of the CHN content was carried out on CHN analyzer "CHN-3 KBA". Determination of the phosphorus content was provided by combustion in an oxygen stream.

Starting phosphines **2** and **3** were prepared by the method<sup>1</sup>.

### Preparations

**Tetrachloro(1<sup>3</sup>,1<sup>7</sup>,5<sup>3</sup>,5<sup>7</sup>-tetra[2'-(pyridine-2''-yl)ethyl]-1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphane)tetrargold (I) (4).**

To a solution of **2** (0.0632 g, 0.0603 mmol) in chloroform (3 ml) a solution of Au(THT)Cl (0.0773 g, 0.2411 mmol) in chloroform (5 ml) was added. The reaction mixture was stirred for 2 h with the exclusion of light by wrapping the reaction flask in aluminium foil. The precipitate was separated by the centrifugation, washed triple with chloroform with the centrifugation and dried at 0.05 torr for 1.5 h. The crude **4** was recrystallized from DMF in air with the exclusion of light and the fine dark precipitate of colloid gold was filtered off the hot solution. The recrystallization gave pure **4** as colourless moderately light-sensitive crystals. Yield of **4**: 0.061 g (51 %). Single crystals of **4** suitable for X-ray crystal structure analysis were obtained by slow crystallization from DMF. M.p. >260°C. Found, % :C 37.51; H 3.74; N 5.81; P 6.69. C<sub>62</sub>H<sub>68</sub>N<sub>8</sub>P<sub>4</sub>Au<sub>4</sub>Cl<sub>4</sub>

Calculated, %: C 37.63; H 3.46; N 5.66; P 6.26. <sup>1</sup>H NMR (400 MHz, DMF-d<sub>7</sub>, 303 K) δ<sub>H</sub>, ppm, *J*, Hz : 8.59 (4H, d, <sup>3</sup>J<sub>HH</sub> = 4.1, C<sup>3</sup>H), 7.76 (4H, ddd, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>3</sup>J<sub>HH</sub> = 6.8, <sup>4</sup>J<sub>HH</sub> = 1.9, C<sup>5</sup>H), 7.39 (4H, d, <sup>3</sup>J<sub>HH</sub> = 7.6, C<sup>6</sup>H), 7.27 (8H, d, <sup>3</sup>J<sub>HH</sub> = 8.6, C<sup>9</sup>H), 7.26-7.30 (4H, m, C<sup>4</sup>H, overlaps with C<sup>9</sup>H), 6.95 (8H, d, <sup>3</sup>J<sub>HH</sub> = 8.6, C<sup>8</sup>H), 4.56 (8H, dd, <sup>2</sup>J<sub>HH</sub> = 15.8, <sup>2</sup>J<sub>PH</sub> = 5.3, C<sup>1</sup>H<sub>a</sub>), 4.46 (8H, d, <sup>2</sup>J<sub>HH</sub> = 15.8, C<sup>1</sup>H<sub>b</sub>), 3.90 (4H, s, C<sup>11</sup>H), 3.16-3.24 (8H, m, C<sup>12</sup>H), 2.64-2.71 (8H, m, C<sup>13</sup>H). <sup>31</sup>P NMR (162 MHz, DMF-d<sub>7</sub>, 303 K) δ<sub>P</sub>, ppm.: 10.96 (s). MS (ESI), m/z (%): 1943 (100.0) [M - Cl]<sup>+</sup>, 1987 (85.0) [M - Cl + 2Na<sup>+</sup>]<sup>+</sup>, 2031 (40.0) [M - Cl + 2Na<sup>+</sup> + K<sup>+</sup>]<sup>+</sup>.

**Tetrachloro(1<sup>3</sup>,1<sup>7</sup>,5<sup>3</sup>,5<sup>7</sup>-tetra[2'-pyridine-2''-yl]ethyl)-3,7-dithia-1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphane)tetragold (I) (5)**

Compound **5** (0.05 g, 43%) was prepared by the procedure described above for **4** from **3** (0.0625 g, 0.0576 mmol) and Au(THT)Cl (0.0739 g, 0.2306 mmol). Yield of **5** 0.05 g (43 %). Single crystals of **5** suitable for X-ray crystal structure analysis were obtained by slow crystallization from DMF. M.p.>260°C. Found, %: C 36.08; H 3.57; N 5.45; P 6.09; S 3.76. C<sub>60</sub>H<sub>64</sub>N<sub>8</sub>P<sub>4</sub>S<sub>2</sub>Au<sub>4</sub>Cl<sub>4</sub>. Calculated, %: C 35.77; H 3.20; N 5.56; P 6.15; S 3.18. <sup>1</sup>H NMR (400 MHz, DMF-d<sub>7</sub>, 303 K) δ<sub>H</sub>, ppm, *J*, Hz: 8.59 (4H, d, <sup>3</sup>J<sub>HH</sub> = 4.9, C<sup>3</sup>H), 7.76 (4H, ddd, <sup>3</sup>J<sub>HH</sub> = 7.8, <sup>3</sup>J<sub>HH</sub> = 7.5, <sup>4</sup>J<sub>HH</sub> = 1.6, C<sup>5</sup>H), 7.41 (4H, d, <sup>3</sup>J<sub>HH</sub> = 8.6, C<sup>9</sup>H), 7.39 (4H, d, <sup>3</sup>J<sub>HH</sub> = 7.5, C<sup>6</sup>H), 7.27 (4H, dd, <sup>3</sup>J<sub>HH</sub> = 7.5, <sup>3</sup>J<sub>HH</sub> = 4.9, C<sup>4</sup>H), 7.09 (4H, d, <sup>3</sup>J<sub>HH</sub> = 8.6, C<sup>8</sup>H), 4.60 (8H, dd, <sup>2</sup>J<sub>HH</sub> = 15.4, <sup>2</sup>J<sub>PH</sub> = 5.3, C<sup>1</sup>H<sub>a</sub>), 4.52 (8H, d, <sup>2</sup>J<sub>HH</sub> = 15.4, C<sup>1</sup>H<sub>b</sub>), 3.15-3.25 (8H, m, C<sup>12</sup>H), 2.64-2.73 (8H, m, C<sup>13</sup>H). <sup>31</sup>P NMR (162 MHz, DMF-d<sub>7</sub>, 303 K) δ<sub>P</sub>, ppm. : 10.95 (s). MS (ESI) m/z (%): 1979 (100.0) [M - Cl]<sup>+</sup>, 2023 (35.0) [M - Cl + 2Na<sup>+</sup>]<sup>+</sup>.

## Methods

### Crystallographic data for **4** and **5**

**X-Ray Crystallography.** Crystal of **4** were placed in glass capillary in mother liquor. Data of **4** were collected on a Bruker Smart Apex II CCD diffractometer using graphite monochromated MoKα(λ = 0.71073 Å) radiation and ω-scan rotation at room temperature. Data collection images were indexed, integrated, and scaled using the APEX2 data reduction package<sup>2</sup> and corrected for absorption using SADABS<sup>3</sup>. The structure was solved by direct methods and refined using SHELX<sup>4</sup> program. Were solved 3 solvate molecules of DMF, and 3 strong peaks in difference Fourier map, which was

interpreted as disordered molecule of water. All non-hydrogen atoms of molecule **4** and nitrogen and oxygen atoms of DMF molecules were refined anisotropically, H atoms were calculated on idealized positions and refined as riding atoms. Carbon atoms of solvate molecules and disordered molecule of water was refined isotropically. Solvate molecules of DMF were placed at centers of symmetry and have short contacts with its centrosymmetric dependent DMF molecules. This means that DMF molecules are disordered by 2 position, and refinement of this molecules with occupancies 0.5 give the best R-factors and parameter Goodnes of fit. So, the stehiometry of cystal are one molecule of **4**, 3 molecules of DMF and 2 molecules of water.

Data Crystal of **5** were collected on a RigakuXcalibur, Sapphire3, Gemini CCD diffractometer using graphite monochromated MoK $\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ ) radiation and  $\omega$ -scan rotation at 130 K. Data collection images were indexed, integrated, and scaled using the CrysAlisPro 1.171.38.43 (Rigaku Oxford Diffraction, 2015) data reduction package and corrected for absorption using Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.. The structure was solved by direct methods and refined using SHELX<sup>4</sup> program. Were solved 3 solvate molecules of DMF, which was disordered on 2 positions. All non-hydrogen atoms were refined anisotropically, H atoms were calculated on idealized positions and refined as riding atoms. So, the stehiometry of cystal are one molecule of **5**, and 6 molecules of DMF.

CCDC 1829646 (**4**), 1829645 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12 Union Road, CambridgeCB2 1EZ, UK; fax: +44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

### **Photophysical measurements**

UV/VIS spectra were registered at room temperature on a Perkin-Elmer Lambda 35 spectrometer with a scan speed of 480 nm min<sup>-1</sup>, using a spectral width of 1 nm. All samples were prepared as solutions in dimethylformamide with concentrations of ca. 1-0.5 x 10<sup>-5</sup>mol l<sup>-1</sup> and placed in 10 mm quartz cells. The excitation and emission spectra for solid-state samples at room temperature and at 77 K were measured on Fluorolog 3 (Horiba JobinYvon) spectrofluorimeter of the Center for optical and laser materials research of Saint-Petersburg State University. The powder samples were supported on the

quartz glass plates. LEDs (maximum of emission at 265 nm, 340 nm and 390 nm) were used in pulse mode to pump the luminescence in lifetime measurements (pulse width 0.9 ns, repetition rate 100 Hz to 10 kHz). The integration sphere was used to measure the solid state emission quantum yield for the complexes **4** and **5**.

### Computations

All calculations were performed with the ORCA program of version 4.0.<sup>5</sup> The hybrid PBE0 functional<sup>6</sup> and the Ahlrichs' triple- $\zeta$  def-TZVP AO basis set<sup>7</sup> were used for optimization of all structures. In all geometry optimizations the D3 approach<sup>8</sup> to describe the London dispersion interactions together with the Becke–Johnson (BJ) damping function<sup>9-11</sup> were employed as implemented in the ORCA program. Time-dependent density functional theory (TD-DFT) has been employed to compute the vertical excitation energies (i.e., absorption wavelengths) and oscillator strengths for the ground-state optimized geometries. 50 lowest singlet excited states were taken into account. The procedure was analogous to the one described elsewhere,<sup>12</sup> except that the range-separated CAM-B3LYP functional<sup>13</sup> was used instead of PBE0. The vertical  $T_1 - S_0$  transition energy were computed at the triplet geometries optimized by UPBE0-D3(BJ)/def-TZVP with ih  $\Delta$ -SCF approach.<sup>14</sup>

Table S1. The photophysical properties of compound **2-5**

Compound	Abs. <sup>a</sup> , $\lambda_{\text{abs}}/\text{nm}$ ( $\epsilon$ , $\text{Lmol}^{-1}\text{cm}^{-1}$ )	Exc. <sup>b</sup> , $\lambda_{\text{exc}}/\text{nm}$	Em. <sup>b</sup> , $\lambda_{\text{em}}/\text{nm}$	$\tau_{\text{obs}}$ , $\mu\text{s}$ (fractional intensity*)	Q.Y. <sup>b</sup> , %
<b>2</b>	318 (12000)				
<b>3</b>	291 (167870), 321 (55957)				
<b>4</b>	322 (9600)	<330	505	0,3 (0,37); 1,5 (0,64)	0.8
<b>5</b>	286 (51000), 322 (13000)	340	520	0,3 (0,39); 1,5 (0,61)	1.8

Table S2. Crystal Data and Refinement Details for compounds **4** and **5**

	<b>4</b>	<b>5</b>
chemical_formula_moiety	$\text{C}_{62}\text{H}_{68}\text{Au}_4\text{Cl}_4\text{N}_8\text{P}_4 \cdot 3(\text{C}_3\text{H}_7\text{NO}) \cdot 2(\text{H}_2\text{O})'$	$\text{C}_{60}\text{H}_{64}\text{Au}_4\text{Cl}_4\text{N}_8\text{P}_4\text{S}_2 \cdot 6(\text{C}_3\text{H}_7\text{NO})$

chemical_formula_sum	C <sub>71</sub> H <sub>93</sub> Au <sub>4</sub> Cl <sub>4</sub> N <sub>11</sub> O <sub>5</sub> P <sub>4</sub>	C <sub>78</sub> H <sub>106</sub> Au <sub>4</sub> Cl <sub>4</sub> N <sub>14</sub> O <sub>6</sub> P <sub>4</sub> S <sub>2</sub>
fw	2230.03	2453.43
temp.	296 K	130(2) K
radiation	MoK $\alpha$ , 0.71073	
cryst syst	Triclinic	Monoclinic
space group	P-1	C 2/c
unit cell parametrs		
<i>a</i> (Å)	12.294(4)	31.5754(6)
<i>b</i> (Å)	14.695(5)	9.8714(2)
<i>c</i> (Å)	14.999(5)	28.6481(5)
$\alpha$ (deg)	90.376(4)	90
$\beta$ (deg)	101.121(4)	102.042(2)
$\gamma$ (deg)	105.999(4)	90
vol (Å <sup>3</sup> )	2550.7(15)	8732.9(3)
Z (Z')	1 (1/2) (molecule on a special position)	4 (1/2) (molecule on a special position on a center of symmetry)
density (calcd) (Mg/m <sup>3</sup> )	1.452	1.866
abs coeff (mm <sup>-1</sup> )	5.943	7.001
F(000)	1076	4784
cryst size (mm <sup>3</sup> )	0.080 x 0.09 x 0.10	0.30 x 0.20 x 0.20
$\theta$ range (deg)	1.76, 26.0	2.166 to 32.014°
index ranges	-15: 15 ; -18: 18 ; -18: 18	-45<= <i>h</i> <=46, -14<= <i>k</i> <=14, -37<= <i>l</i> <=42
reflns collected	33494	58404
Independent, observed (I $\geq$ 2 $\sigma$ ), (Rint)	10009, 7155, (0.0339)	14320, 11445, 0.041
data/restraints/parameters	10009/24/448	14320/183 / 509
final R indices		
R1	0.0473,	0.0359,

wR2	0.1521	0.0674.
R indices (all data)		
R1	0.0708,	0.0527,
wR2	0.1700,	0.0736,
goodness-of-fit on F2	1.049	1.052
largest difference peak and hole (e Å <sup>-3</sup> )	-1.150, 1.192	-1.102 , 1.473

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