Synthesis, Structures and Stability of Amido Gold(III) Complexes with

2,2':6',2"-Terpyridine

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Figure S1. ¹H NMR spectrum of $[2](ClO_4)_2$ in DMSO-d₆. a): without D₂O, b): addition of D₂O. The signal at 7.77 ppm which diminished upon the addition of D₂O is assigned to that of the amido proton.

Figure S2. ¹H NMR spectrum of $[\mathbf{2}](ClO_4)_2$ in DMSO-d₆. a): without D₂O, b): addition of D₂O. The signal at 7.64 ppm which diminished upon the addition of D₂O is assigned to that of the amido proton. Because free NH₂pym coexist in the crystal of $[\mathbf{3}](ClO_4)_2$, signals of

NH₂pym are observed at 8.27 and 6.63 ppm (•). $[3](ClO_4)_2$ is not very stable in DMSO and released trpy was also observed.

Figure S3. ORTEP drawing of $[3]^{2+}$. Hydrogen atoms are omitted for clarity.

Figure S4. Electronic spectrum of $[3](ClO_4)_2$. Because of the concentrated solution was required to hamper the dissociation, a DMSO solution of $[Au(trpy)(NHpym)](ClO_4)_2 \cdot 0.2NH_2pym \cdot 0.3H_2O$ (3.0 mg / 1.0 ml) in a thin-layer cell (path length = 1 mm) was used.

Figure S5. Contour diagrams of [1]2+; a): H-3, b): H-2, c): H-1, d): HOMO, e): LUMO, f): L+1, g): L+2, h): L+3, and i): L+4.

Figure S6. 1H NMR spectra of $[1](ClO_4)_2$ in DMSO-d₆ upon the addition of the HClO₄ aq.;

a): without $HClO_4$, b): addition of 1 eq. $HClO_4$ aq., c): NH_2pyCl in $DMSO-d_6$ with $HClO_4$.

The signals newly appearing in b) are assigned to those of protonated NH₂pyCl.

Figure S7. ¹H NMR spectra of $[Au(trpy)(NHpyCl)](ClO_4)_2$ in DMSO-d₆ upon the addition of NaOH aq. a): without NaOH, b): addition of 1eq NaOH aq, c): addition of 2 eq of NaOH aq. The signals in c) are coincident with those of non-coordinating trpy.

Experimental Section

Caution Perchlorate salts are potentially explosive. The salts should be prepared in the minimum amount and treated carefully.

Synthesis

All reagents were purchased from Aldrich, Wako, and TCI. $[Au(trpy)(OH)](ClO_4)_2$ was prepared according to the literature.¹

Preparation of [Au(trpy)(NHpyCl)](ClO₄)₂· H₂O (NH₂pyCl: 2-amino-5-chloropyridine)

[Au(trpy)(OH)](ClO₄)₂ (16.6 mg, 0.025 mmol) was dissolved in 4 ml of water by heating to afford a yellow solution, whose pH was adjusted to 5 by the addition of aqueous HClO₄ (60%). Then, an aqueous solution of NH₂pyCl (16.2 mg, 0.13 mmol, 0.7 mL) whose pH was adjusted to 5 by HClO₄ was added to the solution to afford a red purple solution. Red purple powder was obtained by cooling in a refrigerator, which was filtrated and recrystallized from water to yield red crystalline powder. Yield 2.1 mg (11%).

Elementary Analysis: Obsd(%); C: 31.07, H; 2.28, N; 8.97%. Calcd for [Au(trpy)(NHpyCl)](ClO₄)₂· H₂O; C: ; 31.01, H; 2.21, N; 9.04%. ¹H NMR: δ/ ppm, in DMSO-d₆; 9.01-8.99 (5H, m), 8.86-8.78 (4H, m), 8.22 (2H, t), 7.92 (1H, d), 7.42 (1H, s), 7.00 (1H, s), 6.78 (1H, d).

Preparation of [Au(trpy)(NHpymCl)](ClO₄)₂· H₂O (NH₂pymCl: 2-amino-4-chloropyrimidine)

 $[Au(trpy)(OH)](ClO_4)_2$ (16.6 mg, 0.025 mmol) was dissolved in 4 ml of water by heating to afford a yellow solution, whose pH was adjusted to 5 by the addition of aqueous HClO4 (60%). Then, an aqueous solution of NH₂pymCl (16.2 mg, 0.13 mmol, 0.7 mL) whose pH

was adjusted to 5 by $HClO_4$ was added to the solution to afford red orange solution. Red orange powder was obtained by cooling in a refrigerator, which was filtrated and recrystallized from water to yield red crystalline powder. Yield 3.1 mg (16%).

Elementary Analysis: Obsd(%);C; 30.00, H; 2.20, N; 11.0%. Calcd for [Au(trpy)(NHpymCl)](ClO₄)₂ : C; 30.16, H; 1.73, N; 11.11%. ¹H NMR: δ/ ppm, in DMSO-d₆; 8.99-8.97 (5H, m), 8.90 (2H, d), 8.83 (2H, t), 8.39 (2H, s), 8.17 (2H, s), 7.77 (1H, s).

Preparation of [Au(trpy)(NHpym)](ClO₄)₂ (NH₂pym: 2-aminopyrimidine)

[Au(trpy)(OH)](ClO₄)₂ (16.6 mg, 0.025 mmol) was dissolved in 4 ml of water by heating to afford a yellow solution, whose pH was adjusted to 6 by the addition of aqueous HClO₄ (60%). Then, an aqueous solution of NH₂pym (11.9 mg, 0.13 mmol, 1 mL) whose pH was adjusted to 5 by HClO₄ was added to the solution to afford a red orange solution. Red orange powder was obtained by cooling in a refrigerator, which was filtrated and recrystallized from water to yield red crystalline powder, which was filtered and washed with ether to remove trpy. Yield 2.3 mg (12%).

Elementary Analysis: Obsd(%);C; 31.37, H; 2.41, N; 12.34%. Calcd for $[Au(trpy)(NHpym)](ClO_4)_2 \cdot 0.2NH_2pym \cdot 0.3H_2O : C; 31.81, H; 2.24, N; 12.36\%. ¹H NMR: <math>\delta/$ ppm, in DMSO-d₆; 8.99-8.97 (5H, m), 8.89 (2H, d), 8.82 (2H, t), 8.34 (2H, d), 8.27 (2H, d), 8.18 (2H, d), 7.64 (1H, s), 6.70 (1H, t).

The reaction with aniline in the similar conditions only produced free trpy and unidentified insoluble materials.

Crystal Structure Analysis

Suitable single crystals of $[1](ClO_4)_2 \cdot H_2O$, $[2](ClO_4)_2$, and $[3](ClO_4)_2 \cdot 0.5NH_2pym$ were obtained as described in the preparation section. The selected crystals were mounted onto loops. Measurements of the crystals were made on a Rigaku VariMax RAPID-DW/NAT with Cu K α radiation at -100 °C. Final cell parameters were obtained from a least-squares analysis of reflections with $I > 10\sigma(I)$. Space group determinations were made on the basis of systematic absences, a statistical analysis of intensity distribution, and the successful solution and refinement of the structures. Data were collected and processed using RapidAuto. An empirical absorption correction resulted in acceptable transmission factors. The data were corrected for Lorentz and polarization factors.

All the calculations were carried out using CrystalStructure² and SHELX-97.³ The structures were solved by direct methods and expanded using Fourier and difference Fourier techniques. Details of crystal parameters and structure refinement are given in Table S1. Selected atomic distances and bond angles are shown in Tables S2.

CCDC-1016165 – 1016167 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 (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail deposit@ccdc.cam.ac.uk).

Molecular Orbital Calculation

Single point energy calculation about $[1]^{2+}$ was performed using Gaussian 09W⁴ on the basis of the crystal structure. Excited states were calculated by the method of TD-DFT.

In the calculation, the hybrid functional B3LYP and the basis set LanL2DZ were used. The effects from aqueous solution was evaluated by the self-consisted reaction field method with the polarizable continuum model.

References

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 J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT,

			1	
formula	$C_{20}H_{17}AuCl_3N_5O_9$	$C_{19}H_{13}AuCl_3N_6O_8$	C21H17.5 AuCl2N7.5O8	
formula weight	774.71	756.67	770.79	
crystal dimensions /mm ³	$0.05\times0.05\times0.025$	$0.16 \times 0.01 \times 0.01$	$0.13 \times 0.08 \times 0.02$	
crystal system	monoclinic	orthorhombic	triclinic	
space group	$P2_{1}/c$	Pbca	рĪ	
a /Å	8.46477(15)	7.4498(3)	8.13140(18)	
b /Å	15.5297(3)	23.1880(8)	11.2285(3)	
c /Å	18.5374(4)	26.8342(8)	13.7736(3)	
$\alpha /^{\circ}$	90	90	103.9027(13)	
eta /°	95.4706(10)	90	93.7274(14)	
γ /°	90	90	90.9481(14)	
$V/Å^3$	2425.74(8)	4635.5(3)	1217.47(5)	
Z	4	8	2	
$\rho_{\text{calcd}} (g/cm^3)$	2.121	2.168	2.102	
$2\theta_{max}$ /°	136.48	136.46	136.46	
radiation	Cu Ka	Cu Ka	Cu Ka	
wavelength / Å	1.54187	1.54187	1.54187	
temperature /°C	-100	-100	-100	
no. of refs measured	27092	50300	14071	
no. of refs independent	4448	4230	4376	
no. of refs with $I > 2\sigma(I)$	3903	1806	3221	
no. of variables	343	334	345	
R1, wR2, GOF	0.041, 0.100, 1.087	0.061, 0.144, 0.83	0.062, 0.164, 1.09	
residual, <i>e</i> ⁻ /Å ³	2.34	2.24	2.74	

Table S1. Crystallographic data of complexes $[1](ClO_4)_2$ · H₂O, $[2](ClO_4)_2$, and $[3](ClO_4)_2$ · 0.5NH₂pym^{*a*}

^{*a*} R1 = $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ for reflections with $I > 2\sigma(I)$, wR2 = $[\Sigma(w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2)]^{1/2}$ for all reflections, GOF = $[\Sigma w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$ for all reflections where N_o and N_v are number of independent reflections and variables.

				[1](ClO ₄) ₂ · H ₂ O	[2](ClO ₄) ₂	[3](ClO ₄) ₂ · 0.5NH ₂ pym
atomi	atomic distances					
A	Au1	N1		2.031(5)	2.001(10)	2.023(10)
A	Au1	N2		1.960(5)	1.947(11)	1.940(10)
A	Au1	N3		2.032(5)	2.014(11)	2.053(11)
A	Au1	N4		1.984(5)	1.966(10)	1.961(11)
A	Au1	N5		2.963(5)	3.023(11)	3.056(10)
bond angles						
N1	А	u1	N2	80.9(2)	81.4(5)	80.8(4)
N1	А	ul	N3	161.7(2)	162.5(5)	161.1(4)
N1	А	ul	N4	102.5(2)	97.0(5)	98.6(4)
N2	А	ul	N3	80.9(2)	81.5(5)	80.4(4)
N2	А	ul	N4	176.0(2)	178.1(4)	178.5(4)
N3	A	u1	N4	95.8(2)	100.1(4)	100.3(4)

Table S2. Selected atomic distances and bond angles of $[1](ClO_4)_2$ · H₂O, $[2](ClO_4)_2$, and $[3](ClO_4)_2$ · 0.5NH₂pym.

	AE		2		f	major con	ntribution	0/_
1	1 7079	eV	726	nm	J 0.0127	HOMO	$\rightarrow I I MO$	60
1	1.7079	CV	720	11111	0.0127	номо	$\rightarrow LOMO$	38
						HOMO	$\rightarrow \Gamma \perp I$	30
2	2.0541	eV	604	nm	0.0059	НОМО	\rightarrow LUMO	39
						НОМО	\rightarrow L+1	60
3	2.6481	eV	468	nm	0.0002	НОМО	\rightarrow L+2	99
4	3.0676	eV	404	nm	0.0049	H-1	→ LUMO	63
						H-1	\rightarrow L+1	36
5	3.3678	eV	368	nm	0.0090	H-1	→ LUMO	36
						H-1	\rightarrow L+1	63
6	3.4493	eV	359	nm	0.0012	НОМО	\rightarrow L+3	98
7	3.5140	eV	353	nm	0.0014	Н-2	\rightarrow LUMO	32
						Н-2	\rightarrow L+1	6
						НОМО	\rightarrow L+4	60
8	3.5157	eV	353	nm	0.0033	Н-2	→ LUMO	50
						Н-2	\rightarrow L+1	8
						НОМО	\rightarrow L+4	38
9	3 5912	eV	345	nm	0.0561	Н_3	→ LUMO	76
,	5.5712		575		0.0201	н.3	\rightarrow L+1	20
						Н-2	\rightarrow LUMO	3
10	3.7322	eV	332	nm	0.0029	Н-2	\rightarrow LUMO	14
						Н-2	\rightarrow L+1	85

Table S3. Calculated low energy excited states and oscillator strengths of $[1]^{2+}$.



Figure S1. ¹H NMR spectrum of $[2](ClO_4)_2$ in DMSO-d₆. a): without D₂O, b): addition of D₂O. The signal at 7.77 ppm which diminished upon the addition of D₂O is assigned to that of the amido proton.



Figure S2. ¹H NMR spectrum of $[\mathbf{3}](ClO_4)_2$ in DMSO-d₆. a): without D₂O, b): addition of D₂O. The signal at 7.64 ppm which diminished upon the addition of D₂O is assigned to that of the amido proton. Because free NH₂pym coexist in the crystal of $[\mathbf{3}](ClO_4)_2$, signals of NH₂pym are observed at 8.27 and 6.63 ppm (•). $[\mathbf{3}](ClO_4)_2$ is not very stable in DMSO and released trpy was also observed.



Figure S3. ORTEP drawing of $[3]^{2+}$. Hydrogen atoms are omitted for clarity.



Figure S4. Electronic spectrum of [**3**](ClO₄)₂. Because of the concentrated solution was required to hamper the dissociation, a DMSO solution of $[Au(trpy)(NHpym)](ClO_4)_2 \cdot 0.2NH_2pym \cdot 0.3H_2O$ (3.0 mg / 1.0 ml) in a thin-layer cell (path length = 1 mm) was used.



Figure S5. Contour diagrams of [1]²⁺; a): H-3, b): H-2, c): H-1, d): HOMO, e): LUMO, f): L+1, g): L+2, h): L+3, and i): L+4.



Figure S6. ¹H NMR spectra of $[1](ClO_4)_2$ in DMSO-d₆ upon the addition of the HClO₄ aq.; a): without HClO₄, b): addition of 1 eq. HClO₄ aq., c): NH₂pyCl in DMSO-d₆ with HClO₄. The signals appearing in b) correspond to those of protonated NH₂pyCl.



Figure S7. ¹H NMR spectra of $[Au(trpy)(NHpyCl)](ClO_4)_2$ in DMSO-d₆ upon the addition of NaOH aq. a): without NaOH, b): addition of 1eq NaOH aq, c): addition of 2eq of NaOH aq. The signals in c) are coincident with those of non-coordinating trpy.