# Tetra- and Hexanuclear String Complexes of the Coinage Metals

Milena Dahlen,<sup>[a]</sup> Tim P. Seifert,<sup>[a]</sup> Sergei Lebedkin,<sup>[b]</sup> Michael T. Gamer,<sup>[a]</sup> Manfred M. Kappes,<sup>[b,c]</sup>

and Peter W. Roesky\*<sup>[a]</sup>

а.	Institute of Inorganic Chemistry; Karlsruhe Institute of Technology (KIT)
	Engesserstr. 15, 76131 Karlsruhe (Germany); E-mail: roesky@kit.edu
b.	Institute of Nanotechnology; Karlsruhe Institute of Technology (KIT)
	Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen (Germany)
С.	Institute for Physical Chemistry; Karlsruhe Institute of Technology (KIT)
	Fritz-Haber-Weg 2, 76131 Karlsruhe (Germany)

## Content

1	General procedures				
2 Synthetic procedures					
	2.1	[dpfam(AuCl)₃Au(tht)] ( <b>1</b> )	4		
	2.2	[dpfam2Cu2(AuMes)2] ( <b>2</b> )	4		
	2.3	[dpfam2Ag2(AuMes)2] ( <b>3</b> )	5		
	2.1	[dpfam2Au2(AuC6F5)4] <b>(4)</b>	5		
3	Pho	otoluminescence measurements	6		
4 Spectra (ESI MS and ATR IR) and additional figures					
	4.1	[dpfam2Cu2(AuMes)2] ( <b>2</b> )	8		
	4.2	[dpfam2Ag2(AuMes)2 ( <b>3</b> )	. 10		
	4.3	[dpfam2Au2(AuC6F5)4] <b>(4)</b>	. 12		
5	Cry	Crystallographic Data14			
6	References				

#### Synthesis and analytics

#### **1** General procedures

All herein reported reactions were carried out using common Schlenk technique (dual manifold Schlenk line with a vacuum up to  $1\cdot 10^{-3}$  mbar, N<sub>2</sub>.as inert gas) or an MBraun glove box (argon atmosphere) in order to exclude air and moisture.All reactions, crystallization and product storage was done in the dark using common aluminum foil to wrap all respective glassware.

Dry diethyl ether and *n*-pentane were obtained from an MBraun solvent purification system (SPS-800). THF was dried trough distillation over potassium and benzophenone. All dried solvents were stored under a nitrogen atmosphere in Schlenck glassware.

IR spectra were recorded on a Bruker Tensor 37 FTIR spectrometer equipped with a DLaTGS detector, a diamond ATR (attenuated total reflection) unit and a nitrogen flushed chamber. The intensity of signals was classified into the categories vs = very strong, s = strong, m = medium, w = weak and vw = very weak.

A LTQ Orbitrap XL Q Exactive mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe was used to obtain ESI mass spectra. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific).

Elemental analyses were carried out on a Vario MICRO cube instrument from *Elementar Analysensysteme GmbH*.

Ligand precursor Kdpfam,<sup>1</sup> [AuCl(tht)],<sup>1,2</sup> [AuC<sub>6</sub>F<sub>5</sub>(tht)],<sup>3</sup> [CuMes]<sub>5</sub><sup>4</sup> and [AgMes]<sub>4</sub><sup>4</sup> were prepared according to literature procedures.

Tetrahydrothiophene wasobtained from common commercial sources and used without further purification.

Single crystals for diffraction analysis were taken from the crystallization mother liquor and transferred directly into the instrument (see section 5). For all other analytical methods the crystalline product was isolated from the mother liquorby decantation and dried under reduced pressure.

#### 2 Synthetic procedures

## 2.1 [dpfam(AuCl)<sub>3</sub>Au(tht)] (1)



Kdpfam (100 mg, 166  $\mu$ mol, 1.00 eq) and [AuCl(tht)] (213 mg, 664  $\mu$ mol, 4.00 eq) were dissolved in in 12 mL of cold THF (precooled with an iPrOH/liquid N<sub>2</sub> bath) and the mixture was allowed to warm up to room temperature. Ten drops of tetrahydrothiophene were added and the mixture was stirred for another 2 h. After filtration (PTFE syringe filter) and diffusion of diethylether into the solution, the product was obtained as colorless crystals which were partly

suitable for X-ray diffraction. Due to the products instability upon drying, no yield was determined and no further analytics were possible.

#### 2.2 [dpfam<sub>2</sub>Cu<sub>2</sub>(AuMes)<sub>2</sub>] (2)



Kdpfam (250 mg, 415  $\mu$ mol, 5.00 eq) and 133 mg [AuCl(tht)] (133 mg, 415  $\mu$ mol, 5.00 eq) were stirred in 12 mL THF for 1.5 h (room temperature). The yellow suspension was filtered through a PTFE syringe filter\* and given to a solution of [CuMes]<sub>5</sub> (75.8 mg, 83  $\mu$ mol, 1.00 eq) in 5 mL of THF. The orange solution was stirred for another 1.5 h. The orange crystalline product (141 mg, 74.7  $\mu$ mol, 36% calculated without solvents) was obtained by diffusion of pentane into the THF solution.

\*Alternatively, the filtration might be done after the reaction prior to crystallization.

**MS** (ESI): m/z (%) = 1886.333 [M]+(calc. 1886.323), 1767.245 [M-Mes]<sup>+</sup> (calc. 1767.237). – **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 3053 (w), 1590 (m), 1571 (m), 1546 (vs), 1530 (s), 1480 (w), 1460 (w), 1434 (s), 1360 (s), 1346 (m), 1265 (w), 1216 (w), 1201 (m), 1128 (w), 1096 (w), 966 (w), 747 (w), 735 (w), 691 (m), 524 (w), 505 (w), 482 (w). – **EA**: C<sub>92</sub>H<sub>80</sub>N<sub>4</sub>P<sub>4</sub>Cu<sub>2</sub>Au<sub>2</sub>: calculated C 58.57; H 4.27; N 2.97; found C 58.50; H 4.06; N 2.99.

The crystalline product showed too low solubility to get interpretable NMR spectra.

## 2.3 [dpfam<sub>2</sub>Ag<sub>2</sub>(AuMes)<sub>2</sub>] (3)



Kdpfam (150 mg, 249  $\mu$ mol, 4.00 eq) and[AuCl(tht)] (79.8 mg, 249  $\mu$ mol, 4.00 eq) were stirred for 1.5 h in 10 mL of THF. The yellow suspension was filtered via a PTFE syringe filter onto a cooled (with liquid N<sub>2</sub>/*i*PrOH bath) solution of [AgMes]<sub>4</sub> (56.5 mg, 62.2  $\mu$ mol, 1.00 eq) in 5 mL of THF and stirred for another 1.5 h. The pale amber crystalline product (82 mg, 41.5  $\mu$ mol, 33% calculated without solvent) was obtained by diffusion of pentane into the THF solution.

**MS** (ESI): m/z (%) = 989.147 [0.5M+H]<sup>+</sup> (cal. 989.145), 1855.198 [M-Mes]<sup>+</sup>(cal. 1855.190). – **IR** (ATR):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3070 (w), 3051 (w), 2912 (vw), 2857 (w), 1586 (w), 1564 (m), 1530 (vs), 1477 (m), 1457 (m), 1433 (s), 1349 (s), 1309 (w), 1285 (w), 1261 (w), 1218 (w), 1203 (w), 1156 (w), 1127 (vw), 1094 (w), 1066 (m), 1027 (w), 998 (vw), 925 (w), 903 (w), 843 (w), 775 (w), 745 (m), 694 (m), 520 (w), 506 (m), 474 (w), 445 (w), 413 (vw). – **EA:** C<sub>92</sub>H<sub>80</sub>N<sub>4</sub>P<sub>4</sub>Ag<sub>2</sub>Au<sub>2</sub>: calculated C 55.94; H 4.08; N 2.84; found C 56.07; H 4.05; N 2.80.

The crystalline product showed too low solubility to get interpretable NMR spectra.

## 2.1 [dpfam<sub>2</sub>Au<sub>2</sub>(AuC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (4)



Kdpfam (150 mg, 249  $\mu$ mol, 1.00 eq) and [AuCl(tht)] (79.8 mg, 249  $\mu$ mol, 1.00 eq) were stirred overnight in 12 mL of THF before the solvent was removed under reduced pressure. The remaining solids were extracted with toluene (~10 mL) and the suspension was filtered onto 225 mg [AuC<sub>6</sub>F<sub>5</sub>(tht)] (498  $\mu$ mol, 2.00 eq) in a cooled flask (N<sub>2</sub>/*i*PrOH bath). The mixture was allowed to stir overnight while warming up to room temperature. The solvent was removed

under reduced pressure and the pale yellow solids were suspended in ~15 mL of diethyl ether. After storing over 2-3 days at room temperature the product was obtained as colorless crystals in a pale yellow mother liquor. (100 mg, 32.8  $\mu$ mol, 26% calculated containing one molecule of diethylether).

**MS** (ESI): m/z (%) = 2613.183 [M-AuC<sub>6</sub>F<sub>5</sub>+H]<sup>+</sup> (cal. 2613.177), 2249.223 [M-2(AuC<sub>6</sub>F<sub>5</sub>)+2H]<sup>+</sup> (cal. 2249.219). – **IR** (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 1544 (s), 1499 (s), 1454 (s), 1435 (vs), 1353 (m), 1203 (w), 1101 (w), 1056 (w), 953 (s), 798 (w), 749 (m), 693 (m), 545 (w). – **EA**: C<sub>98</sub>H<sub>58</sub>N<sub>4</sub>P<sub>4</sub>Au<sub>6</sub>F<sub>20</sub>+Et<sub>2</sub>O: calculated C 40.15; H 2.25; N 1.84; found C 40.26; H 2.28; N 2.01.

Despite some solubility in e.g. THF- $d_8$ , **4** shows uninterpretable resonances in NMR spectra which might be due to decomposition in solution.

#### **3** Photoluminescence measurements

PL measurements were performed with a Horiba Jobin Yvon Fluorolog-322 spectrometer equipped with a closed-cycle optical cryostat (Leybold) operating within a temperature range of ca. 15-300 K. Solid samples (crystalline powders) were measured as dispersions in a thin layer of viscous polyfluoroester oil placed between two 1 mm quartz plates. The latter were mounted on the cold finger of the cryostat. Sample emission was collected at *ca*. 30° angle relative to the excitation light beam. All emission spectra were corrected for the wavelength-dependent response of the spectrometer and detector (in relative photon flux units). Emission decay traces were recorded by connecting a photomultiplier to a 500 MHz oscilloscope (via a 50, 500 or 2.500  $\Omega$  load, depending on the decay time scale) and using a nitrogen laser (~2 ns, ~5  $\mu$ J per pulse) for pulsed excitation at 337 nm. Several hundred traces were usually acquired and averaged. PL quantum yields at ambient temperature were determined using an integrating sphere out of optical PTFE, which was installed into the sample chamber of the spectrometer, according to the method of de Mello et al.<sup>5</sup> The uncertainty of these measurements was estimated to be ±10%.



**Figure S 3-1:** Emission decay traces (black) of solid **2-4** at low (20 K) and ambient temperatures and ns-pulsed laser excitation at 337 nm. The red lines indicate decay fits with monoexponential and biexponential curves.

#### 4 Spectra (ESI MS and ATR IR) and additional figures

## 4.1 [dpfam<sub>2</sub>Cu<sub>2</sub>(AuMes)<sub>2</sub>] (2)



**Figure S 4-1:**Graphic of the solid state structure of **2** with highlighted  $\pi$ -stacking (selection) between the parallel-displaced phenyl rings.



Figure S 4-2:ESI-MS analytics of 2. Shown is the signal for the [M]<sup>+</sup> ion. Top: experimental spectrum; Bottom: simulated signals.



Figure S 4-3: ESI-MS analytics of 2. Shown is the signal for the [M-Mes]<sup>+</sup> ion. Top: experimental spectrum; Bottom: simulated signals.



Figure S 4-4: ATR IR spectra of 2.

## 4.2 [dpfam<sub>2</sub>Ag<sub>2</sub>(AuMes)<sub>2</sub> (3)



**Figure S 4-5:**Graphic of the solid state structure of **3** with highlighted  $\pi$ -stacking between the parallel-displaced phenyl rings (selection).



Figure S 4-6: ESI-MS analytics of 3. Shown is the signal for the [M-Mes]<sup>+</sup> ion. Top: experimental spectrum; Bottom: simulated signals.



**Figure S 4-7:** ESI-MS analytics of **3**. Shown is the signal for the [0.5 M+H]<sup>+</sup> ion. Top: experimental spectrum; Bottom: simulated signals.



Figure S 4-8: ATR IR spectrum of 3.

## 4.3 [dpfam<sub>2</sub>Au<sub>2</sub>(AuC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (4)



**Figure S 4-9:** Graphic of the solid state structure of **4** with highlighted  $\pi$ -stacking (selection) between the parallel-displaced phenyl rings.



**Figure S 4-10:** ESI-MS analytics of **4**. Shown is the signal for the  $[M-AuC_6F_5+H]^+$  ion. Top: experimental spectrum; Bottom: simulated signals.



**Figure S 4-11:** ESI-MS analytics of **4**. Shown is the signal for the [M-2AuC<sub>6</sub>F<sub>5</sub>+2H]<sup>+</sup> ion. Top: experimental spectrum; Bottom: simulated signals.



Figure S 4-12:ATR IR spectrum of 4.

## 5 Crystallographic Data

A crystal suitable for single X-ray diffraction was covered in mineral oil (Aldrich) and mounted on a glass fiber. The selected crystal was directly transferred to the cold stream of a STOE IPDS 2 or a STOE StadiVari diffractometer. All structures were solved by using the programs SHELXS/T<sup>6</sup> and Olex2.<sup>7</sup> Remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on  $F^2$  by using the program SHELXL.<sup>6</sup> In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 2117887-2117890. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Substance	1 [dpfam(AuCl)₃(Au( <i>tht</i> )]	2 [dpfam <sub>2</sub> Cu <sub>2</sub> (AuMes) <sub>2</sub> ]	3 [dpfam <sub>2</sub> Ag <sub>2</sub> (AuMes) <sub>2</sub> ]	4 [dpfam <sub>2</sub> Au <sub>2</sub> (AuC <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]
Identification code	MD126	MD143	MD147	MD183
Empirical formula	C <sub>41</sub> H <sub>37</sub> Au <sub>4</sub> Cl <sub>3</sub> N <sub>2</sub> P <sub>2</sub> S ·1.5 THF	C <sub>92</sub> H <sub>80</sub> Au <sub>2</sub> Cu <sub>2</sub> N <sub>4</sub> P <sub>4</sub> , 0.5 (THF), 0.5 (C <sub>5</sub> H <sub>12</sub> )	) C <sub>92</sub> H <sub>80</sub> Ag <sub>2</sub> Au <sub>2</sub> N <sub>4</sub> P <sub>4</sub> , 2 (THF)	C <sub>98</sub> H <sub>58</sub> Au <sub>6</sub> F <sub>20</sub> N <sub>4</sub> P <sub>4</sub> , Et <sub>2</sub> O
Formula weight	1654.10	1958.61	2119.36	3051.28
Temperature/K	100.0	150	150	100.0
Crystal system	monoclinic	trigonal	triclinic	monoclinic
Space group	P21/c	R3c	PĪ	P21/c
a/Å	27.7643(13)	35.0732(3)	12.1796(5)	17.0505(7)
b/Å	12.9640(4)	35.0732(3)	12.4715(5)	22.6822(7)
c/Å	31.9939(16)	39.2104(4)	15.0606(6)	13.1960(6)
α/°			85.096(3)	
β/°	109.695(4)		71.854(3)	99.353(3)
γ/°			80.296(3)	
Volume/ų	10842.1(9)	41771.7(8)	2141.46(16)	5035.6(3)
Z	8	18	1	2
ρ <sub>calc</sub> g/cm <sup>3</sup>	2.027	1.401	1.643	2.012
µ/mm⁻¹	11.071	3.717	3.993	8.857
F(000)	6160.0	17586.0	1052.0	2860.0
Crystal size/mm <sup>3</sup>	0.408 × 0.179 × 0.037	0.497 × 0.347 × 0.162	$0.227 \times 0.194 \times 0.102$	0.272 × 0.141 × 0.043
Radiation	ΜοΚα (λ = 0.71073 Å)	ΜοΚα (λ = 0.71073 Å)	ΜοΚα (λ = 0.71073 Å)	Μο Κα (λ = 0.71073 Å)
20 range for data collection/°	4.926 to 56.412	3.696 to 50.684	3.316 to 58.982	3.014 to 63.012
Index ranges	-36 ≤ h ≤ 32, -17 ≤ k ≤ 15, -35 ≤ l ≤ 42	$-42 \le h \le 42, -39 \le k \le 42, -47 \le l \le 47$	$-16 \le h \le 16, -14 \le k \le 17, -19 \le l \le 20$	$0 - 21 \le h \le 22, -31 \le k \le 26, -13 \le l \le 18$
Reflections collected	48035	74831	21888	27656
Independent reflections	24014 [R <sub>int</sub> = 0.0714, R <sub>sigma</sub> = 0.0965]	8416 [R <sub>int</sub> = 0.0280, R <sub>sigma</sub> = 0.0111]	11667 [R <sub>int</sub> = 0.0275, R <sub>sigma</sub> = 0.0417]	13692 [R <sub>int</sub> = 0.0457, R <sub>sigma</sub> = 0.0708]
Data/restraints/parameters	24014/60/1090	8416/48/517	11667/0/517	13692/24/642
Goodness-of-fit on F <sup>2</sup>	0.989	1.120	1.030	0.980
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0803, wR <sub>2</sub> = 0.2077	R <sub>1</sub> = 0.0269, wR <sub>2</sub> = 0.0756	$R_1 = 0.0323$ , $wR_2 = 0.0747$	$R_1 = 0.0497$ , $wR_2 = 0.1209$
Final R indexes [all data]	R <sub>1</sub> = 0.1191, wR <sub>2</sub> = 0.2324	R <sub>1</sub> = 0.0322, wR <sub>2</sub> = 0.0809	R <sub>1</sub> = 0.0476, wR <sub>2</sub> = 0.0792	$R_1 = 0.0767$ , $wR_2 = 0.1323$
Largest diff. peak/hole / e Å <sup>-3</sup>	5.78/-4.36	0.74/-0.30	3.57/-0.93	2.52/-2.66



**Figure S 5-1:** Molecular structure of **1** in the solid state. Hydrogen atoms and non-coordinating solvent molecules are omitted for clarity. Thermal ellipsoids displayed to encompass 40 % probability.Please note, two molecules crystallized in the asymmetric unit. Due to only minor differences in both molecules and for better visibility, just one molecule is displayed. Selected bond lengths [Å] and angles [°]: Au1-Au2 2.9579(8), Au2-Au3 2.9529(9), Au1-P1 2.245(4), P2-Au4 2.254(4), N1-Au2 2.096(13), N2-Au3 2.019(11), S1-Au2 2.284(4), Cl1-Au1 2.302(4), Cl2-Au3 2.259(4), N1-C1 1.30(2), C1-N2 1.33(2), Au3-Au2-Au1 98.45(2), P1-Au1-Cl1 171.46(14), N1-Au2-S1 172.2(4), N2-Au3-Cl2 171.6(4), P2-Au4-Cl3 177.67(14), N1-C1-N2 123.3(14).



**Figure S 5-2:**Molecular structure of the tetranuclear bimetallic complex **2** in the solid state. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity. Atoms labelled with a dash are symmetry generated. Selected bond lengths [Å] and angles [°]: Au-Cu 2.9960(4), Au-P1 2.2951(9), Au-C39 2.062(4), Cu-Cu' 2.7939(9), Cu-P2 2.4106(10), Cu-N1 1.929(3), Cu-N2 1.948(3), N1-C1 1.320(4), N2-C20 1.317(4), Cu-Cu-Au 111.62(2), C39-Au-P1 167.67(10), N1-Cu-P2 109.73(9), N1-Cu-N2 165.63(12), N2-Cu-P2 84.39(9), N1-C1-N1' 123.9(5), N2-C20-N2' 124.7(5).



**Figure S 5-3:** Molecular structure of **3** in the solid state. Hydrogen atoms and non-coordinating solvent molecules are omitted for clarity. Thermal ellipsoids displayed to encompass 40 % probability. Selected bond lengths [Å] and angles [°]: Au-Ag 2.9756(3), Ag-Ag' 2.9009(5), Au-P1 2.3110(9), Au-C38 2.057(4), Ag-P2 2.5934(9), Ag-N1 2.171(3), Ag'-N2 2.186(3), N1-C1 1.315(4), N2-C1 1.313(5), Ag'-Ag-Au 102.197(13), C38-Au-P1 173.80(10), N1-Ag-N2' 164.18(11), N2'-Ag-P2' 78.86(8).



**Figure S 5-4:**Molecular structure of the homometallic hexanuclear complex **4** in the solid state. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity. Atoms labelled with a dash are symmetry generated. Selected bond lengths [Å] and angles [°]: Au1-Au1' 2.9221(6), Au1-Au2' 3.0017(4), Au1-N1' 2.076(5), Au1-P1 2.246(2), N1-C19 1.305(9), N2-C19 1.328(9), Au2-N2 2.095(6), Au2-C38 2.013(8), P2-Au3 2.283(2), Au3-C44 2.041(8), Au1-Au1'-Au2 103.118(14), N1'-Au1-P1 176.7(2), C38-Au2-N2 170.9(3), C44-Au3-P2 170.5(2), N1-C19-N2 127.4(6).

#### 6 References

- M. Dahlen, M. Kehry, S. Lebedkin, M. M. Kappes, W. Klopper and P. W. Roesky, *Dalton Trans.*, 2021, **50**, 13412-13420.
- S. Ahrland, K. Dreisch, B. Norén and Å. Oskarsson, *Mater. Chem. Phys.*, 1993, **35**, 281-289.
- T. Lauterbach, M. Livendahl, A. Rosellón, P. Espinet and A. M. Echavarren, *Org. Lett.*, 2010, **12**, 3006-3009; C. Kaub, PhD thesis, Karlsruhe Institute of Technology, 2016.
- E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1989, **8**, 1067-1079.
- J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9**, 230-232.
- G. M. Sheldrick, Journal, 1997; G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112-122; G. M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 3-8.
- O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339-341.