Electronic Supplementary Information

Mononuclear gold(III) complexes with diazanaphthalenes: the influence of the position of nitrogen atoms in the aromatic rings on the complex crystalline properties

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Abstract

A series of mononuclear gold(III) complexes of the general formula [$AuCl_3$(diazanaphthalene)], where diazanaphthalene is quinazoline (qz, **1**), phthalazine (phtz, **2**), 1,5-naphthyridine (1,5-naph, **3**), 1,6-naphthyridine (1,6-naph, **4**) or 1,8-naphthyridine (1,8-naph, **5**), were prepared and fully characterized. The complexes **1–5** consist of discrete monomeric species with the Au(III) cation in a square planar coordination geometry surrounded by three chloride anions and one diazanaphthalene ligand. Crystallographic studies indicate the presence of an extended 4 + 1 or 4 + 2 geometry around the square planar [$AuCl_3$(diazanaphthalene)] center due to Au···Cl and Au···N interactions. The crystal structures of these complexes are controlled by a variety of intermolecular interactions that utilize the amphiphilic properties of the coordinated chloride anions and involve C–H groups, π-electrons, and an uncoordinated nitrogen atom of the diazanaphthalene ligand. The usual offset π-stacking between the N-heteroaromatic ligands appears to be completely hindered between the 1,5-naph fragments and significantly weakened between the 1,6-naph and 1,8-naph in their respective complexes **3**, **4** and **5**, for which the average molecular polarizability (α) values are the lowest in the series. It is remarkable that the [$AuCl_3$(benzodiazine)] complexes **1** and **2** form centrosymmetric crystals, but the [$AuCl_3$(naphthyridine)] complexes **3–5** assemble into non-centrosymmetric aggregates, making them potential alternatives to the previously studied systems for application in various fields by taking advantage of their polarity.

Keywords: Gold(III) complexes; Diazanaphthalenes; Spectroscopy; X-ray crystallography; Non-centrosymmetric crystals; DFT calculations.

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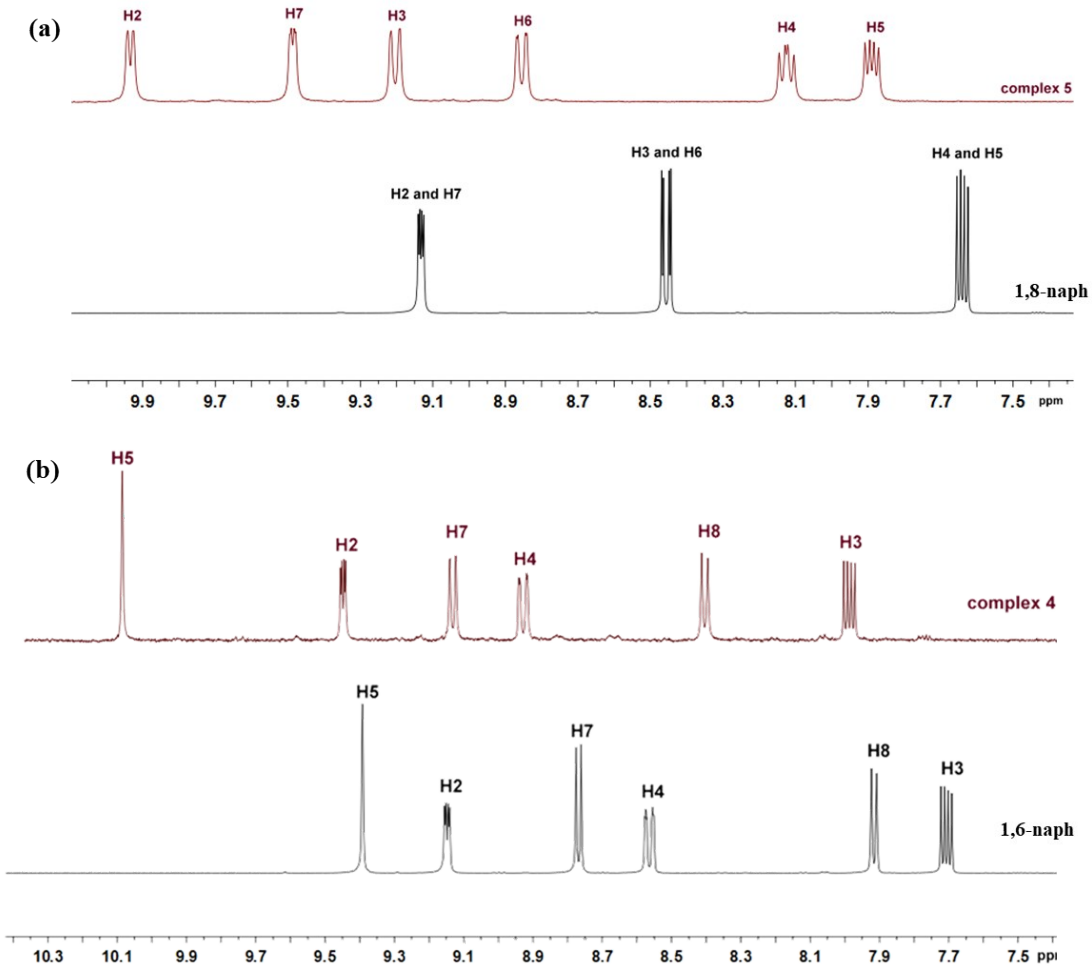

Fig. S1 ^{1}H NMR spectra of (a) symmetrical 1,8-naph ligand and the corresponding gold(III) complex **5**, and (b) asymmetrical 1,6-naph ligand and the corresponding gold(III) complex **4** recorded in acetone-d_6 at ambient temperature (400 MHz).

Table S1 Crystal data for complexes **1-5**. For all structures: molecular formula $C_8H_6AuCl_3N_2$ and MW = 433.46.

	1	**2**	**3**	**4**	**5**
Crystal data					
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Orthorhombic, $Pna2_1$	Monoclinic, $P2_1$	Monoclinic, Cc
a, b, c (Å)	7.6012(4), 7.6086(5), 9.9648(4)	7.8424(4), 8.1614(4), 9.7794(5)	12.9111(4), 12.1129(4), 6.7647(2)	4.0553(1), 11.2233(2), 11.6686(3)	7.5601(2), 22.2124(5), 13.5335(3)
α, β, γ (°)	111.477(5), 92.248(4), 92.294(5)	113.353(5), 95.989(4), 104.639(4)	90, 90, 90	90, 93.193(2), 90	90, 103.107(3), 90
V (Å^3)	534.96(5)	541.06(5)	1057.94(6)	530.26(2)	2213.45(9)
Z	2	2	4	2	8
D_x (Mg m^{-3})	2.691	2.661	2.721	2.715	2.601
Packing Index [%]	69.1	69.8	70.7	70.5	67.5
μ (mm^{-1})	14.46	14.29	14.62	14.59	13.98
Crystal size (mm)	0.35 × 0.18 × 0.10	0.20 × 0.20 × 0.10	0.23 × 0.20 × 0.16	0.23 × 0.20 × 0.05	0.35 × 0.25 × 0.10
Data collection					
T_{min}, T_{max}	0.045, 0.293	0.050, 0.216	0.074, 0.210	0.324, 0.733	0.023, 0.338
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8983, 1874, 1774	9111, 1914, 1817	7169, 1871, 1747	9371, 1878, 1828	22331, 3878, 3804
R_{int}	0.044	0.038	0.027	0.042	0.051
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.595	0.595	0.595	0.595

Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.044, 1.07	0.018, 0.040, 1.12	0.017, 0.035, 1.06	0.020, 0.047, 1.08	0.020, 0.044, 1.04
No. of reflections	1874	1914	1871	1878	3878
No. of parameters	128	128	128	127	254
No. of restraints	0	0	1	1	2
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.88, -0.70	0.65, -0.64	0.38, -0.49	0.53, -0.68	0.39, -0.49
Absolute structure	–	–	Refined as an inversion twin.	Flack x determined using 838 quotients [(I+)-(I-)]/[(I+)+(I-)]	Refined as an inversion twin.
Absolute structure parameter	–	–	0.608(14)	-0.030(6)	0.442(11)

Table S2 Selected bond distances (Å) and valence angles (°) in gold(III) complexes with diazanaphthalene ligands **1-5**. DFT calculations were performed at M06-2X/(LanL2TZ(f)+cc-pVTZ)//M06-2X/(LanL2TZ(f)+cc-pVDZ) level of theory *in vacuo*.

	1			**2**			**3**			**4**			**5**		
	calc.	**X-ray**		**calc.**	**X-ray**		**calc.**	**X-ray**		**calc.**	**X-ray**		**calc.**	**X-ray**	
Au—C11	2.303	2.2819(13)	Au—C11	2.314	2.2724(13)	Au—C11	2.308	2.283(2)	Au—C11	2.308	2.277(3)	Au—C11	2.307	2.275(3)	2.281(3)
Au—Cl2	2.255	2.2590(13)	Au—Cl2	2.256	2.2662(12)	Au—Cl2	2.257	2.2709(18)	Au—Cl2	2.256	2.258(2)	Au—Cl2	2.257	2.257(3)	2.265(3)
Au—Cl3	2.309	2.2698(12)	Au—Cl3	2.297	2.2797(12)	Au—Cl3	2.303	2.2763(19)	Au—Cl3	2.303	2.275(3)	Au—Cl3	2.307	2.268(3)	2.271(3)
Au—N3	2.097	2.049(4)	Au—N2	2.070	2.027(4)	Au—N1	2.083	2.053(6)	Au—N6	2.096	2.057(8)	Au—N1	2.081	2.052(9)	2.037(8)
N1—C2	1.300	1.297(6)	N2—N3	1.344	1.372(5)	N1—C2	1.418	1.337(11)	N6—C5	1.322	1.320(12)	N1—C2	1.318	1.323(14)	1.328(12)
N1—C9	1.365	1.351(6)	N2—C1	1.313	1.308(6)	N1—C9	1.372	1.361(12)	N6—C7	1.371	1.362(13)	N1—C9	1.369	1.366(13)	1.384(12)
N3—C2	1.378	1.367(6)	N3—C4	1.306	1.301(6)	N5—C6	1.311	1.324(14)	N1—C2	1.313	1.326(16)	N8—C8	1.313	1.338(14)	1.335(14)
N3—C4	1.321	1.322(6)				N5—C10	1.361	1.355(11)	N1—C9	1.361	1.344(16)	N8—C9	1.348	1.322(13)	1.341(13)
N3—Au—Cl1	89.77	91.72(11)	N2—Au—Cl1	87.75	89.80(11)	N1—Au—Cl1	88.92	89.64(17)	N6—Au—Cl1	89.55	89.6(3)	N1—Au—Cl1	88.37	88.5(3)	88.5(2)
N3—Au—Cl2	179.70	178.03(11)	N2—Au—Cl2	179.40	176.18(11)	N1—Au—Cl2	179.30	178.0(3)	N6—Au—Cl2	179.83	178.5(3)	N1—Au—Cl2	179.36	179.0(3)	178.0(3)
N3—Au—Cl3	89.25	88.56(11)	N2—Au—Cl3	89.37	88.22(10)	N1—Au—Cl3	88.28	88.31(17)	N6—Au—Cl3	89.71	89.3(3)	N1—Au—Cl3	87.90	90.2(3)	90.2(2)
Cl1—Au—Cl2	90.50	90.24(6)	Cl1—Au—Cl2	91.65	91.52(5)	Cl1—Au—Cl2	91.24	91.75(8)	Cl1—Au—Cl2	90.35	89.56(11)	Cl1—Au—Cl2	91.89	91.21(12)	90.88(12)
Cl1—Au—Cl3	178.77	178.36(5)	Cl1—Au—Cl3	175.99	178.01(5)	Cl1—Au—Cl3	176.97	174.80(9)	Cl1—Au—Cl3	179.11	178.41(10)	Cl1—Au—Cl3	175.86	178.67(13)	178.68(13)
Cl2—Au—Cl3	90.47	89.49(5)	Cl2—Au—Cl3	91.23	90.46(5)	Cl2—Au—Cl3	91.55	90.42(7)	Cl2—Au—Cl3	90.39	91.50(11)	Cl2—Au—Cl3	91.83	90.12(12)	90.43(12)
Au—N3—C2	120.59	120.5(3)	Au—N2—C1	120.92	120.9(3)	Au—N1—C2	117.42	116.5(6)	Au—N6—C5	119.92	119.0(7)	Au—N1—C2	121.91	121.4(8)	124.4(7)
Au—N3—C4	120.87	120.9(3)	Au—N2—N3	115.58	115.8(3)	Au—N1—C9	122.29	121.8(6)	Au—N6—C7	120.11	120.7(6)	Au—N1—C9	117.58	116.5(7)	115.8(6)
C2—N3—C4	118.53	118.4(4)	C1—N2—N3	123.49	122.9(4)	C2—N1—C9	120.28	121.7(7)	C5—N6—C7	119.98	120.3(8)	C2—N1—C9	120.50	122.0(10)	119.8(9)
C2—N1—C9	117.75	118.2(4)	N2—N3—C4	117.71	116.0(4)	C6—N5—C10	117.29	118.5(8)	C2—N1—C9	116.70	117.3(9)	C8—N8—C9	117.16	115.9(10)	114.8(10)

Table S3 Geometrical parameters describing Au···Cl and Cl···Cl interactions in **1-5**.

Cl···Cl Au···Cl	X···X [Å]	d [Å]	θ_1 / θ_2 [°]*	Symmetry operations
1	Cl1···Cl3	3.582(2)	138.47(7) / 137.54(6)	*x+1,+y,+z*
	Cl3···Cl3	3.462(2)	132.68(8) / 132.68(8)	*-x+1,-y+1,-z+2*
	Cl1···Au1	3.295(2)		*-x+2,-y,-z+2*
	Cl2···Au1	3.665(2)		*-x+2,-y+1,-z+2*
2	Cl1···Cl3	3.444(2)	158.32(7) / 156.37(6)	*x+1,+y,+z*
	Cl2···Cl2	3.548(2)	136.77(8) / 136.77(8)	*-x+1,-y,-z*
	Cl3···Au1	3.530(2)		*-x+1,-y+1,-z+1*
3	Cl1···Cl2	3.721(3)	110.03(8) / 175(9)	*x+1/2,-y+1/2,+z*
	Cl2···Cl3	3.694(4)	59.78(8) / 108.35(8)	*-x+1,-y,+z+1/2*
	Cl3···Cl3	3.684(3)	73.83(9) / 59.96(8)	*-x+1,-y,+z-1/2*
	Cl3···Au1	3.218(2)		*-x+1,-y,+z-1/2*
4	Cl1···Cl2	3.328(4)	141.49(12) / 169.22(14)	*-x+1,+y-1/2,-z+1*
	Cl1···Au1	3.427(3)		*x+1,+y,+z*
	Cl3···Au1	3.378(3)		*x-1,+y,+z*
5	Cl1···Au2	3.465(3)		*x-1/2,-y+1/2,+z-1/2*
	Au1···Cl4	3.553(3)		*x-1/2,-y+1/2,+z-1/2*
	Cl3···Cl5	3.684(4)	165.06(14) / 115.71(14)	
	Cl4···Cl6	3.731(4)	109.91(12) / 163.25(14)	*x,-y+1,+z+1/2*

*θ_1 and θ_2 are two Au-Cl···Cl angles

Table S4 Geometrical parameters for the shortest intra- and intermolecular hydrogen bonds.

	D–H [Å]	H···A [Å]	D···A [Å]	D-H···A [°]	Symmetry operations on A
1_qz					
C2–H2···Cl1	0.93	2.76	3.247(5)	114	
C4–H4···Cl3	0.93	2.72	3.104(4)	105	
C2–H2···N1	0.93	2.49	3.167(7)	129	*-x+2,-y,-z+1*
C6–H6···Cl2	0.93	2.90	3.524(5)	126	*x-1,+y-1,+z-1*
C7–H7···Cl2	0.93	2.91	3.531(5)	126	*x-1,+y-1,+z-1*
2_phtz					
C1–H1···Cl1	0.93	2.85	3.740(6)	161	*-x+2,-y+1,-z+1*
C1–H1···Cl3	0.93	2.89	3.469(7)	122	*-x+1,-y+1,-z+1*
C4–H4···Cl2	0.93	2.98	3.847(6)	156	*x,+y,+z+1*
C4–H4···Cl2	0.93	2.95	3.524(6)	121	*-x+1,-y,-z+1*
C5–H5···Cl2	0.93	3.00	3.846(6)	151	*-x+1,-y,-z+1*
C6–H6···Cl3	0.93	2.97	3.645(6)	130	*-x+1,-y+1,-z+2*
C7–H7···Cl3	0.93	2.86	3.725(4)	155	*x+1,+y+1,+z+1*
3_1,5-naph					
C8–H8···Cl1	0.93	2.98	3.471(8)	114	
C4–H4···N5	0.93	2.58	3.340(11)	139	*-x+2,-y,+z+1/2*
C2–H2···Cl2	0.93	2.90	3.730(9)	149	*-x+1,-y,+z+1/2*
C2–H2···Cl3	0.93	2.58	3.752(9)	144	*-x+1,-y,+z+1/2*
C8–H8···Cl3	0.93	2.88	3.285(8)	108	*-x+1,-y,+z-1/2*
4_1,6-naph					
C5–H5···Cl1	0.93	2.98	3.307(10)	102	
C7–H7···N1	0.93	2.66	3.551(15)	160	*-x+1,+y+1/2,-z+2*
C2–H2···Cl3	0.93	3.03	3.864(11)	150	*x,+y-1,+z*
C3–H3···Cl2	0.93	3.00	3.907(12)	164	*x-1,+y-1,+z*
C4–H4···Cl1	0.93	2.90	3.610(12)	134	*-x,+y-1/2,-z+1*
C4–H4···Cl2	0.93	3.05	3.935(12)	160	*-x,+y-1/2,-z+1*
C5–H5···Cl1	0.93	2.84	3.506(10)	130	*x-1,+y,+z*
C8–H8···Cl3	0.93	2.92	3.770(10)	153	*-x+1,+y-1/2,-z+2*
5_1,8-naph					
C7–H7···N18	0.93	2.70	3.301(14)	124	*x,-y+1,+z-1/2*
C2–H2···Cl4	0.93	2.84	3.683(13)	152	*x-1/2,-y+1/2,+z-1/2*
C2–H2···Cl5	0.93	3.02	3.511(13)	115	*x-1/2,-y+1/2,+z-1/2*
C3–H3···Cl1	0.93	2.97	3.882(14)	168	*x-1,+y,+z*
C5–H5···Cl4	0.93	3.01	3.662(11)	128	*x-1,+y,+z-1*
C5–H5···Cl6	0.93	2.81	3.634(14)	149	*x-1,-y+1,+z-1/2*
C7–H7···Cl6	0.93	2.98	3.751(14)	141	*x,-y+1,+z-1/2*
C17–H17···N8	0.93	2.65	3.283(14)	126	*x,-y+1,+z+1/2*
C12–H12···Cl1	0.93	2.80	3.631(11)	149	*x+1/2,-y+1/2,+z+1/2*
C13–H13···Cl4	0.93	2.95	3.870(13)	170	*x+1,+y,+z*

C15–H15···Cl3	0.93	2.78	3.605(13)	148	*x+1,-y+1,+z+1/2*
C15–H15···Cl5	0.93	3.04	3.667(11)	126	*x+1,-y+1,+z+1/2*
C16–H16···Cl1	0.93	2.82	3.319(11)	115	*x+1/2,+y+1/2,+z+1*
C17–H17···Cl3	0.93	2.92	3.656(14)	138	*x,-y+1,+z+1/2*

Table S5 Geometrical parameters describing π···π interactions in **1, 2, 4** and **5**.*

	h(Å)	r(Å)	Θ(°)	Symmetry code
1				
Ar/Ar	3.381	1.348	0	*-x+1,-y-1,-z+1*
Ar/Pm	3.469	1.189	0	*-x+1,-y,-z+1*
2				
Ar/Ar	3.447	1.109	0	*-x+2,-y+1,-z+2*
Ar/Pz	3.447	1.268	0	*-x+2,-y+1,-z+2*
4				
Py/Py	3.617	1.793	0	*x+1,y,z*
Py/Py	3.617	1.833	0	*x+1,y,z*
5				
Py/Py	3.686	1.249	1.8	*x-1,-y+1,+z-1/2*

*Ar = arene ring;
Pm = pyrimidine ring;
Pz = pyridazine ring;
Py= pyridine ring;
h = distance between planes defined by diazanaphthalene fragments;
r = displacement parameter defined as a distance between the centers of the six-membered rings engaged in stack projected on a plane defined by atoms of one of the two interacting rings;
Θ = inclination of one ring plane in relation to the other ring plane.