Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

for

Gold(III) Six-membered N^C^N Pincer Complexes: Synthesis, Structure, Reactivity and Theoretical Calculations.

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Description of the supramolecular structure of 1[$AuCl_4$]Cl

In compound **1**[$AuCl_4$]Cl the HN^CH^NH dications and counterions $[AuCl_4]^-$ and Cl^- are linked into a complex three-dimensional framework by a combination of two weak independent C-H···Cl interactions and one N-H···Cl hydrogen bond (Figure S1 and Table S2). However, the structure of **1**[$AuCl_4$]Cl can be easily analyzed in terms of two more simple one- and two-dimensional substructures. In the first substructure the two N-H protons of the $[HN^CH^NH]^{2+}$ moiety are hydrogen bonded to the Cl(4) chloride anion. Propagation by translation then generates helical chains running along the [1 0 0] direction (Figure S2). The second substructure consist of layers parallel to (1 0 0), as shown in Figure S2, generated by weak C-H···Cl interactions (H···Cl distances 2.826 and 2.897 Å)[1]. The Cl(3) chloride ligand of the tetrachloroaurate anion, and the symmetry generated Cl(3') atom, located in *trans* position, are hydrogen bonded to a methylenic group and a aryl ring of two different HN^CH^NH dications (Figure S3). In the literature there exist many examples of structures containing the same type of intermolecular interactions to form a supramolecular architecture.[2]

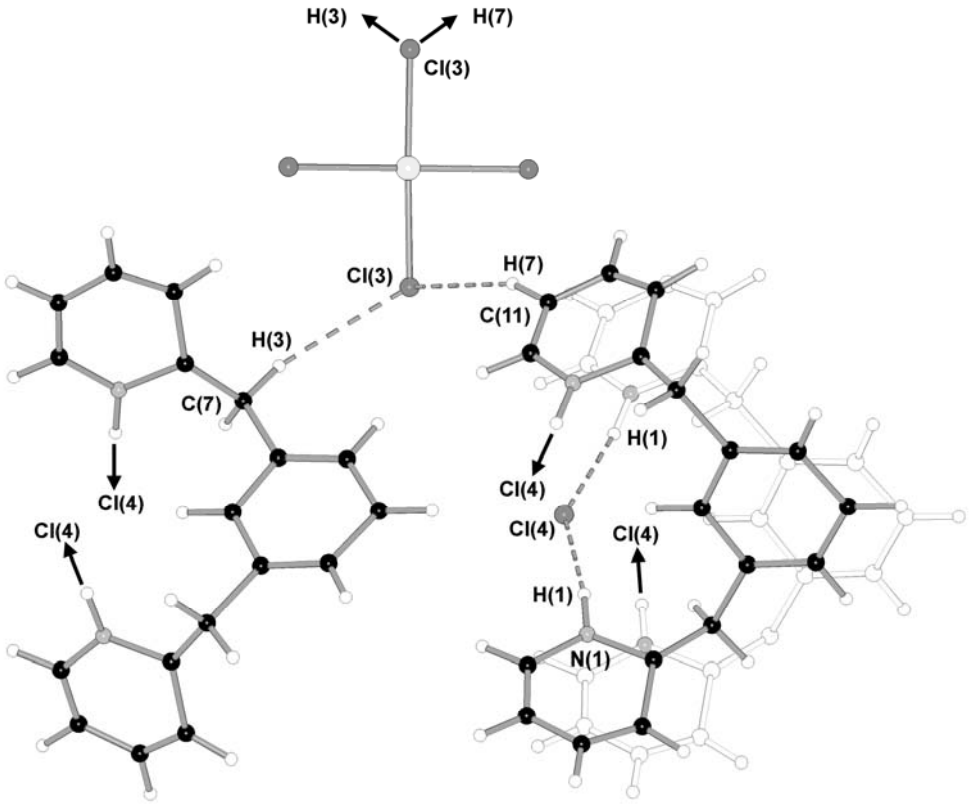

Figure S1. A schematic representation of the hydrogen bonding structure in [HN^CH^NH][$AuCl_4$]Cl, **1**[$AuCl_4$]Cl. Only atoms involved in hydrogen bonding are labeled. Hydrogen bonds are represented by dotted lines. The arrows indicate the continuation of the hydrogen-bonded network.

Table S1. Hydrogen-bond geometry (Å, °) for **1**[$AuCl_4$]Cl[1]

Donor – H…*Acceptor*	*D* – H	H…*A*	*D*…*A*	*D* – H…*A*
N(1) – H(1)···Cl(4)	0.970	2.063	3.026(12)	171.8
C(11) – H(7)···Cl(3)	0.970	2.826	3.737(23)	156.8
C(7) – H(3)^{i}···Cl(3)	0.970	2.896	3.847(27)	166.7

Symmetry codes: (i) –*x*, *y*, *z*+½

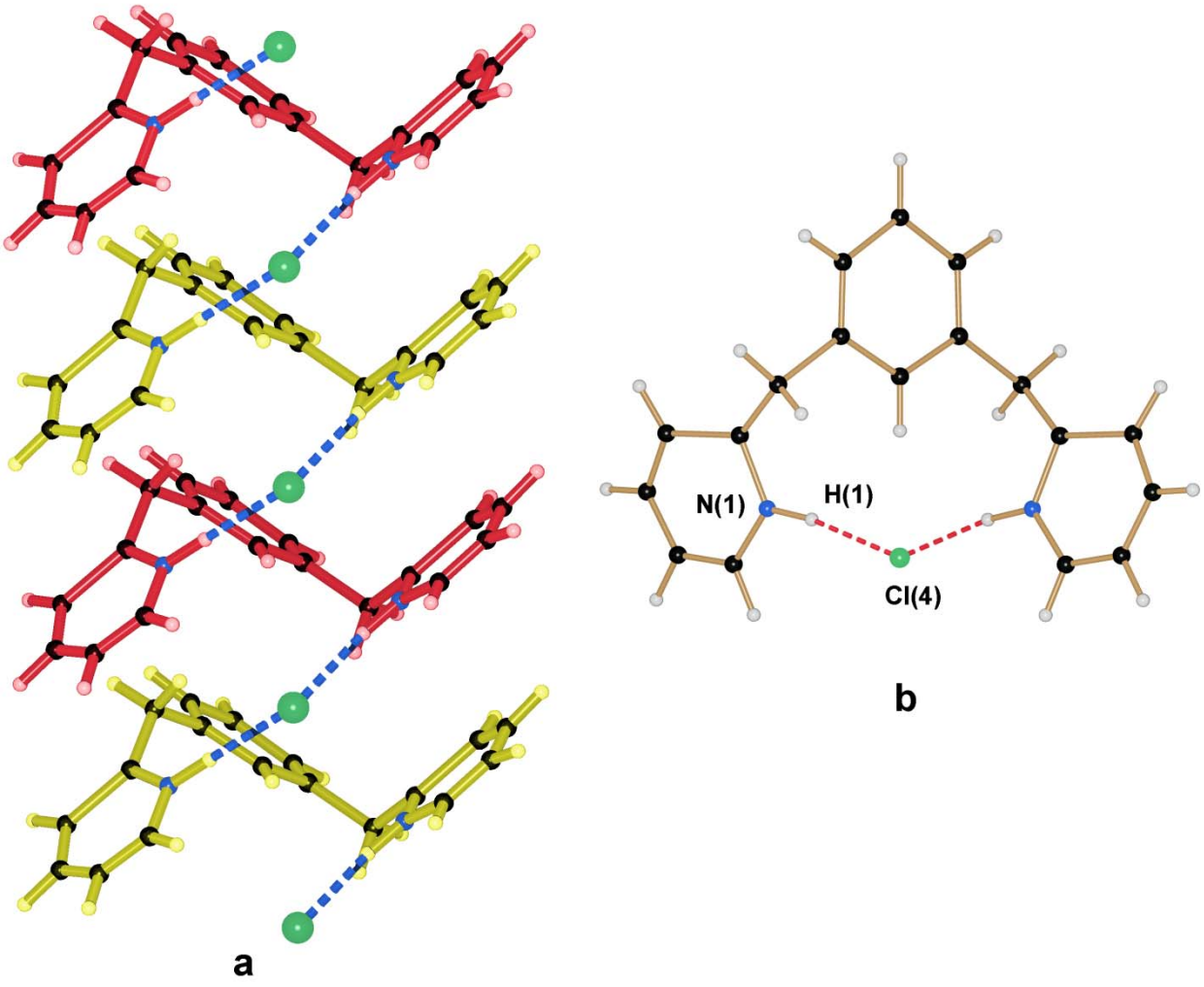

Figure S2 a) Part of the crystal structure of **1**[$AuCl_4$]Cl, showing the formation of helical chains parallel to the [1 0 0] direction. The broken lines indicate the N-H···Cl hydrogen bond between dipyridinium dications and chloride anion. b) A view of the helical chain along *a*-axis.

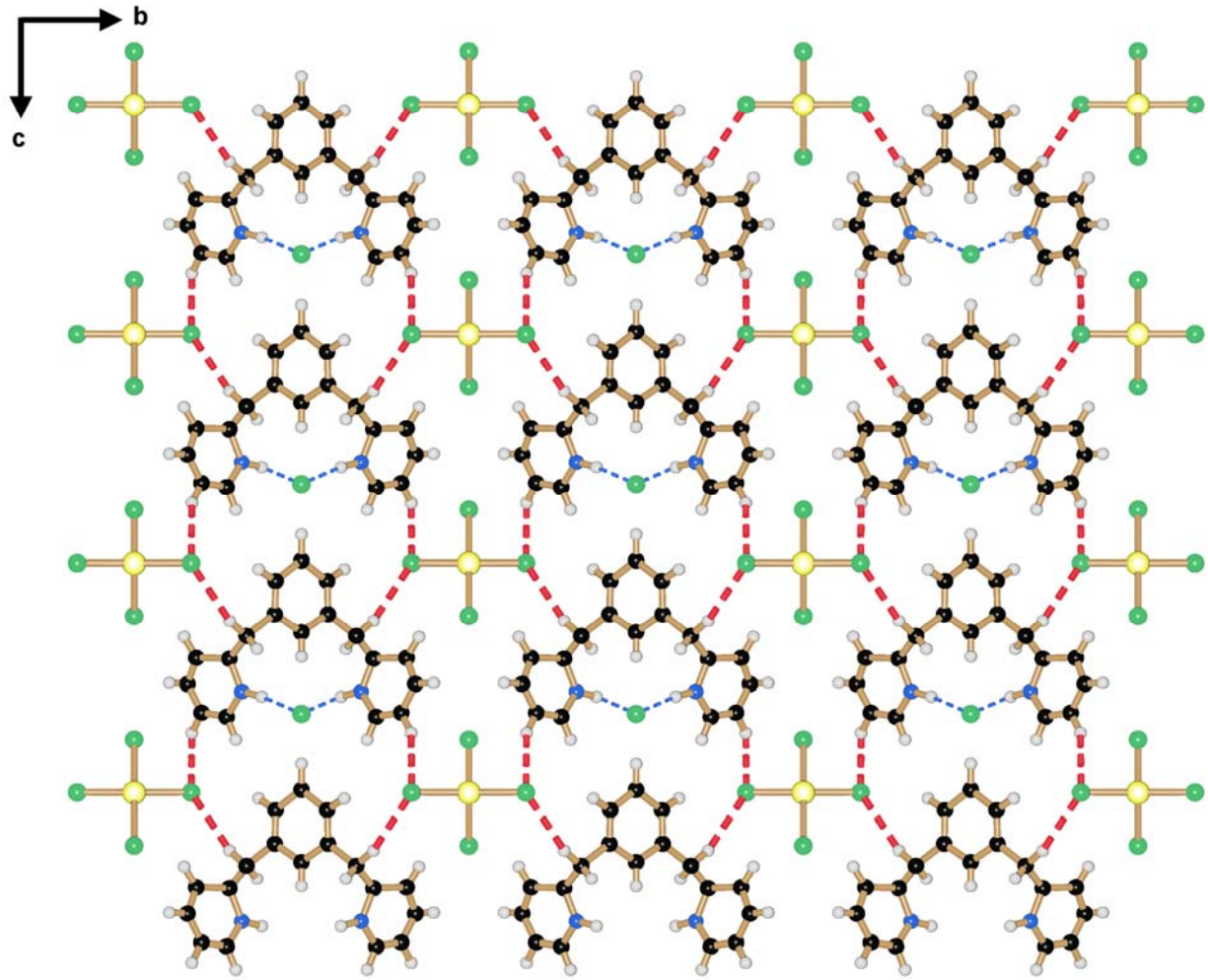

Figure S3. A partial packing diagram for **1**[$AuCl_4$]Cl, viewed along the *a*-axis, showing the hydrogen-bonded layer structure. Dashed lines show C-H···Cl hydrogen bonds.

Table S2. Principal bond and non-bond parameters of compound **2**.

Distances, Å

Hg – Cl 2.308(2)	Hg – C(2) 2.066(7)
Hg···N(1) 2.730(7)	Hg···N(2) 2.820(9)
N(1) – C(12) 1.280(12)	N(1)-C(8) 1.330(9)
C(8)-C(7) 1.502(11)	C(7) – C(1) 1.594(16)
C(1) – C(2) 1.417(11)	C(1) – C(6) 1.367(16)
N(2) – C(18) 1.291(13)	N(2) – C(14) 1.340(10)
C(14) – C(13) 1.489(11)	C(13) – C(3) 1.529(11)
C(3) – C(2) 1.397(13)	C(3) – C(4) 1.347(11)

Angles, °

Cl – Hg – C(2) 173.6(2)	N(1)···Hg···N(2) 108.2(2)
C(12) – N(1) – C(8) 119.3(7)	N(1) – C(8) – C(7) 116.7(7)
C(8) – C(7) – C(1) 114.1(8)	C(7) – C(1) – C(2) 117.8(8)
C(7) – C(1) – C(6) 120.0(8)	C(2) – C(1) – C(6) 122.2(10)
C(1) – C(2) – C(3) 116.7(8)	C(18) – N(2) – C(14) 116.0(9)
N(2) – C(14) – C(13) 116.6(8)	C(14) – C(13) – C(3) 112.5(7)
C(13) – C(3) – C(2) 119.2(6)	C(13) – C(3) – C(4) 119.7(9)
C(2) – C(3) – C(4) 121.0(8).	

Table S3. ^{1}H NMR data of N^CH^N, Hg(N^C^N)Cl, **2**, and [Au(N^C^N)Cl][X], **3**[X], in DMSO-d_6

	CH_2	H^2	H^5	H^4, H^6	$H^{3'}$, $H^{3''}$	$H^{4'}$, $H^{4''}$	$H^{5'}$, $H^{5''}$	$H^{6'}$, $H^{6''}$
N^CH^N	4.05	7.17-7.21	7.17-7.21	7.08	7.25	7.68	7.17-7.21	8.46
2	4.10		7.24-7.27	7.24-7.27	7.38	7.71	7.11	8.43
3[X] X = ½ [Hg_2Cl_6]	4.46 4.94		7.24-7.30	7.24-7.30	8.10	8.37	7.81	9.21
3[X] X = Cl	4.46 5.09		7.23-7.27	7.23-7.27	8.09	8.35	7.78	9.28
3[X] X = [PF_6]	4.45 4.95		7.20-7.32	7.20-7.32	8.10	8.37	7.81	9.21

References

[1] a) A. Bondi, *J. Phys. Chem.*, 1964**, 68**, 441; b) L.Brammer, E. A. Bruton and P. Sherwood, *Cryst. Growth Des.*, 2001, **1**, 277.

[2] a) T.K. Hagos, S. D. Nogai, L. Dobrzańska and S. Cronje, *Acta Cryst.*, 2008**, E64**, m1357; b) Z.-F. Zhang, J.-H. Qin, S.-Q. Wang and G.-R. Qua, *Acta Cryst.*, 2007, **C63**, o622; c) X.-P. Zhang, G. Yanga and N. S. Weng *Acta Cryst.*, 2006, **E62**, m2018; d) S.A. Bourne and L. J. Moitsheki, *Polyhedron*, 2008, **27**, 263.