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Electronic supporting information for manuscript

Unprecedented [d^9]Cu·· [d^{10}]Au Coinage Bonding Interactions in $\{Cu(NH_3)_4[Au(CN)_2]\}^+[Au(CN)_2]^-$ salt

by

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1. X ray crystallography

Single-crystal data were collected with a Gemini R Ultra diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) for (**1**) with ω-scan method at 150 K. Data collection, data reduction and multi-scan absorption collection were performed the CrysAlisPro software [CrysAlis PRO 1.171.38.46 (Rigaku OD, 2015)]. Using the program Olex[2],[1] all structures were solved with Direct Methods with SHELXS-14 solution program [2]and refined with full-matrix least-squares techniques on F^2 with SHELXL-14 refinement program[3]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms positions were calculated and refined riding on the corresponding bonded atoms. CCDC code 2085287 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://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.

Table S1 Crystal data and structure refinement for Cu-Au.

Empirical formula	$C_4H_{12}Au_2Cu_1N_4$
Formula weight	629.71
Temperature/K	100
Crystal system	orthorhombic
Space group	Pnma
a/Å	11.2665(4)
b/Å	7.2480(3)
c/Å	15.2490(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1245.22(8)
Z	5
ρ_{calc}g/cm^3	3.3585
μ/mm^{-1}	25.182
F(000)	1116.0
Crystal size/mm^3	0.5 × 0.3 × 0.25
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.5 to 64.2
Index ranges	-16 ≤ h ≤ 15, -10 ≤ k ≤ 10, -22 ≤ l ≤ 21
Reflections collected	16746
Independent reflections	2240 [R_{int} = 0.0575, R_{sigma} = 0.0245]
Data/restraints/parameters	2240/0/87
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0299, wR_2 = 0.0787
Final R indexes [all data]	R_1 = 0.0348, wR_2 = 0.0815
Largest diff. peak/hole / e Å^{-3}	2.29/-2.03

Table S2 Bond Lengths for Cu-Au.

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**

Au1	C1	1.991(7)		Cu1	N6[2]	2.028(4)
Au1	C2	1.992(7)		Cu1	N6	2.028(4)
Au2	C3	1.995(7)		N1	C1	1.134(10)
Au2	C4	1.990(7)		N2	C2	1.140(9)
Cu1	N4[1]	2.231(7)		N3	C3	1.128(10)
Cu1	N5[2]	2.041(4)		N4	C4	1.132(10)
Cu1	N5	2.041(4)				

[1]-1/2+X,1/2-Y,1/2-Z; [2]+X,1/2-Y,+Z

Table S3 Bond Angles for Cu-Au.

Atom	**Atom**	**Atom**	**Angle/˚**		**Atom**	**Atom**	**Atom**	**Angle/˚**
C2	Au1	C1	174.1(3)		N6[1]	Cu1	N5[1]	171.66(18)
C4	Au2	C3	172.3(3)		N6	Cu1	N5[1]	89.95(17)
N5[1]	Cu1	N4[2]	96.90(17)		N6	Cu1	N6[1]	89.5(2)
N5	Cu1	N4[2]	96.90(17)		C4	N4	Cu1[3]	172.4(6)
N5[1]	Cu1	N5	89.4(2)		N1	C1	Au1	176.2(7)
N6[1]	Cu1	N4[2]	91.43(17)		N2	C2	Au1	177.5(6)
N6	Cu1	N4[2]	91.43(17)		N3	C3	Au2	175.2(7)
N6	Cu1	N5	171.66(18)		N4	C4	Au2	171.6(7)
N6[1]	Cu1	N5	89.95(17)					

[1]+X,1/2-Y,+Z; [2]-1/2+X,1/2-Y,1/2-Z; [3]1/2+X,1/2-Y,1/2-Z

Table S4 Hydrogen bonding Bond Lengths for Cu-Au.

Atom1	**Atom2**	**Length**	**Length-VdW**	**Symm. op. 1**	**Symm. op. 2**
C1	H5b	2.811	-0.089	x,y,z	x,1/2-y,z
N2	H5a	2.345	-0.405	x,y,z	1/2+x,1/2-y,1/2-z
N2	H6b	2.279	-0.471	x,y,z	1/2+x,y,1/2-z
N1	H5c	2.336	-0.414	x,y,z	-x,1/2+y,1-z
N1	H6a	2.376	-0.374	x,y,z	1/2-x,1-y,1/2+z
C3	H5b	2.826	-0.074	x,y,z	-1/2+x,1/2-y,1/2-z
C4	H6c	2.719	-0.181	x,y,z	-1/2+x,1/2-y,1/2-z

2. Experimental details

Synthesis of $\{Cu(NH_3)_4[Au(CN)_2]\}[Au(CN)_2]$: 20 mg $CuNO_3.5/2H_2O$ has been dissolved in 5 ml of water. Addition of 2 ml of concentrated ammonia brings to the immediate formation of $[Cu(NH_3)_4]^{2+}$ complex. After complete reaction, 50 mg of $K[Au(CN)_2]$ have been added, forming a deep blue solution. This solution has been tapped and refrigerated to 10 °C. After one day, deep blue crystals start crystallizing. These crystals are not stable outside to the mother liquor after few ours, and after the choice of a suitable crystal for SCXRD, the measurement has been done at low temperature, to prevent decomposition. This is probably due to loss of ammonia. (Yield: 99.9 %, Elemental analysis (%): Calcd for $C_4H_{12}Au_2CuN_8$: C, 7.63%; H, 1.92%; N, 17.79%; Found: C, 7.57%; H, 1.98%; N, 17.75%.)

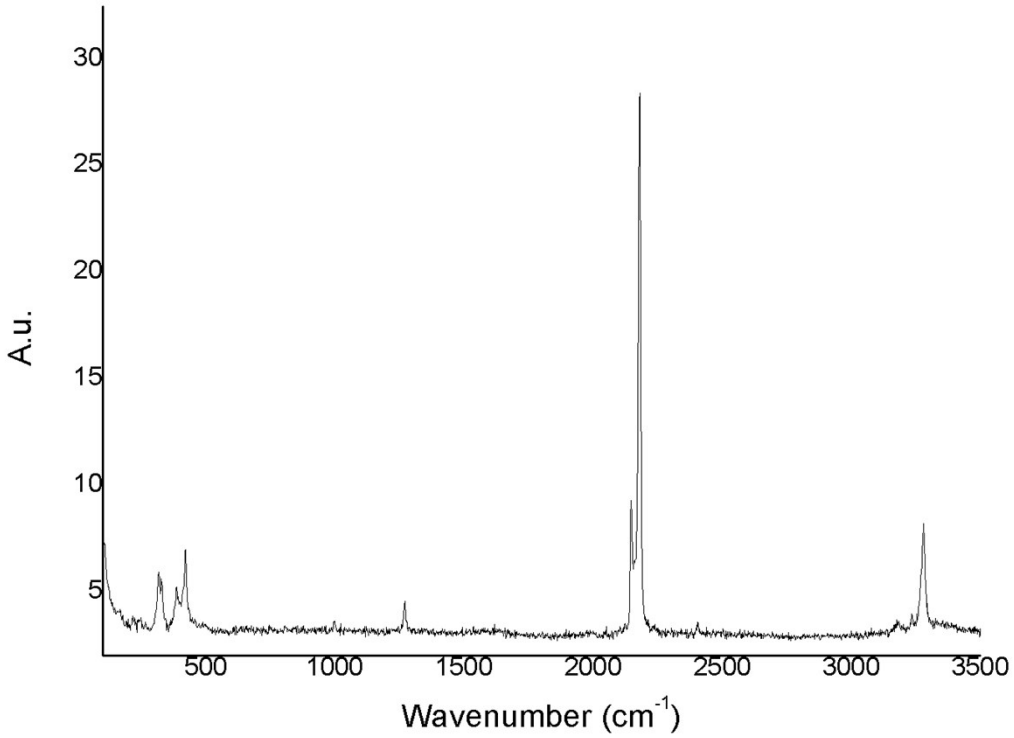

Fig. S Raman Spectrum of Cu-Au.

Table S5: Raman and IR modes assignation of Cu-Au.

Assignation	IR	Raman
ν(Cu-N)	324	324
δ(Au-C)	395	395
ν(Au-C)	423	423
δ(N-H)	1277	1277
ν(C-N)	2144	2144
ν(C-N)	2179	2179
ν(N-H)	3282	3282

3. Theoretical Methods.

The energetic features of the adducts analyzed in this work were calculated at the PBE0[4]-D3[5][/ def2-TZVP[6] level of theory using the crystallographic coordinates. For Gold, the inner shell electrons are modelled by ECPs (ECP-60 scheme),[7] which also accounts for scalar relativistic effects. The GAUSSIAN-16 program has been used for the energetic calculations and NBO analysis.[8] The basis set superposition error for the calculation of interaction energies has been corrected using the counterpoise method.[9] Molecular electrostatic potential (MEP) surfaces have been computed at the same level of theory and represented using several isovalues of electron density to map the electrostatic potential. The QTAIM analysis[10] has been performed using the AIMAll program[11] at the same level of theory.

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