Electronic Supplementary Information for: Probing halogen···halogen interactions via thermal expansion analysis

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Experimental

General procedures and materials

All reactions were performed in air. $[Cu(MeCN)_4]OTf$ and all $[Cat][AuX_2(CN)_2]$ starting materials were synthesized using literature procedures.[1–7] All other reagents were obtained from commercial sources and used as received.

Infrared spectra were measured on a Thermo Nicolet Nexus 670 FT-IR spectrometer equipped with Pike MIRacle attenuated total reflection (ATR) sampling accessory. Raman spectra were measured using a Renishaw inVia Raman microscope equipped with 785 and 514 nm lasers. Microanalyses (C, H, N) were performed by Paul Mulyk at Simon Fraser University on a Carlo Erba EA 1110 CHN elemental analyzer.

Synthetic procedures

$Cu(MeCN)_2[AuCl_2(CN)_2]$. A 2 mL MeCN solution of $[Cu(MeCN)_4]OTf$ (0.05 mol·L^{-1}; 0.1 mmol) was diluted to 5 mL with CH_2Cl_2. To this a 5 mL colourless solution of $[^nBu_4N][AuCl_2(CN)_2]$ (58 mg; 0.10 mmol) was added, resulting in a yellow solution. This solution was partially covered and set aside for slow evaporation. After a few hours, red block-shaped crystals of $Cu(MeCN)_2[AuCl_2(CN)_2]$ (**1**) formed, were collected by pipette and gently rinsed three times with CH_2Cl_2 (19 mg; 41% yield). IR (cm^{-1}): 2246(w; ν_{CN}), 2202 (s; ν_{CN}), 2163 (w; ν_{CN}), 1362 (s), 1032 (w). Raman (cm^{-1}): 2299 (br; ν_{CN}), 2247(s; ν_{CN}), 2217 (vs; ν_{CN}), 1363 (m), 933 (w), 546 (m), 518 (m), 374 (m), 335 (vs; ν_{AuCl}), 273 (sh). Anal calcd. for $C_6H_6N_4AuCl_2Cu$: C 15.48%, H 1.30%, N 12.03%; Found: C 15.31%, H 1.28%, N 11.90%.

$Cu(MeCN)_2[AuBr_2(CN)_2]$ (2). A 2 mL MeCN solution of $[Cu(MeCN)_4]OTf$ (0.05 mol·L^{-1}; 0.1 mmol) was diluted to 5 mL with MeCN. To this a 10 mL yellow solution of $[^nBu_4N][AuBr_2(CN)_2]$ (62 mg; 0.095 mmol) was added, resulting in a yellow solution. This solution was partially covered and set aside for slow evaporation. After three days, red block-shaped crystals of $Cu(MeCN)_2[AuBr_2(CN)_2]$ (**2**) formed, were collected manually with tweezers then air dried (< 2 mg; < 5% yield). The low yield precluded EA and IR analysis. Raman (cm^{-1}): 2303 (m; ν_{CN}), 2273 (s; ν_{CN}), 2207 (s; ν_{CN}), 1362 (m), 936 (s), 522 (s), 395 (w), 206 (vs; ν_{AuBr}).

$Cu(MeCN)_2[AuI_2(CN)_2]$ (3). A 2 mL MeCN solution of $[Cu(MeCN)_4]OTf$ (0.05 mol·L^{-1}; 0.1 mmol) was diluted to 5 mL with MeCN. To this a 10 mL red solution of $[^nBu_4N][AuI_2(CN)_2]$ (77 mg; 0.10 mmol) was added, resulting in an orange solution. This solution was partially covered and set aside for slow evaporation. After three days, red plate-shaped crystals of $Cu(MeCN)_2[AuI_2(CN)_2]$ (**3**) formed, were collected manually with tweezers, then air dried (13 mg; 20% yield). IR (cm^{-1}): 2207 (s; ν_{CN}), 1472 (m), 1269 (m), 1029 (m). Raman (cm^{-1}): 2205 (s; ν_{CN}), 555 (m; shoulder), 527 (s), 376 (w), 327 (w), 142 (vs; ν_{AuI}). Anal calcd. for $C_6H_6N_4AuCuI_2$: C 11.11%, H 0.93%, N 8.64%; Found: C 11.06%, H 0.95%, N 8.46%.

X-ray crystallographic analysis

Data collection. All crystallographic data were collected on a Bruker SMART ApexII Duo diffractometer equipped with a Mo Kα ($\lambda = 0.7109$ Å) Triumph-monochromated source and an Oxford Cryosystems cold stream. Single crystals of **1**, **2** and **3** were mounted on MiTeGen sample holders using paratone oil.

To prevent premature desolvation, crystals were introduced to the cold stream with a starting temperature of 270 K. Complete data sets were then collected at decreasing temperatures (every 15 K) from 270 K to 105 K, after which data were collected at increasing temperatures (every 40 K) from 120 K to 240 K, then 285 K and 300 K. The data collected upon heating from 120 K to 240 K were to confirm the absence of hysteresis effects. Data for each temperature was collected using three ω scans, achieving a minimum completeness of 99.5% (to a resolution of 0.7 Å) for all data sets.

Data analysis. All single crystal diffraction data were processed and initial solutions found with the Bruker ApexIII software suite. Subsequent refinements were performed in ShelXle.[8] Hydrogen atoms were placed geometrically and refined using a riding model. Thermal expansion coefficients along primary axes were determined using PASCal.[9]

Structural diagrams were made using ORTEP-3[10] and POV-ray.[11] Additional crystallographic information can be found in Table S1, below.

Table S1: Crystallographic data (150 K) for compounds **1**, **2** and **3**.

	1	**2**	**3**
empirical formula	$C_6H_6AuCl_2CuN_4$	$C_6H_6AuBr_2CuN_4$	$C_6H_6AuCuI_2N_4$
formula weight ($g{\cdot}mol^{-1}$)	465.55	554.47	648.45
crystal system	monoclinic	monoclinic	monoclinic
space group	$C\,2/c$	$C\,2/c$	$C\,2/c$
a (Å)	15.304(3)	15.5179(11)	16.5670(16)
b (Å)	6.2273(12)	5.9393(4)	5.5064(5)
c (Å)	14.009(3)	14.8526(10)	15.8161(15)
α (deg)	90	90	90
β (deg)	115.285(2)	112.7690(10)	108.2580(10)
γ (deg)	90	90	90
V (Å^3)	1207.2(4)	1262.22(15)	1370.2(2)
Z	4	4	4
T (K)	150(2)	150(2)	150(2)
ρ_{calcd} ($g{\cdot}cm^{-3}$)	2.561	2.918	3.143
μ (mm^{-1})	14.310	19.594	16.725
$2\theta_{max}$ (deg)	61.010	61.012	60.986
total/unique reflections	7610/1838	8073/1930	8733/2088
reflections $[I_0 \geq 2\sigma(I_0)]$	1589	1735	1990
R_1, wR_2 $[I_0 \geq 2\sigma(I_0)]^a$	0.0181, 0.0424	0.0158, 0.0352	0.0208, 0.0519
goodness of fit	1.059	1.040	1.129
CCDC number	1574364	1574365	1574366

[a] Function minimized: $\Sigma w(F_o^2 - F_c^2)^2$. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$.

Additional thermal expansion data

Table S2: Temperature dependence of unit cell parameters for **1**.

Temperature	a /Å	b /Å	c /Å	β /°
105	15.267(3)	6.644(1)	13.936(3)	115.469(2)
120	15.280(3)	6.237(1)	13.961(3)	115.409(2)
135	15.293(3)	6.233(1)	13.986(3)	115.351(2)
150	15.304(3)	6.227(1)	14.009(3)	115.285(2)
165	15.311(3)	6.221(1)	14.032(3)	115.210(2)
180	15.324(2)	6.217(1)	14.062(2)	115.143(2)
195	15.343(1)	6.209(1)	14.092(1)	115.096(1)
210	15.366(1)	6.203(1)	14.128(1)	115.027(1)
225	15.383(1)	6.195(1)	14.159(1)	114.957(1)
240	15.406(1)	6.189(1)	14.194(1)	114.899(1)
255	15.429(1)	6.181(1)	14.227(1)	114.832(1)
270	15.453(1)	6.174(1)	14.261(1)	114.762(1)
285	15.486(1)	6.170(1)	14.305(1)	114.700(1)
300	15.513(1)	6.164(1)	14.341(1)	114.626(1)

Table S3: Temperature dependence of unit cell parameters for **2**.

Temperature	a /Å	b /Å	c /Å	β /°
105	15.473(1)	5.960(1)	14.768(1)	113.019(1)
120	15.484(1)	5.952(1)	14.793(1)	112.936(1)
135	15.500(1)	5.946(1)	14.822(1)	112.853(1)
150	15.518(1)	5.939(1)	14.853(1)	112.769(1)
165	15.538(1)	5.934(1)	14.886(1)	112.681(1)
180	15.554(1)	5.927(1)	14.916(1)	112.593(1)
195	15.575(1)	5.919(1)	14.952(1)	112.493(1)
210	15.595(1)	5.910(1)	14.988(1)	112.395(1)
225	15.617(1)	5.903(1)	15.026(1)	112.296(1)
240	15.637(1)	5.895(1)	15.063(1)	112.200(1)
255	15.654(1)	5.886(1)	15.095(1)	112.106(1)
270	15.678(1)	5.879(1)	15.132(1)	112.012(1)
285	15.706(1)	5.869(1)	15.172(1)	111.897(1)
300	15.729(1)	5.861(1)	15.207(1)	111.806(1)

Table S4: Temperature dependence of unit cell parameters for **3**.

Temperature	a /Å	b /Å	c /Å	β /°
105	16.536(2)	5.5137(5)	15.755(2)	108.425(1)
120	16.548(2)	5.5114(5)	15.776(2)	108.368(1)
135	16.556(2)	5.5082(5)	15.795(1)	108.316(1)
150	16.567(2)	5.5064(5)	15.816(2)	108.258(1)
165	16.577(2)	5.5055(6)	15.838(2)	108.203(2)
180	16.586(2)	5.5039(7)	15.861(2)	108.146(2)
195	16.591(2)	5.5000(6)	15.877(2)	108.097(2)
210	16.599(1)	5.4965(4)	15.898(1)	108.046(1)
225	16.610(1)	5.4943(4)	15.922(1)	108.001(1)
240	16.618(1)	5.4925(4)	15.943(1)	107.962(1)
255	16.630(1)	5.4922(4)	15.966(1)	107.916(1)
270	16.640(1)	5.4922(4)	15.992(1)	107.872(1)
285	16.650(1)	5.4904(4)	16.012(1)	107.820(1)
300	16.658(1)	5.4893(4)	16.033(1)	107.777(1)

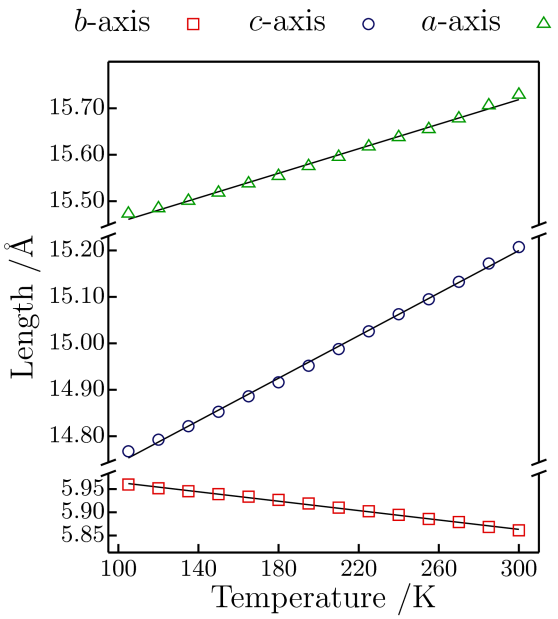

Figure S1: Plot of unit cell length parameter vs. temperature for **2** (error bars are within the points). Solid lines depict linear least squares fits to the data.

Table S5: Thermal expansion coefficients $/\times 10^{-6}\,\mathrm{K}^{-1}$ for $Cu(MeCN)_2[AuX_2(CN)_2]$ (X = Cl, Br, I) along primary orthogonal axes.

Compound	α_{X1}	α_{X2}	α_{X3}
1	76(4)	−66.1(14)	190(4)
2	71.7(17)	−84.8(14)	215(3)
3	31.7(4)	−23.6(11)	115.2(3)

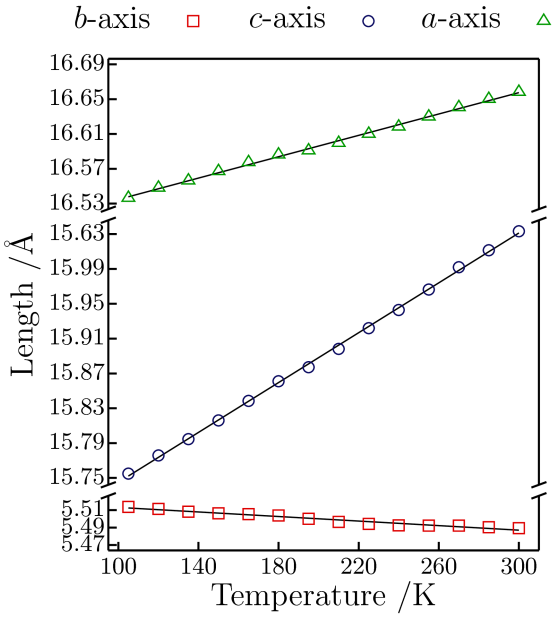

Figure S2: Plot of unit cell length parameter vs. temperature for **3** (error bars are within the points). Solid lines depict linear least squares fits to the data.

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