Electronic Supplementary Material (ESI) for Dalton Transactions.

Cyclic Trinuclear Copper(I), Silver(I), and Gold(I) Complexes: A Theoretical Insight.

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Supporting Information

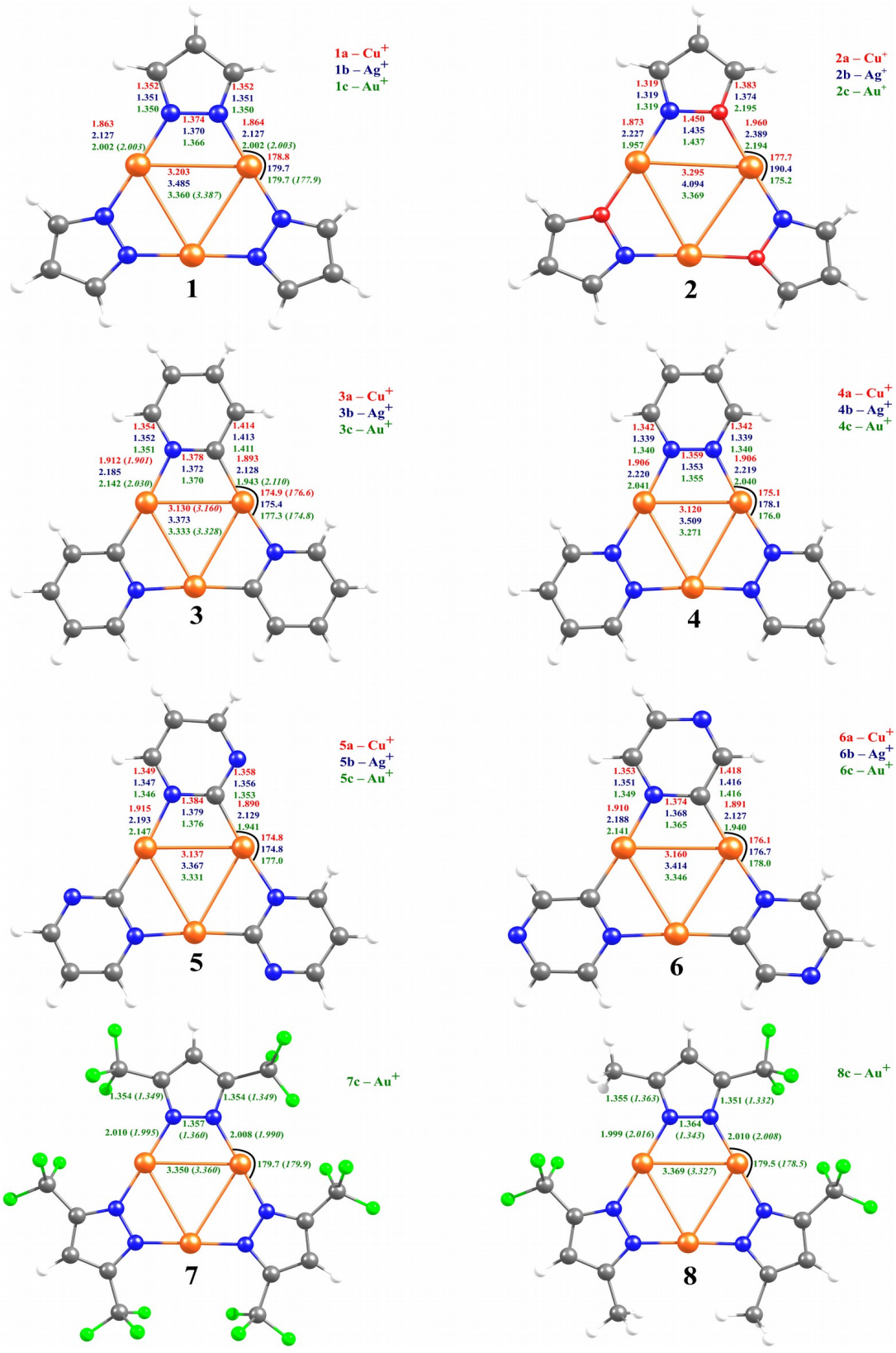

Figure S1. Optimized structures of model complexes **1**-**8** at the BP86-D3/def2-TZVP level of theory. Values in parentheses depict experimental data available.[3,19,21,23,24] Color code (M = orange, C = gray, N = blue, O = red, F = green, H = white).

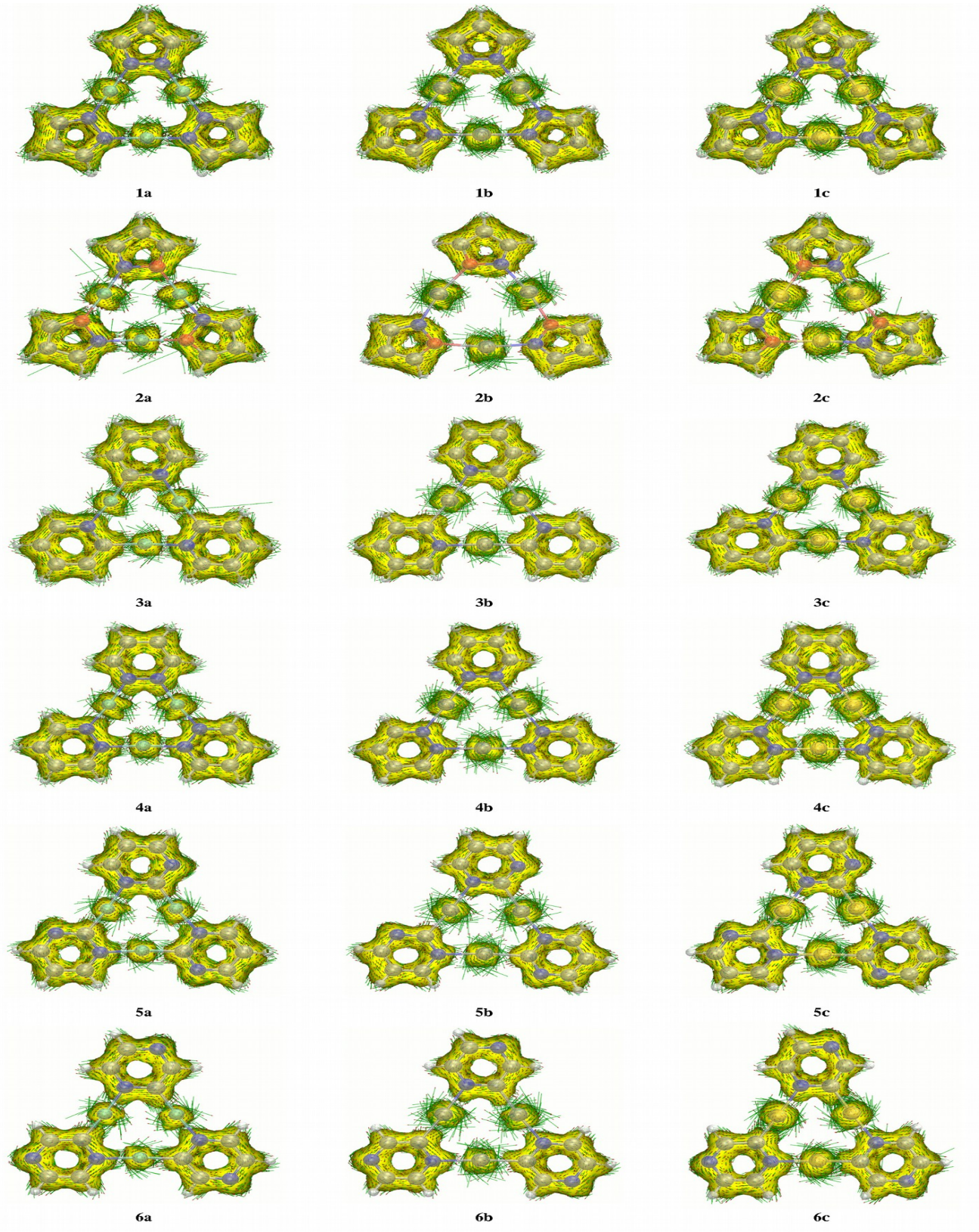

Figure S2. ACID plots for complexes **1a-6c**.

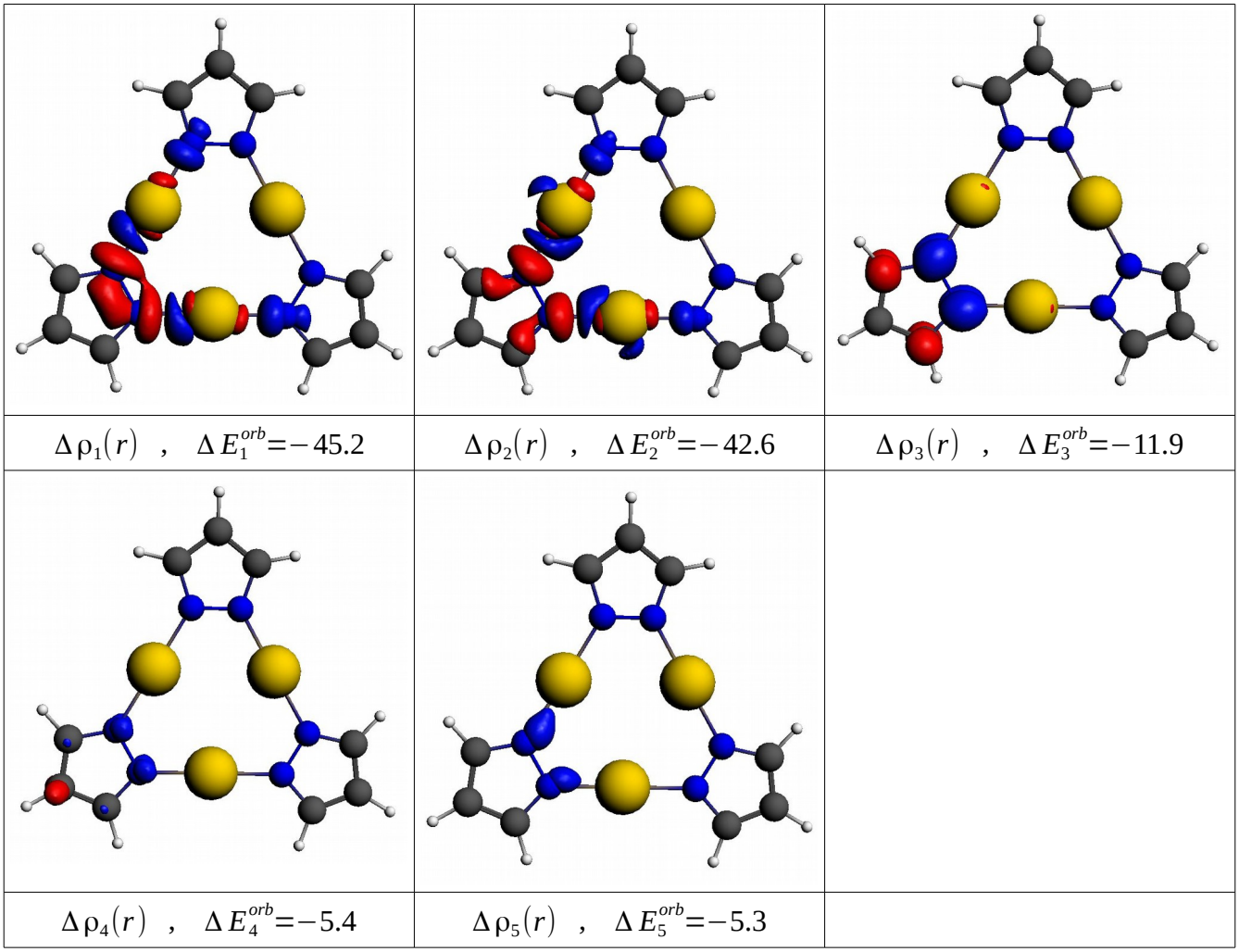

Figure S3. Contours of deformation densities (contour value 0.003), $\Delta\rho_i(r)$, describing the density inflow (blue) and outflow (red) between the interacting fragments **1c** and their corresponding energy ΔE_i^{orb} (kcal.mol^{-1})

Table S1. Bond orders and natural atomic charges obtained by NBO for some selected systems.

CTC	bond	bond order (b_{AB}^{wa})	atom	atomic charge (q^{NPA})
1a	Cu–N	0.298	Cu	0.722
	Cu–Cu	0.017	N	-0.463
1b	Ag–N	0.340	Ag	0.594
	Ag–Ag	0.015	N	-0.396
1c	Au–N	0.455	Au	0.458
	Au–Au	0.013	N	-0.357
7c	Au–N	0.447	Au	0.465
	Au–Au	0.017	N	-0.344
8c	Au–N	0.457	Au	0.438
	Au–Au	0.016	N	-0.366
2a	Cu–N	0.292	Cu	0.844
	Cu–O	0.133	O	-0.386
	Cu–Cu	0.026	N	-0.333
2b	Ag–N	0.266	Ag	0.817
	Ag–O	0.100	O	-0.334
	Ag–Ag	0.009	N	-0.281
2c	Au–N	0.548	Au	0.633
	Au–O	0.200	O	-0.316
	Au–Au	0.036	N	-0.227
4a	Cu–N	0.268	Cu	0.800
	Cu–Cu	0.022	N	-0.377
4b	Ag–N	0.282	Ag	0.689
	Ag–Ag	0.017	N	-0.306
4c	Au–N	0.438	Au	0.540
	Au–Au	0.019	N	-0.274

Table S2. Second order stabilization energies, ΔE^2(kcal.mol^{-1})difference of energy, $\varepsilon_i - \varepsilon_j$ (a.u.) from NBO analysis for some selected systems.

CTC	donor (occup.)	Acceptor (occup.)	ΔE^2	$\varepsilon_i - \varepsilon_j$
		L→M donation		
1a	$n_{sp^{2.73}}$N (1.79)	σ*Cu−N (0.20)	59.1	0.42
1b	$n_{sp^{2.73}}$N (1.75)	σ*Ag−N (0.20)	70.6	0.37
1c	$n_{sp^{2.73}}$N (1.70)	σ*Au−N (0.33)	137.7	0.40
7c	$n_{sp^{2.73}}$N (1.68)	σ*Au−N (0.33)	124.6	0.42
8c	$n_{sp^{2.73}}$N (1.68)	σ*Au−N (0.33)	127.2	0.41
2a	$n_{sp^{1.15}}$O (1.92)	*s* Cu (0.24)	25.6	0.62
	$n_{sp^{1.30}}$N (1.83)	*s* Cu (0.24)	45.4	0.46
2b	$n_{sp^{1.11}}$O (1.94)	*s* Ag (0.24)	11.9	0.60
	$n_{sp^{1.23}}$N (1.84)	*s* Ag (0.24)	35.3	0.43
2c	$n_{sp^{1.11}}$O (1.87)	σ*Au−N (0.16)	40.0	0.66
4a	$n_{sp^{2.02}}$N (1.98)	*s* Cu (0.30)	51.0	0.40
4b	$n_{sp^{2.02}}$N (1.98)	*s* Ag (0.35)	47.6	0.38
4c	$n_{sp^{2.02}}$N (1.69)	*s* Au (0.59)	130.3	0.33
		M→L back-donation		
1a	d_{xz}Cu (2.00)	σ*N−N (0.05)	1.30	0.50
	d_{yz}Cu (2.00)	π*N−C (0.55)	2.77	0.18
1b	d_{xz}Ag (2.00)	σ*N−N (0.05)	0.98	0.56
	d_{yz}Ag (2.00)	π*N−C (0.54)	1.67	0.23
1c	d_{xz}Au (2.00)	σ*N−N (0.05)	2.50	0.54
	d_{yz}Au (2.00)	π*N−C (0.54)	4.32	0.22
7c	d_{xz}Au (2.00)	σ*N−N (0.05)	2.13	0.54
	d_{yz}Au (2.00)	π*N−C (0.56)	4.14	0.22
8c	d_{xz}Au (2.00)	σ*N−N (0.04)	2.50	0.54
	d_{yz}Au (2.00)	π*N−C (0.60)	4.05	0.22
2a	d_{xz}Cu (2.00)	σ*N−O (0.09)	2.38	0.30
2b	d_{xz}Ag (2.00)	σ*N−O (0.07)	1.03	0.37
2c	d_{yz}Au (2.00)	π*N−C (0.37)	4.87	0.23
	d_{xz}Au (2.00)	σ*N−O (0.11)	2.06	0.31
4a	d_{yz}Cu (2.00)	π*N−C (0.36)	2.42	0.18
4b	d_{yz}Ag (2.00)	π*N−C (0.35)	1.20	0.22
4c	d_{xz}Au (2.00)	σ*N−N (0.05)	2.09	0.54
	d_{yz}Au (2.00)	π*N−C (0.37)	3.93	0.21