Supporting Information

The Control of the Electronic Structure of Dinuclear Copper Complexes of Redox-Active Tetrakisguanidine Ligands by the Environment

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Content

1) Additional information for the computational investigation

Table S1. The following table contain a summary of the calculations for all complexes $[GFA(CuX_2)_2]$ (GFA = **1**, **2** or **3**, X = Cl or Br).

$[\mathbf{1}(CuBr_2)_2]$		BP86/SVP	BP86/TZVP	B3LYP/SVP	B3LYP/TZVP
	E(el) / H	-15254,49563	-15258,03142	-15251,16273	-15254,71481
	ZPE / H	0,75338		0,77569	
	G(corr) / H	0,66573		0,68899	
sing	**E(tot) / H**	-15253,74225	-15257,27804	-15250,38703	-15253,93912
	G(tot) / H	-15253,82990	-15257,36569	-15250,47373	-15254,02582
	E(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	G(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	E(el) / H	-15254,49587	-15258,02994	-15251,18263	-15254,72807
	ZPE / H	0,75336		0,77733	
	G(corr) / H	0,66439		0,69182	
trip	**E(tot) / H**	-15253,74251	-15257,27658	-15250,40530	-15253,95074
	G(tot) / H	-15253,83148	-15257,36555	-15250,49081	-15254,03624
	<S2>**	2,00215	2,00265	2,00678	2,00791
	E(rel) / kJ mol-1	**-0,7**	**3,8**	**-48,0**	**-30,5**
	G(rel) / kJ mol-1	**-4,2**	**0,4**	**-44,8**	**-27,4**
	E(el) / H		-15258,03137		-15254,72812
	E(tot) / H		-15257,27801		-15253,95079
	G(tot) / H		-15257,36698		-15254,03629
BS	**<S**2>**		0,767248		1,00610
	J / cm-1		-253,36		-10,91
	E(rel) / kJ mol-1		**0,1**		**-30,6**
	G(rel) / kJ mol-1		**-3,4**		**-27,5**

$[\mathbf{1}(CuCl_2)_2]$		BP86/SVP	BP86/TZVP	B3LYP/SVP	B3LYP/TZVP
	E(el) / H	-6798,40194	-6801,31747	-6796,23644	-6799,16345
	ZPE / H	0,75513		0,77771	
	G(corr) / H	0,66966		0,69066	
sing	**E(tot) / H**	-6797,64681	-6800,56234	-6795,45872	-6798,38574
	G(tot) / H	-6797,73227	-6800,64781	-6795,54577	-6798,47279
	E(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	G(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	E(el) / H	-6798,40322	-6801,31835	-6796,26225	-6799,186233
	ZPE / H	0,75481		0,77906	
	G(corr) / H	0,66929		0,69570	
trip	**E(tot) / H**	-6797,64841	-6800,56355	-6795,48319	-6798,40718
	G(tot) / H	-6797,73393	-6800,64906	-6795,56655	-6798,49054
	<S2>**	2,00224	2,00276	2,00610	2,007123
	E(rel) / kJ mol-1	**-4,2**	**-3,2**	**-64,3**	**-56,3**
	G(rel) / kJ mol-1	**-4,4**	**-3,3**	**-54,6**	**-46,6**
	E(el) / H		-6801,31964		-6799,186268
	E(tot) / H		-6800,56484		-6798,40721
	G(tot) / H		-6800,65035		-6798,49057
BS	**<S**2>**		0,799299		1,00625
	J / cm-1		-234,93		-7,8
	E(rel) / kJ mol-1		**-6,5**		**-56,4**
	G(rel) / kJ mol-1		**-6,7**		**-46,7**

[2(CuBr$_2$)$_2$]		BP86/SVP	BP86/TZVP	B3LYP/SVP	B3LYP/TZVP
	E(el) / H	-15270,54223	-15274,09863	-15267,19626	-15270,77337
	ZPE / H	0,74246		0,76368	
	G(corr) / H	0,65662		0,68174	
sing	**E(tot) / H**	-15269,79977	-15273,35616	-15266,43259	-15270,00969
	G(tot) / H	-15269,88562	-15273,44201	-15266,51452	-15270,09163
	E(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	G(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	E(el) / H	-15270,54592	-15274,10005	-15267,22498	-15270,79237
	ZPE / H	0,74246		0,76476	
	G(corr) / H	0,65604		0,67955	
trip	**E(tot) / H**	-15269,80347	-15273,35760	-15266,46021	-15270,02760
	G(tot) / H	-15269,88989	-15273,44401	-15266,54542	-15270,11281
	<S2>**	2,00247	2,00297	2,00661	2,00791
	E(rel) / kJ mol-1	**-9,7**	**-3,8**	**-72,5**	**-47,0**
	G(rel) / kJ mol-1	**-11,2**	**-5,3**	**-81,1**	**-55,6**
	E(el) / H		-15274,10114		-15270,79249
	E(tot) / H		-15273,35869		-15270,02773
	G(tot) / H		-15273,44511		-15270,11294
BS	**<S**2>**		0,864388		1,00258
	J / cm-1		-210,39		-27,33
	E(rel) / kJ mol-1		**-6,6**		**-47,4**
	G(rel) / kJ mol-1		**-8,1**		**-55,9**

[2(CuCl$_2$)$_2$]		BP86/SVP	BP86/TZVP	B3LYP/SVP	B3LYP/TZVP
	E(el) / H	-6814,44922	-6817,38548	-6812,27441	-6815,2229
	ZPE / H	0,74440		0,76642	
	G(corr) / H	0,65923		0,68346	
sing	**E(tot) / H**	-6813,70483	-6816,64109	-6811,50799	-6814,45648
	G(tot) / H	-6813,78999	-6816,72625	-6811,59094	-6814,53943
	E(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	G(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	E(el) / H	-6814,45380	-6817,38849	-6812,30298	-6815,246229
	ZPE / H	0,74449		0,76719	
	G(corr) / H	0,65883		0,68391	
trip	**E(tot) / H**	-6813,70931	-6816,64399	-6811,53579	-6814,47903
	G(tot) / H	-6813,79498	-6816,72966	-6811,61907	-6814,56232
	<S2>**	2,00261	2,00314	2,00640	2,007519
	E(rel) / kJ mol-1	**-11,8**	**-7,6**	**-73,0**	**-59,2**
	G(rel) / kJ mol-1	**-13,1**	**-8,9**	**-73,9**	**-60,1**
	E(el) / H		-6817,389611		-6815,246321
	E(tot) / H		-6816,64512		-6814,47913
	G(tot) / H		-6816,73078		-6814,56241
BS	**<S**2>**		0,876222		1,004472
	J / cm-1		-218,83		-20,11
	E(rel) / kJ mol-1		**-10,6**		**-59,5**
	G(rel) / kJ mol-1		**-11,9**		**-60,3**

[3(CuBr$_2$)$_2$]		BP86/SVP	BP86/TZVP	B3LYP/SVP	B3LYP/TZVP
	E(el) / H	-15408,00789	-15411,70092	-15404,57578	-15408,28756
	ZPE / H	0,79859		0,82226	
	G(corr) / H	0,70964		0,73206	
sing	**E(tot) / H**	-15407,20930	-15410,90233	-15403,75352	-15407,46530
	G(tot) / H	-15407,29825	-15410,99128	-15403,84372	-15407,55549
	E(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	G(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	E(el) / H	-15408,00990	-15411,70190	-15404,59060	-15408,29689
	ZPE / H	0,79894		0,82308	
	G(corr) / H	0,70772		0,73398	
trip	**E(tot) / H**	-15407,21097	-15410,90296	-15403,76752	-15407,47381
	G(tot) / H	-15407,30218	-15410,99417	-15403,85661	-15407,56291
	<S2>**	2,00362	2,00375	2,00817	2,00966
	E(rel) / kJ mol-1	**-4,4**	**-1,7**	**-36,7**	**-22,3**
	G(rel) / kJ mol-1	**-10,3**	**-7,6**	**-33,9**	**-19,5**
	E(el) / H		-15411,69989		-15408,29742
	E(tot) / H		-15410,90095		-15407,47434
	G(tot) / H		-15410,99217		-15407,56344
BS	**<S**2>**		0,650733		0,99171
	J / cm-1		325,58		-114,20
	E(rel) / kJ mol-1		**3,6**		**-23,7**
	G(rel) / kJ mol-1		**-2,3**		**-20,9**

[3(CuCl$_2$)$_2$]		BP86/SVP	BP86/TZVP	B3LYP/SVP	B3LYP/TZVP
	E(el) / H	-6951,91434	-6954,98879	-6949,64715	-6952,734933
	ZPE / H	0,80032		0,82333	
	G(corr) / H	0,71404		0,73630	
sing	**E(tot) / H**	-6951,11402	-6954,18847	-6948,82381	-6951,91160
	G(tot) / H	-6951,20030	-6954,27475	-6948,91085	-6951,99864
	E(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	G(rel) / kJ mol-1	**0,0**	**0,0**	**0,0**	**0,0**
	E(el) / H	-6951,91536	-6954,99189	-6949,66860	-6952,753653
	ZPE / H	0,80043		0,82448	
	G(corr) / H	0,71102		0,73766	
trip	**E(tot) / H**	-6951,11493	-6954,19145	-6948,84413	-6951,92918
	G(tot) / H	-6951,20434	-6954,28087	-6948,93094	-6952,01599
	<S2>**	2,00401	2,00406	2,00726	2,00878
	E(rel) / kJ mol-1	**-2,4**	**-7,8**	**-53,3**	**-46,1**
	G(rel) / kJ mol-1	**-10,6**	**-16,1**	**-52,7**	**-45,6**
	E(el) / H		-6954,988695		-6952,753888
	E(tot) / H		-6954,18826		-6951,92941
	G(tot) / H		-6954,27768		-6952,01622
BS	**<S**2>**		0,719274		1,003434
	J / cm-1		544,92		-51,16
	E(rel) / kJ mol-1		**0,5**		**-46,8**
	G(rel) / kJ mol-1		**-7,7**		**-46,2**

Figure S1

UV/Vis spectrum of a $1.87 \cdot 10^{-5}$ M solution of [**1**$(CuBr_2)_2$] in CH_3CN.

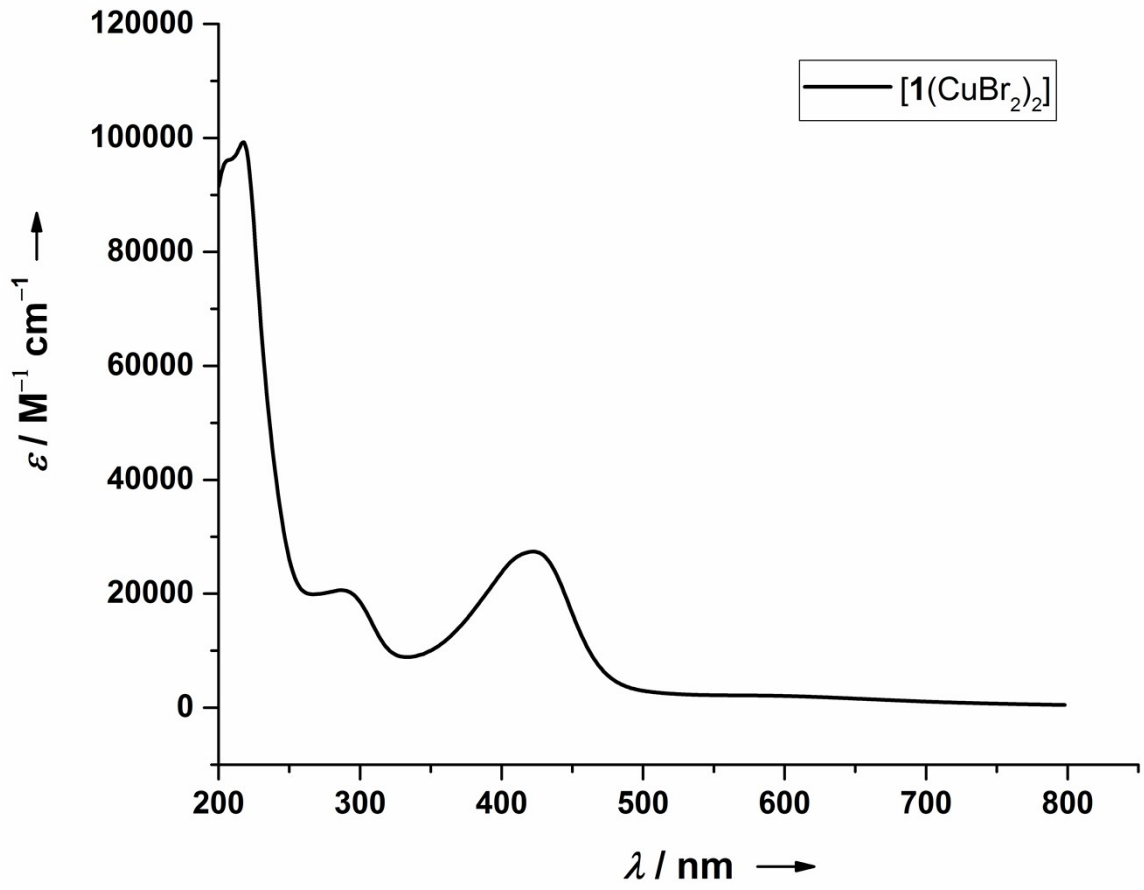


Figure S2

EPR spectrum of [**1**$(CuCl_2)_2$] in a frozen dichloromethane solution at 35 K.

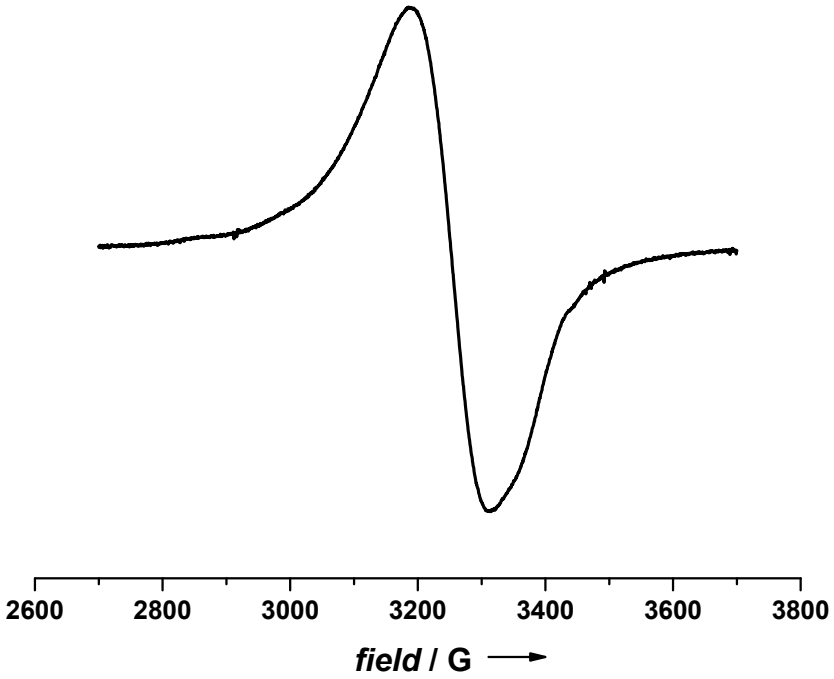
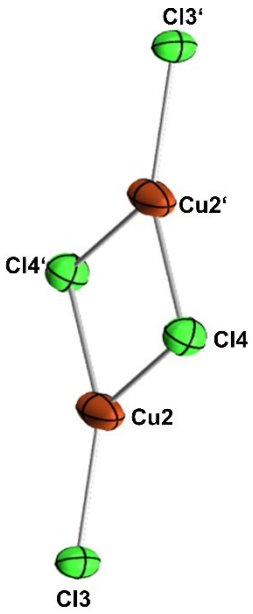


Figure S3.

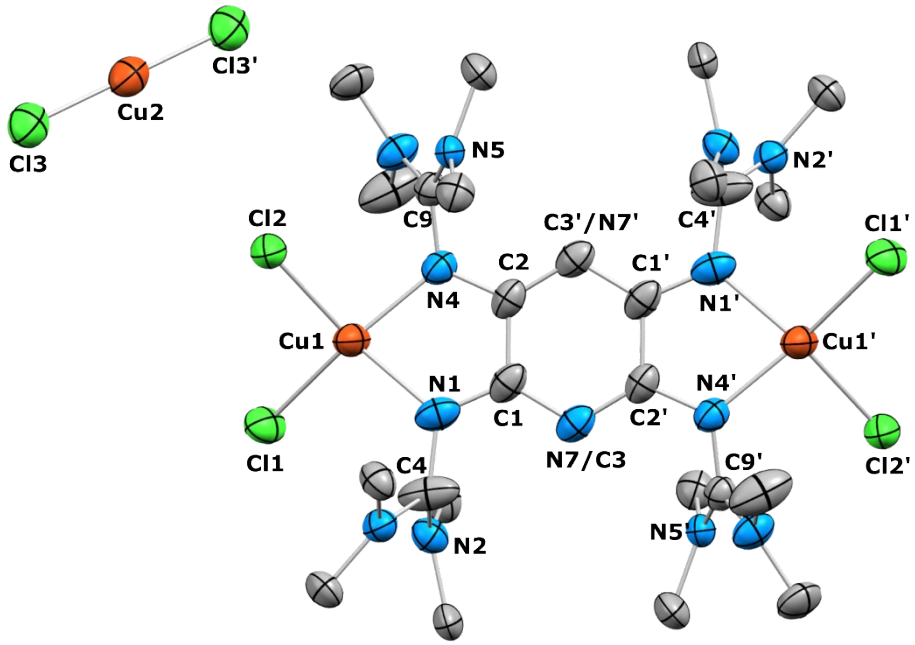
Visualization of the structure of the $[Cu_2Cl_4]^{2-}$ dianion of $[\mathbf{2}(CuCl_2)_2][Cu_2Cl_4]$.



Molecular structure of the dianion $[Cu_2Cl_4]^{2-}$. Vibrational ellipsoids at the 50% probability level. Selected bond distances (in Å) and angles (in °): Cu2–Cl3 2.158(1), Cu2–Cl4 2.313(1), Cu2-Cl4’ 2.392(1), Cu2···Cu2’ 3.126; Cl3-Cu2-Cl4 135.9(7), Cl3-Cu2-Cl4’ 127.2(6).

Figure S4.

Visualization of the structure of [**2**($CuCl_2$)$_2$][$CuCl_2$].



Molecular structure of [**2**($CuCl_2$)$_2$][$CuCl_2$]. Vibrational ellipsoids at the 50% probability level. Hydrogen atoms and co-crystallized acetonitrile molecules are neglected for clarity. Selected bond distances (in Å) and angles (in °): Cu1–Cl1 2.228(1), Cu1–Cl2 2.242(1), Cu1–N1 1.985(4), Cu1–N4 1.977(4), Cu2–Cl3 2.107(1), N1–C1 1.338(6), N1–C4 1.387(6), N2–C4 1.279(6), N4–C2 1.349(5), N4–C9 1.375(5), C1–C2 1.457(6), C1–C3/N7 1.379(6), C2–C3'/N7' 1.351(6); Cl1–Cu–Cl2 97.4(6), N1–Cu–N4 80.6(1), Cl3-Cu2-Cl3' 180.0(7) (Cl1–Cu–Cl2,N1–Cu–N4) 34.3.

Table S2. Energy differences ΔE_{TS} (in kJ mol^{-1}) between triplet and closed-shell singlet electronic states for different solvent permittivity ε_r, according to BP86/def2-TZVP + COSMO calculations. Positive energies mean that the closed-shell singlet electronic state is preferred.

	ΔE_{TS} (in kJ mol^{-1})		
complex	$\varepsilon_r = 1$	$\varepsilon_r = 9.08$	$\varepsilon_r = 36.3$
[**1**($CuCl_2$)$_2$]	-3.2	+12.1	+14.8
[**2**($CuCl_2$)$_2$]	-7.6	+15.3	+19.4
[**3**($CuCl_2$)$_2$]	-7.8	+8.3	+11.9