

Supporting Information

Bimacrocyclic Effect in Anion Recognition by a Copper(II) Bicyclam Complex

Michele Invernici,[¶] Carlo Ciarrocchi,[¶] Daniele Dondi,[¶] Luigi Fabbrizzi,^{*¶} Simone Lazzaroni,[¶]
Maurizio Licchelli,^{*¶} Massimo Boiocchi[§], Marco Bonizzoni^{*†}

[¶] Dipartimento di Chimica, Università di Pavia, via Taramelli 12, I-27100 Pavia, Italy.

[§] Centro Grandi Strumenti, Università di Pavia, via Bassi 21, I-27100 Pavia, Italy.

[†] Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, United States

A. EPR Studies

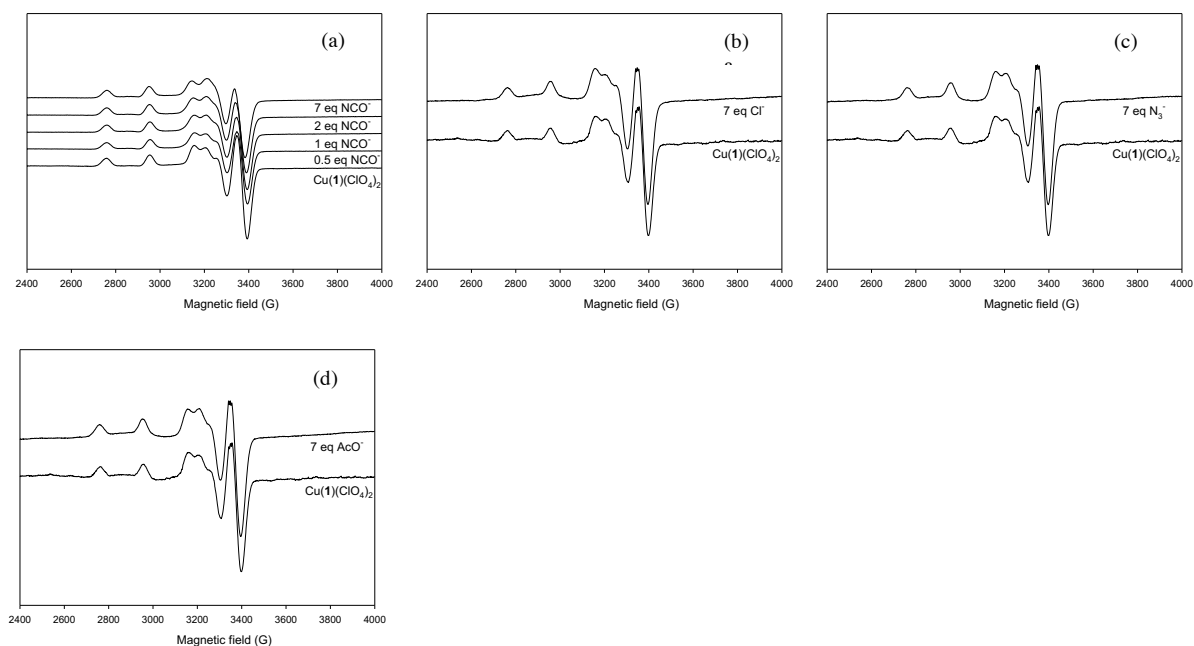


Figure S1. EPR spectra of a solution of $[\text{Cu}(\mathbf{1})](\text{ClO}_4)_2$ ($5 \times 10^{-4} \text{ M}$) in the presence of increasing amounts of (a) cyanate, and in the presence of excess (b) chloride, (c) azide, and (d) acetate.

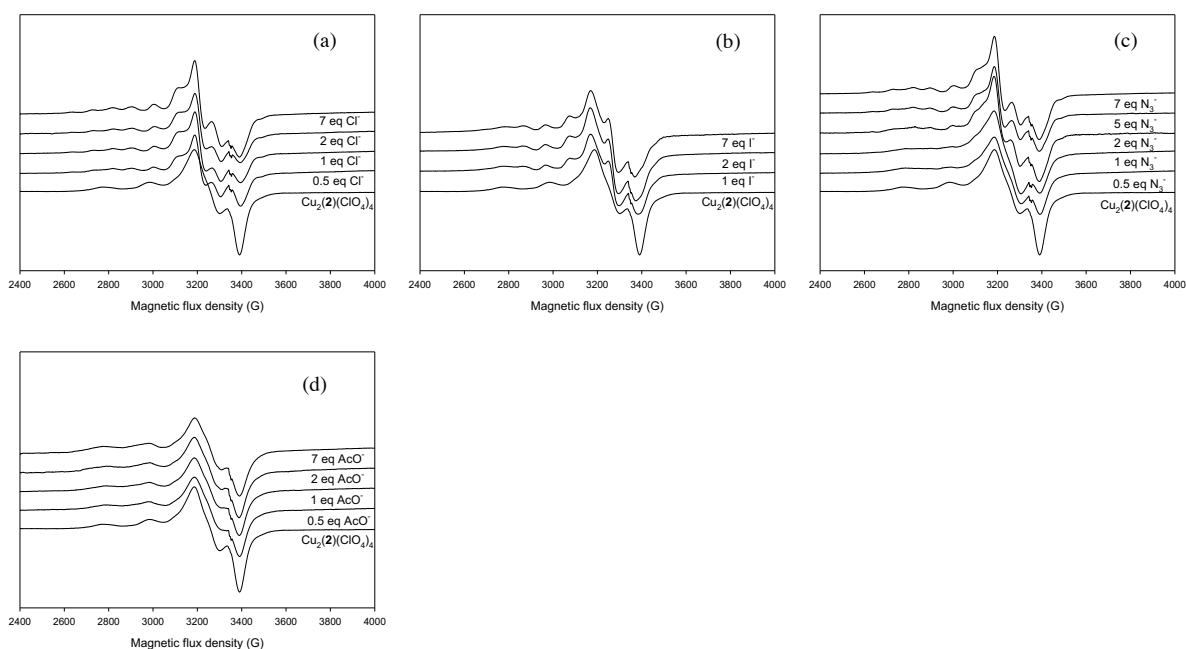


Figure S2. EPR spectra of a solution of $[\text{Cu}_2(\mathbf{2})](\text{ClO}_4)_4$ ($5 \times 10^{-4} \text{ M}$) in the presence of increasing amounts of (a) chloride, (b) iodide, (c) azide, and (d) acetate.

B. Calorimetric Studies

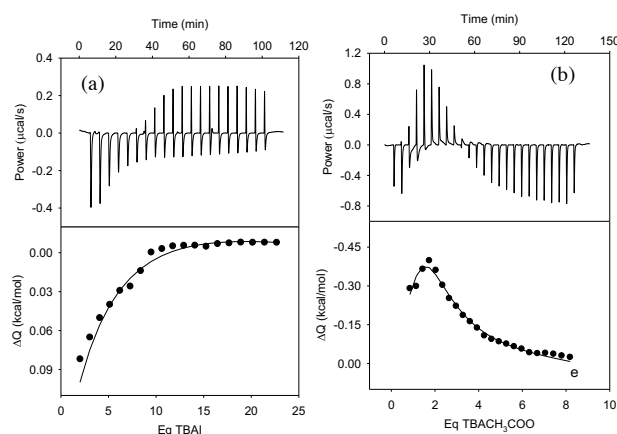


Figure S3. Thermograms and corresponding ITC profiles taken over the course of the titration experiments in DMSO: (a) $[\text{Cu}(\mathbf{1})](\text{ClO}_4)_2$ (1.0×10^{-3} M) titrated with $(\text{TBA})\text{I}$ (6.7×10^{-2} M); (b) $[\text{Cu}(\mathbf{1})](\text{ClO}_4)_2$ (5.1×10^{-3} M) titrated with $(\text{TBA})\text{CH}_3\text{COO}$ (1.2×10^{-1} M). Circles: experimental data; line: fitting profile (sequential two site models; “receptor” complex in the cell); $T = 25^\circ\text{C}$.

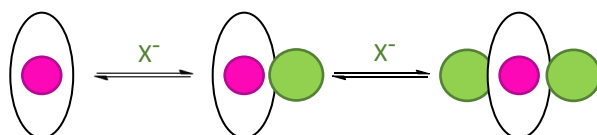


Figure S4. Schematic representation of equilibria taking place over the course of the titrations of $[\text{Cu}(\mathbf{1})]^{2+}$ with different anions (X^- , green spheres = Cl^- , Br^- , I^- , NCO^- , N_3^- , CH_3COO^-).

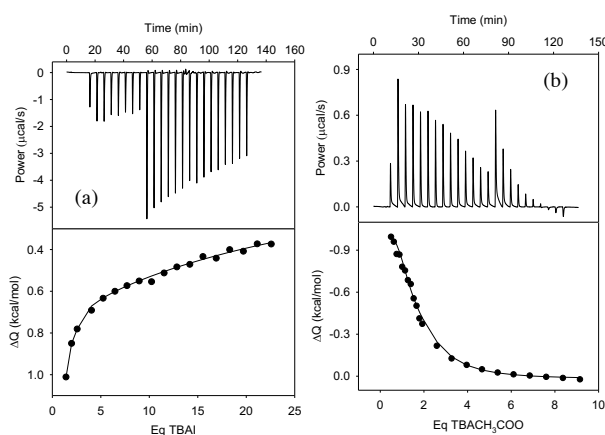


Figure S5. Thermograms and ITC profiles taken over the course of the titration of a solution of $[\text{Cu}_2(\mathbf{2})](\text{ClO}_4)_4$ (1.0×10^{-3} M) in DMSO with a solution of: (a) $(\text{TBA})\text{I}$ (6.7×10^{-2} M); (b) $(\text{TBA})\text{CH}_3\text{COO}$ (3.0×10^{-2} M). Circles: experimental data; line: fitting profile (sequential two site models; “receptor” complex in the cell); $T = 25^\circ\text{C}$. In both experiments the volume of the titrant additions was changed roughly halfway through. This was done in order to achieve the necessary ratios of titrant to Cu^{II} complex without unduly lengthening the experiment. This allowed us to probe the region of the thermogram at low $[\text{anion}]/[\text{complex}]$ with high resolution, while at the same time reaching high values of $[\text{anion}]/[\text{complex}]$ and signal saturation in a single experiment.

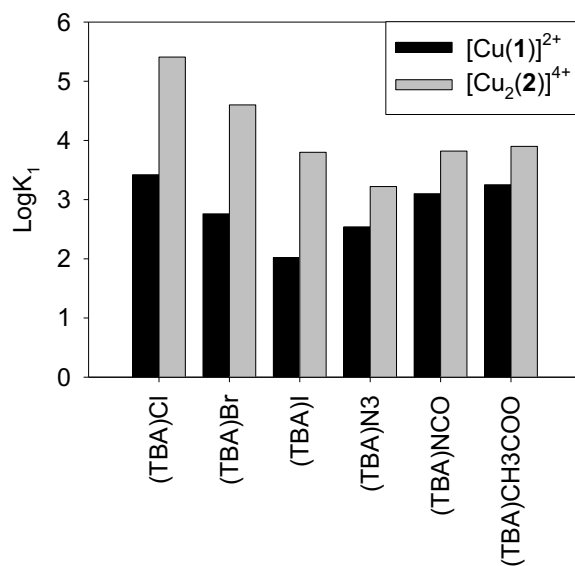


Figure S6. Bar diagram comparing $\log K_1$ values obtained for the interaction of mono- and di-copper(II) complexes with the investigated anions.

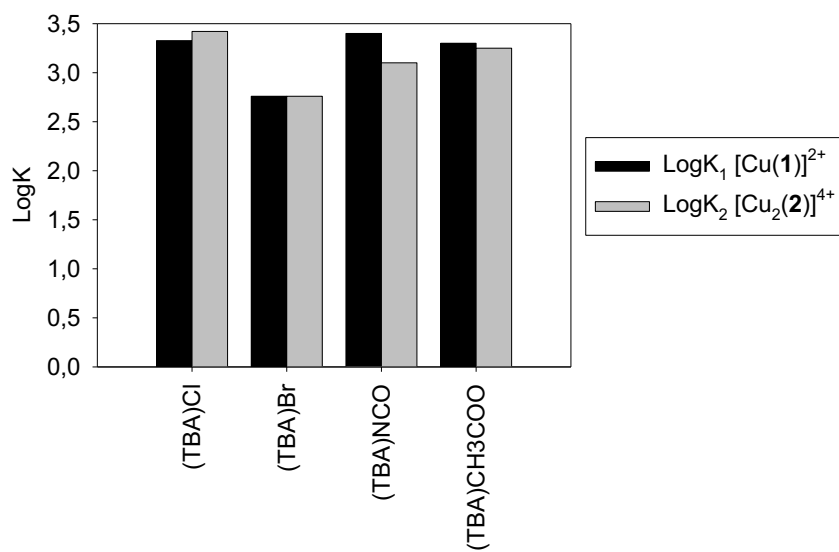


Figure S7. Bar diagram comparing $\log K_2$ values obtained for the interaction of the di-copper(II) complex with the investigated anions and the corresponding $\log K_1$ determined for the mononuclear complex.

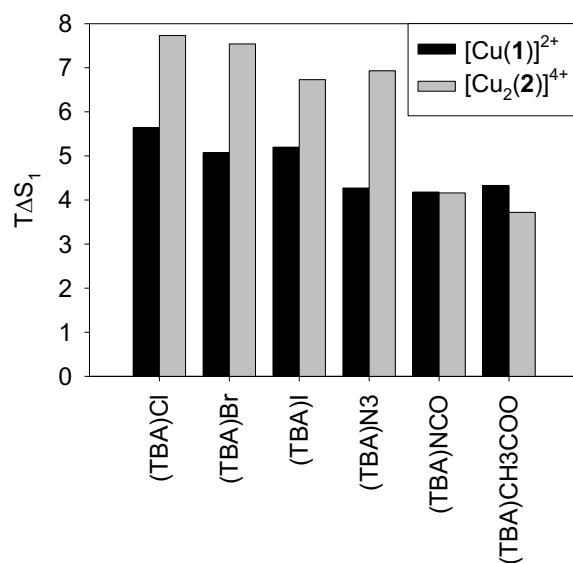


Figure S8. Bar diagram comparing $T\Delta S_1$ values obtained for the interaction of the di-copper(II) complex with the investigated anions and the corresponding values determined for the mononuclear complex.

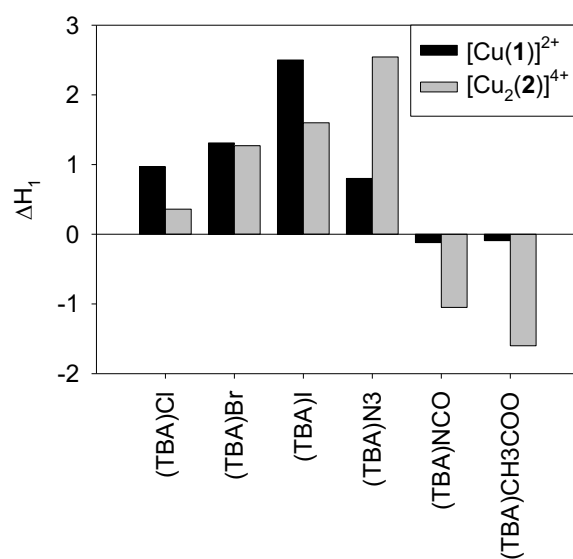


Figure S9. Bar diagram comparing ΔH_1 values obtained for the interaction of the di-copper(II) complex with the investigated anions and the corresponding values determined for the mononuclear complex.

C. Spectrophotometric Studies

The affinity towards anions of $[\text{Cu}(\mathbf{1})]^{2+}$ and $[\text{Cu}_2(\mathbf{2})]^{4+}$ in DMSO was also investigated through spectrophotometric titration experiments. Solutions of $[\text{Cu}(\mathbf{1})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\mathbf{2})](\text{ClO}_4)_4$ were titrated with standard solutions of the tetrabutylammonium (TBA^+) salts of the envisaged anions. After each addition of sub-stoichiometric amounts of the anion, the UV-Vis spectrum of the solution was recorded. The association constants determined by a non-linear least-squares program^{S1} are reported in Table S1.

Table S1. Association constants (as logK values) for the interaction of $[\text{Cu}(\mathbf{1})]^{2+}$ and $[\text{Cu}_2(\mathbf{2})]^{4+}$ with anions (as TBA^+ salts) in pure DMSO at 25°C, determined by UV/Vis spectroscopy. Numbers in parentheses are standard deviations to the last significant figure.

Anion	Receptor	Fitting model	Log K ₁	Log K ₂
Cl^-	$[\text{Cu}(\mathbf{1})]^{2+}$	1:1	3.39(2)	/
	$[\text{Cu}_2(\mathbf{2})]^{4+}$	1:2	5.3(1)	3.0(3)
Br^-	$[\text{Cu}(\mathbf{1})]^{2+}$	1:1	2.9(1)	/
	$[\text{Cu}_2(\mathbf{2})]^{4+}$	1:2	4.8(2)	2.8(5)
I^-	$[\text{Cu}(\mathbf{1})]^{2+}$	1:1	2.1(2)	/
	$[\text{Cu}_2(\mathbf{2})]^{4+}$	1:2	3.89(4)	b
N_3^-	$[\text{Cu}(\mathbf{1})]^{2+}$	1:1	2.98(5)	/
	$[\text{Cu}_2(\mathbf{2})]^{4+}$	1:1	3.4(1)	/
NCO^-	$[\text{Cu}(\mathbf{1})]^{2+}$	1:1	3.6(3)	/
	$[\text{Cu}_2(\mathbf{2})]^{4+}$	a	a	a
CH_3COO^-	$[\text{Cu}(\mathbf{1})]^{2+}$	a	a	a
	$[\text{Cu}_2(\mathbf{2})]^{4+}$	a	a	a

^a No reliable fit. ^b Reliable value cannot be calculated.

As an example, Figure S10 shows the UV-Vis spectra collected over the course of the titrations of receptors $[\text{Cu}(\mathbf{1})]^{2+}$ and $[\text{Cu}_2(\mathbf{2})]^{4+}$ with $(\text{TBA})\text{Br}$, and the related distribution diagrams of species present at the equilibrium. Spectra and distribution diagrams obtained after titrations with $(\text{TBA})\text{Cl}$, $(\text{TBA})\text{I}$, $(\text{TBA})\text{N}_3$, $(\text{TBA})\text{NCO}$, and $(\text{TBA})\text{CH}_3\text{COO}$ are reported in Figures S11 and S12, respectively. No significant spectral variations were observed upon the titration of both complexes with nitrate and thiocyanate, suggesting that weak interactions (if any) take place with these anions, as already observed during ITC experiments. As a consequence, no stability constants have been determined for the adducts with SCN^- and NO_3^- .

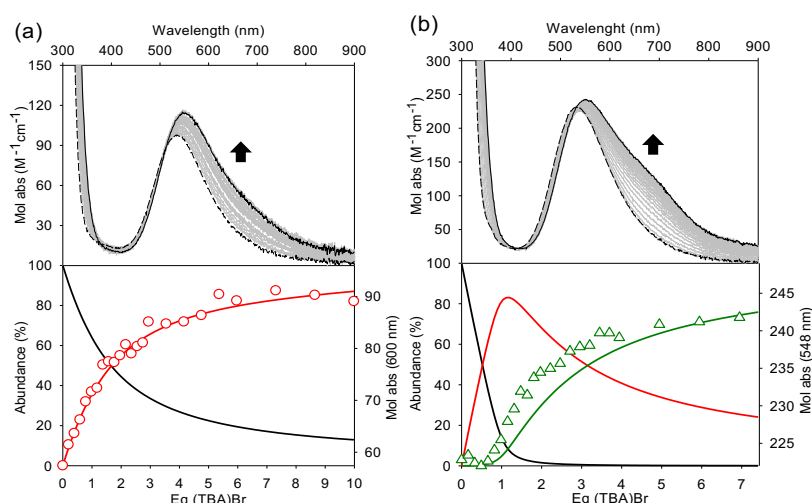


Figure S10. (a) Absorption spectra taken over the course of the titration of $[\text{Cu}(\mathbf{1})](\text{ClO}_4)_2$ (1.0×10^{-3} M in DMSO) with a solution of $(\text{TBA})\text{Br}$ (5.0×10^{-2} M in DMSO), and the related distribution diagram of species present at the equilibrium (black line: free $[\text{Cu}(\mathbf{1})]^{2+}$; red line: $[\text{Cu}(\mathbf{1})\text{Br}]^+$; red circles: superimposed plots of molar absorptivity (at 600 nm) versus the equivalent ratio $\text{Br}/\text{complex}$, $T = 25^\circ\text{C}$). (b) Absorption spectra taken over the course of the titration of $[\text{Cu}_2(\mathbf{2})](\text{ClO}_4)_4$ (1.0×10^{-3} M in DMSO) with a solution of $(\text{TBA})\text{Br}$ (5.0×10^{-2} M in DMSO), and the related distribution diagram of species present at the equilibrium (black line: free $[\text{Cu}_2(\mathbf{2})]^{4+}$; red line: $[\text{Cu}_2(\mathbf{2})\text{Br}]^{3+}$; Green line: $[\text{Cu}_2(\mathbf{2})\text{Br}_2]^{2+}$; circles: superimposed plots of molar absorptivity (at 548 nm) versus the equivalent ratio $\text{Br}/\text{complex}$, $T = 25^\circ\text{C}$).

Both mono- and di-nuclear complexes display a band centered at 533 nm, due to an envelope of d-d transitions.^{S2} As expected, this band in the di-nuclear complex ($\varepsilon = 228 \text{ M}^{-1}\text{cm}^{-1}$) is about twofold more intense than in the mono-nuclear analogue ($\varepsilon = 98 \text{ M}^{-1}\text{cm}^{-1}$). The addition of Br⁻ causes a redshift of the band at 533 nm, which also undergoes a slight intensity increase. In the case of $[\text{Cu}(\mathbf{1})]^{2+}$ the best fit to the titration data is obtained by assuming the occurrence of only one equilibrium for the interaction with bromide, corresponding to the formation of 1:1 adduct. The formation of $[\text{Cu}(\mathbf{1})\text{Br}_2]$, which cannot be ruled out, since this species was observed by ITC experiments, does not seem to induce spectral changes sufficient to be clearly detected during the UV-vis titration experiment. A similar behavior was observed when $[\text{Cu}(\mathbf{1})]^{2+}$ was titrated with Cl⁻, I⁻, N₃⁻, and NCO⁻.

Considering the $[\text{Cu}_2(\mathbf{2})]^{4+}$ complex, data fitting indicates that two equilibria take place in the presence of bromide, corresponding to the formation of $[\text{Cu}_2(\mathbf{2})\text{Br}]^{3+}$ and $[\text{Cu}_2(\mathbf{2})\text{Br}_2]^{2+}$ species (see diagram of species distribution, Figure S10b). The occurrence of two analogous stepwise equilibria is suggested also for the interaction of the di-copper complex with chloride and iodide, while only the formation of 1:1 adduct can be hypothesized in the case of azide on the basis of the UV-Vis titration results, in accordance with the ITC experiments. It should be noted that titration data related to the interactions of NCO⁻ with $[\text{Cu}_2(\mathbf{2})]^{4+}$ and of CH₃COO⁻ with both complexes did not provide a reliable fit, preventing the determination of the corresponding stability constants.

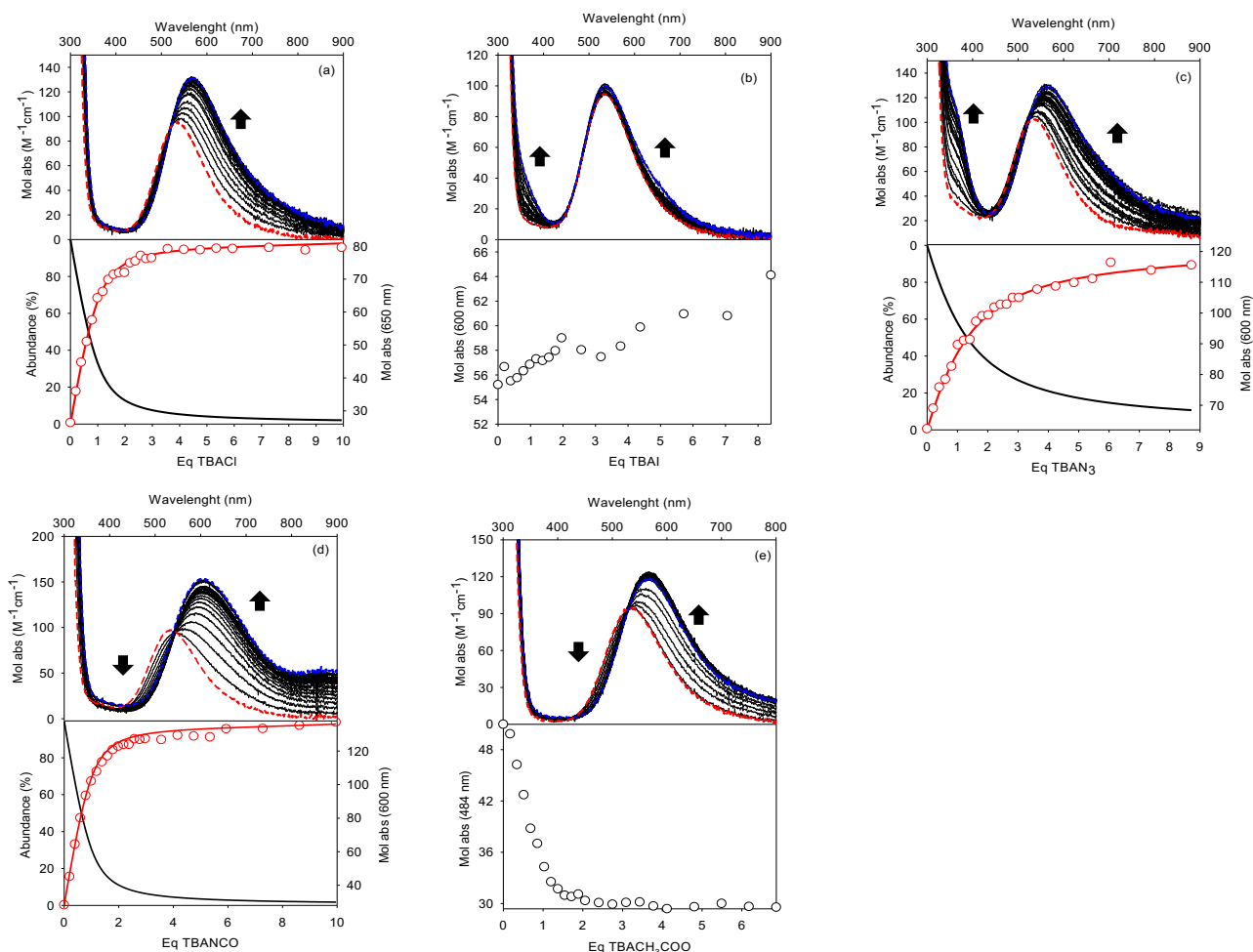


Figure S11. Absorption spectra taken over the course of the titration of $[\text{Cu}(\mathbf{1})](\text{ClO}_4)_2$ ($1.0 \times 10^{-3} \text{ M}$ in DMSO) with a DMSO solution of (a) (TBA)Cl ($5.0 \times 10^{-2} \text{ M}$), (b) (TBA)I ($5.0 \times 10^{-2} \text{ M}$), (c) (TBA)N₃ ($5.2 \times 10^{-2} \text{ M}$), (d) (TBA)NCO ($4.7 \times 10^{-2} \text{ M}$), and (e) (TBA)CH₃COO ($5.2 \times 10^{-2} \text{ M}$), and the related distribution diagrams of species present at the equilibrium (black line: free $[\text{Cu}(\mathbf{1})]^{2+}$; red line: $[\text{Cu}(\mathbf{1})\text{X}]^+$; red circles: superimposed plots of molar absorptivity versus the equivalent ratio X/complex, X=Cl, NCO, N₃, T = 25°C). In the case of iodide and acetate the plot of molar absorptivity versus the equivalent ratio anion/complex is reported (black circles).

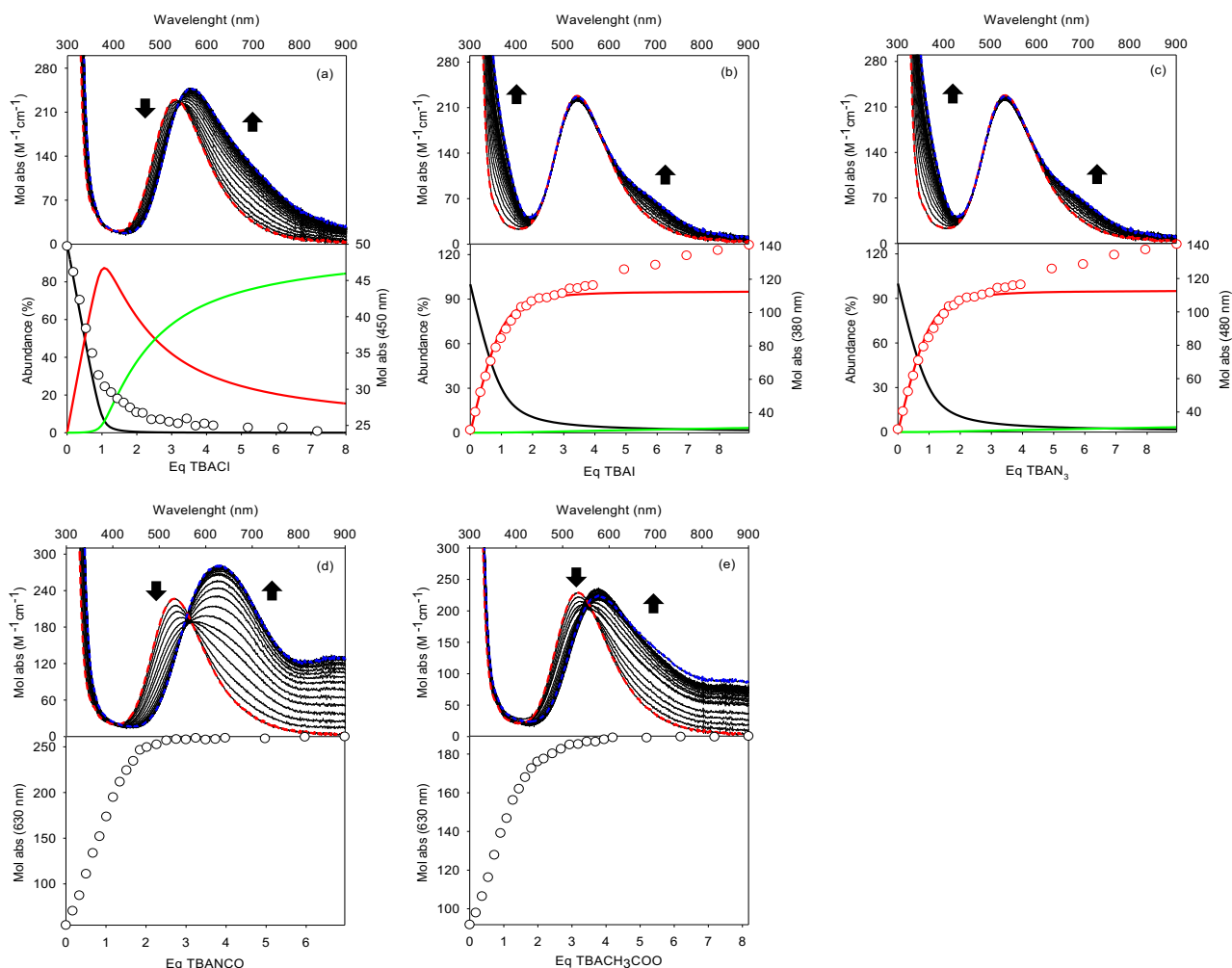


Figure S12. Absorption spectra taken over the course of the titration of $[\text{Cu}_2(\mathbf{2})](\text{ClO}_4)_4$ (1.0×10^{-3} M in DMSO) with a DMSO solution of (a) $(\text{TBA})\text{Cl}$ (5.5×10^{-2} M), (b) $(\text{TBA})\text{I}$ (5.0×10^{-2} M), (c) $(\text{TBA})\text{N}_3$ (5.2×10^{-2} M), (d) $(\text{TBA})\text{NCO}$ (4.7×10^{-2} M), and (e) $(\text{TBA})\text{CH}_3\text{COO}$ (5.2×10^{-2} M), and the related distribution diagram of species present at the equilibrium (black line: free $[\text{Cu}_2(\mathbf{2})]^{4+}$; red line: $[\text{Cu}_2(\mathbf{2})\text{X}]^{3+}$; green line: $[\text{Cu}_2(\mathbf{2})\text{X}_2]^{2+}$; circles: superimposed plots of molar absorptivity versus the equivalent ratio $\text{X}^-/\text{complex}$, $\text{X}=\text{Cl}, \text{I}, \text{N}_3$, $\text{T}=25^\circ\text{C}$). In the case of cyanate and acetate the plots of molar absorptivity versus the equivalent ratio anion/complex are reported (black circles).

D. X-ray Crystallography

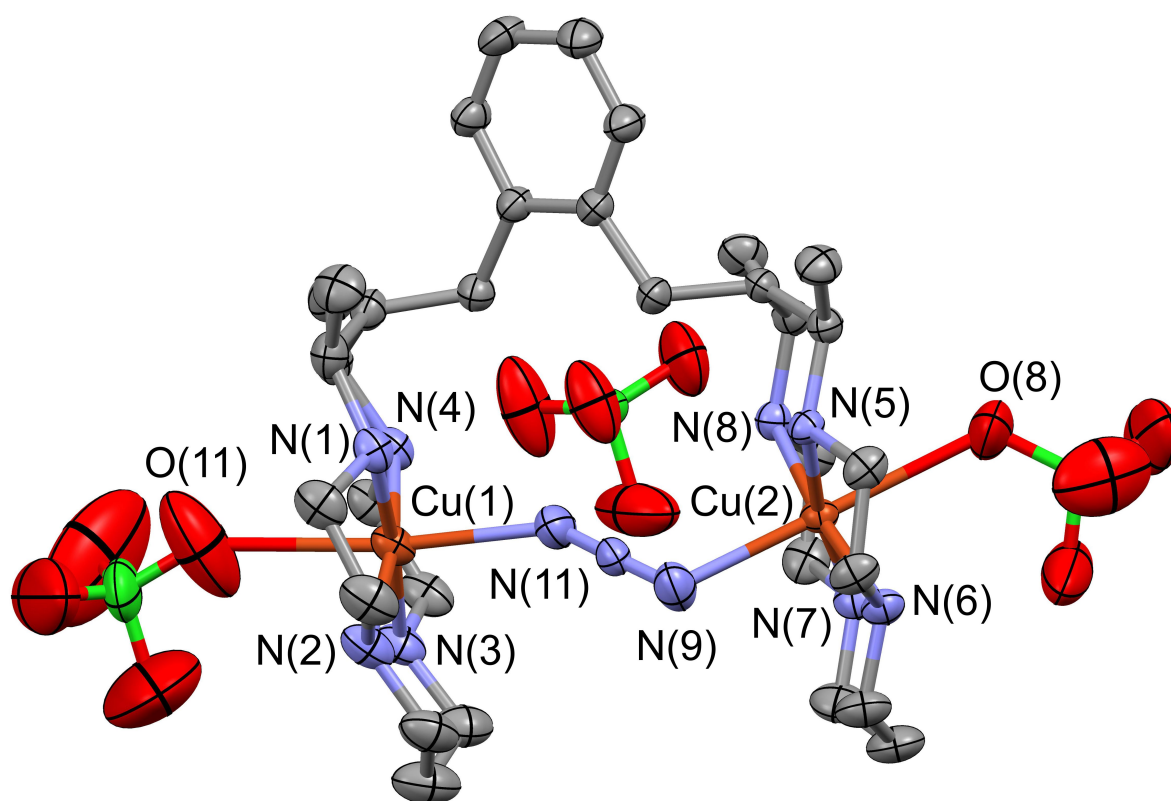


Figure S13. Plot showing thermal ellipsoids of the $[\text{Cu}^{\text{II}}_2(2)\text{N}_3(\text{ClO}_4)_2](\text{ClO}_4)$ molecular compound occurring in the hemihydrate crystal salt (ellipsoids are drawn at the 30% probability level; H atoms and water solvent molecules were omitted for clarity). Atom names were reported only for the copper(II) centers and for their bonded atoms, defining two axially elongated octahedra.

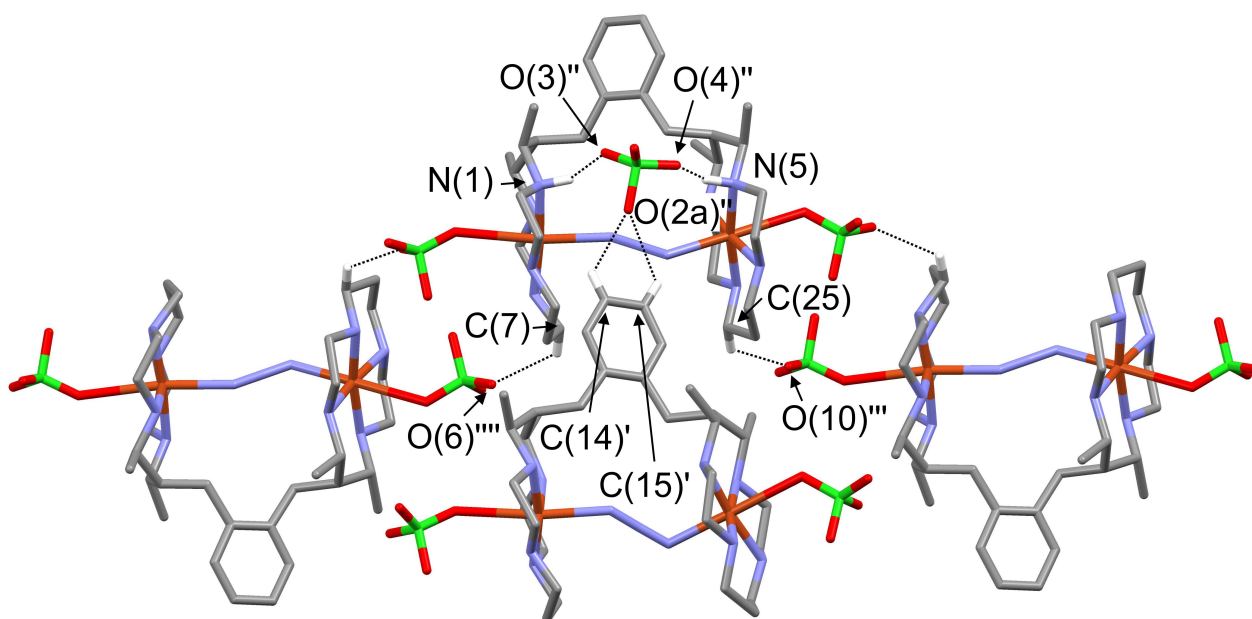


Figure S14. A simplified sketch showing that copper(II) centers of adjacent bimacrocycles are not directly bridged by the perchlorate counterions and intramolecular connections are provided by $\text{NH}\cdots\text{O}$ and unconventional $\text{CH}\cdots\text{O}$ interactions, having the oxygens of perchlorate ions as H-acceptors. Atom names and hydrogen atoms are drawn only for the independent supramolecular interactions, whose geometrical features are reported in the following table:

D donor group	D···A [Å]	H···A [Å]	D-H···A [°]	A acceptor atom
N(1)-H(1a)	3.299(7)	2.569(7)	131.4(3)	O(3)"
N(5)-H(5)	2.942(6)	2.100(6)	142.9(3)	O(4)"
C(7)-H(7b)	3.146(10)	2.470(10)	126.5(5)	O(6)""
C(25)-H(25a)	3.061(15)	2.342(15)	130.4(5)	O(10)'''
C(14)'-H(14)'	3.119(9)	2.508(2)	123.4(4)	O(2a)"
C(15)'-H(15)'	3.152(9)	2.586(8)	119.7(4)	O(2a)"

Symmetry code: (') = $x, -y, -1/2+z$; (") = $1/2-x, -1/2+y, z$; (""') = $1/2+x, 1/2-y, -z$; (""") = $-1/2+x, 1/2-y, -z$

References

- (S1) (a) Gans, P.; Sabatini, A.; Vacca, A. Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs. *Talanta*, **1996**, 43, 1739–1753. (b) Gans, P.; Sabatini, A.; Vacca, A. Determinations of equilibrium constants from spectrophotometric data obtained from solutions of known pH: the program pHab *Ann. Chim.* **1999**, 89, 45-49; <http://www.hyperquad.co.uk/HypSpec2014.htm>.
- (S2) (a) Licchelli, M.; Milani, M.; Pizzo, S.; Poggi, A.; Sacchi, D.; Boiocchi, M. Synthesis of novel diazacyclam copper(II) complexes by template reaction involving sulphonamides as locking fragments. *Inorg. Chim. Acta* **2012**, 384, 210-218. (b) Hathaway, B. J. A new look at the stereochemistry and electronic properties of complexes of the copper(II) ion. *Struct. Bonding (Berlin)* **1984**, 57, 55-118.