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An Electron-Poor Host Receptor for Electron-Rich Guests Involving Anion–π and Lone-Pair–π Interactions

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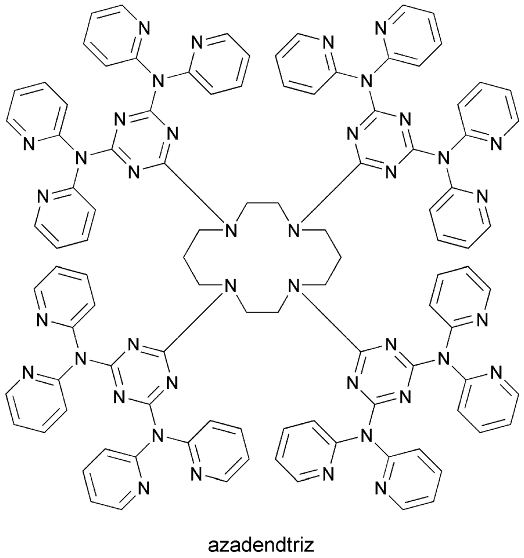
The binding of the ligand *N*,*N*′,*N*′′,*N*′′′-tetrakis{2,4-bis[(dipyridin-2-yl)amino]-1,3,5-triazin-2-yl}-1,4,8,11-tetraazacyclotetradecane (azadendtriz) to four copper(II) ions generates two electron-deficient cavities formed by four coordinated pyridine rings that are capable of hosting electron-rich guests. The molecular structures of $[Cu_4(azadendtriz)Cl_4](Cl)_4(H_2O)_{13}$ (**1**) and $[Cu_4(azadendtriz)Br_4](Br)_4(H_2O)_{28}$ (**2**), determined from single-crystal X-ray data, reveal that the π-acidic receptor binds a chloride anion through anion–π interactions in **1**, whereas it hosts a water molecule through lone-pair–π interactions in **2**. This differentiation between Br^- and Cl^- may be explained by the different size of the (hydrated) anions.

Introduction

The crucial role of anionic species in biochemical processes has triggered considerable research efforts into the design and preparation of synthetic anion-binding hosts.[1–10] These artificial anion receptors find applications in the binding and transport of biologically relevant anions,[11–15] catalysis,[16–19] analytical chemistry,[20,21] (water) waste management,[22,23] and anion-templated reactions.[24–27] These host–guest systems are principally based on hydrogen-bonding interactions (mostly involving positively charged hosts) or Lewis acidity (electroneutral hosts).[28,29] However, over the past two years a new type of supramolecular interaction, namely the anion–π interaction,[30–35] has been considered by the scientific community to rationally design and synthesize anion receptors.[36–38]

In 2004 some of us reported on one of the first crystallographic evidences of such anion–π interactions between chloride ions and π-acidic pyridine rings.[39] The Cl host is obtained by the reaction of copper(II) chloride with the ligand azadendtriz[40] (Scheme 1). The resulting tetracopper(II) coordination compound **1** exhibits two electron-deficient cavities built from four Cu-coordinated pyridine rings, each hosting a chloride anion.[39]



Scheme 1. *N*,*N*′,*N*′′,*N*′′′-tetrakis{2,4-bis[(dipyridin-2-yl)amino]-1,3,5-triazin-2-yl}-1,4,8,11-tetraazacyclotetradecane (azadendtriz).[40]

In the present study, the synthetic receptor, which had primarily been obtained serendipitously, is now purposely generated by the reaction of copper(II) bromide with azadendtriz. The anion-binding properties of the $CuCl_2$ and $CuBr_2$ systems are compared, both experimentally (single-

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crystal X-ray structures) and theoretically (DFT calculations), revealing interesting and new supramolecular features.

Results and Discussion

Reaction between Copper(II) Bromide and azadendtriz

The slow interphase reaction of an aqueous solution of copper(II) bromide with a dichloromethane solution of azadendtriz (ratio $CuBr_2$/azadendtriz = 9:1) produces single crystals of a tetracopper(II) coordination compound, i.e. $[Cu_4(azadendtriz)Br_4](Br)_4(H_2O)_{28}$ (**2**; Figure S1), whose solid-state structure is comparable to the one of the previous chloride analogue $[Cu_4(azadendtriz)Cl_4](Cl)_4(H_2O)_{13}$ (**1**).[39] Like **1**, compound **2** holds four square-pyramidal Cu^{II} centers whose coordination environments consist of four pyridine donors at the basal planes and an anion at the apical positions (Figure 1). The Cu–N [ranging from 2.006(15) to 2.058(14) Å] and Cu–Br [ranging from 2.540(5) to 2.590(6) Å] bond lengths can be considered as normal for these types of copper(II) chromophores and are analogous to those found for **1**.[39] Four bromide ions and 28 water molecules are present in the crystal lattice. As observed before for **1**, the triazine rings are π–π stacked in a face-to-face alignment [the centroid–centroid distances are 3.654(1) Å].

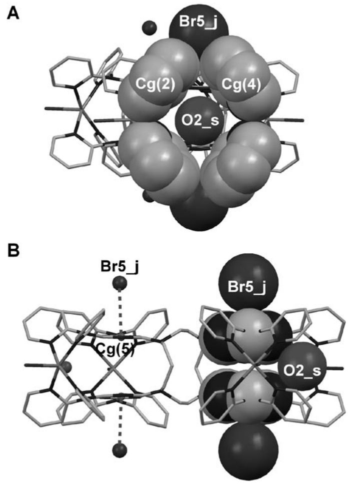

Figure 1. Representations of the cationic part of compound **2** showing (A) the inclusion of a water molecule (O2_s) inside a cavity formed by four pyridine rings and (B) anion(Br5_j)–π(triazine) interactions.

As expected, compound **2** displays electron-poor cavities formed by four coordinated pyridine rings (Figure 1A). However, close examination of the guest molecules in **1** and **2** reveals significant supramolecular disparities between the two molecules (Figure 1 and Figure 2).

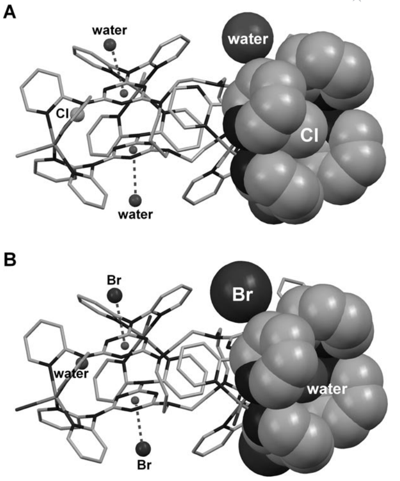

Figure 2. Anion–π and lone-pair–π interactions in the solid-state structures of (A) compound **1** and (B) compound **2**.

Indeed, in the case of compound **1**, the cavities host a chloride anion (Figure 2A), whereas these receptors contain a water molecule in **2** (Figure 1 and Figure 2B). Surprisingly, the bromide ions do interact with the electron-deficient triazine rings through anion–π interactions. The equivalent triazine rings in **1** interact with water molecules by means of lone-pair (l.p.)–π interactions,[41,42] a supramolecular feature that has been overlooked in the earlier description of the molecular structure of **1**. The contact distances characterizing these supramolecular interactions are listed in Table 1. The supramolecular synthons involved in these interactions are labeled in Figure 1 and Figure 3 for compounds **2** and **1**, respectively.

The encapsulated water molecule (see Figure 1) is characterized by O2_s–centroid distances of 3.504(14) Å [Cg(2)···O2_s] and 3.569(13) Å [Cg(4)···O2_s] (Table 1). These distances are comparable to those observed for the guest chloride ions Cl5 and Cl6 in **1** (Table 1) and are about 0.35–0.5 Å above the sums of the van der Waals radii of carbon and nitrogen with oxygen.[30] Remarkably, the bromide ions (Br5_j; Figure 1), although not fitting into the central cavity of four pyridine rings, are nevertheless involved in anion–π interactions with the triazine rings. The centroid···Br^- distance is 3.489(15) Å [Cg(5)···Br5_j] (Table 1), which is below the sum of the van der Waals radii for C + Br = 3.55 Å and just above the sum of the van der Waals radii for N + Br = 3.40 Å.[43] Moreover, the centroid···Br^- distance is slightly longer than the value calculated for the simple model Br···s-triazine, namely 3.34 Å.[44] Amazingly, the equivalent triazine rings in compound **1** interact with water molecules (see Figure 3; oxygen atoms O2 and O3). The contact distances are 3.178(6) Å [Cg(12)···O2] and 3.338(6) Å [Cg(13)···O3] (Table 1), reflecting sensible interactions of the guest water molecules with the host triazine rings, i.e. the sum of the van der Waals radii (C + O) and (N + O) are 3.22 and 3.07 Å, respectively.[30] A significantly different affinity of the four-pyridine host cavity for chloride and bromide ions

Table 1. Characteristic contact distances (in Å) for the anion–π and lone-pair–π interactions observed in the molecular structures of **1** and **2** (see Figure 1 and Figure 3 for the labeling schemes[a]).

Compound **1**			
Cg(4)–Cl5	3.521(6)	Cg(7)–Cl5	3.559(5)
Cg(9)–Cl6	3.697(5)	Cg(11)–Cl6	3.488(5)
N17–O3	3.786(5)	C48–O3	3.414(5)
N18–O3	3.712(6)	C49–O3	3.872(5)
N19–O3	3.324(6)	C50–O3	3.401(6)
Cg(13)–O3	3.338(6)		
N13–O2	3.292(5)	C41–O2	3.372(6)
N14–O2	3.504(6)	C42–O2	3.253(5)
N15–O2	3.585(6)	C43–O2	3.674(5)
Cg(12)–O2	3.178(6)		
Compound **2**			
N52–Br5_j	3.586(14)	N54–Br5_j	3.489(14)
N56–Br5_j	3.679(14)	C51–Br5_j	3.678(16)
C53–Br5_j	3.489(15)	C55–Br5_j	3.585(13)
Cg(5)–Br5_j	3.489(15)		
N41–O2_s	3.470(12)	C42–O2_s	3.425(12)
C43–O2_s	3.789(12)	C44–O2_s	4.159(12)
C45–O2_s	4.195(13)	C46–O2_s	3.871(12)
Cg(4)–O2_s	3.569(13)		
N21–O2_s	3.506(12)	C22–O2_s	3.452(13)
C23–O2_s	3.719(13)	C24–O2_s	4.015(12)
C25–O2_s	4.061(13)	C26–O2_s	3.818(12)
Cg(2)–O2_s	3.504(14)		

[a] Symmetry operations: j: 1/2 – *x*, 1/2*y*, –*z*; s: 1/2 – *x*, –1/2 + *y*, –*z*.

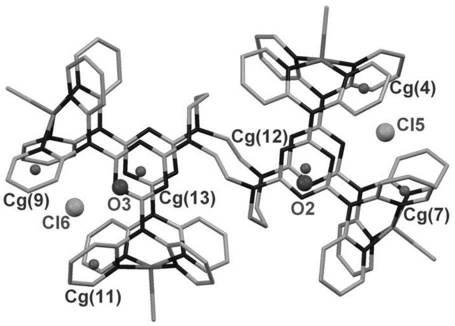

Figure 3. Chloride–π [Cl5···Cg(4) and Cl5···Cg(7) and Cl6···Cg(9) and Cl6···Cg(11)] interactions and l.p.(water)–π [O2···Cg(12) and O3···Cg(13)] interactions in **1**.

is thus observed, which may be due to the different sizes of the anions (the ionic radius is 1.81 Å for Cl^- and 1.96 Å for Br^-).[45] The molecular structures of **1** and **2** have been theoretically investigated.

Theoretical Investigations

The different supramolecular arrangements based on anion–π interactions have also been theoretically examined. In order to estimate the formation energies and to calculate the molecular electrostatic potential (MEP) maps, the BHandH functional coupled with 6-31+G(d) basis sets has been employed (see Computational Studies). The results of these calculations are given in Table 2 and are displayed in Figure 4A–F.

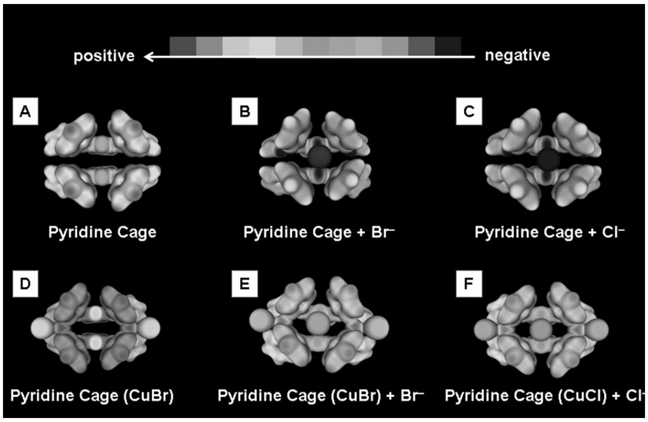

Figure 4. Molecular electrostatic potential on the 0.001 au surface of the studied assemblies. For the sake of clarity, the pyridine cage (CuCl) is not displayed as it is qualitatively equivalent to the pyridine cage (CuBr).

Firstly, the system consisting of the azadendtriz ligand forming the pyridine-based host cage [but non-coordinated to copper(II) ions] and a chloride guest has been investigated (Figure 4C). The formation energy of this supramolecular association is +7.8 kcal mol^{-1} (Table 2), thus reflecting an instability of the host–guest pair.

When the pyridine N donors are coordinated to $Cu^{II}Cl$ units (Figure 4F) then the stability of the cage–Cl supramolecular pairing is significantly enhanced, as is evidenced by the corresponding formation energy of –91.2 kcal mol^{-1} (Table 2). This higher affinity of the host for the chloride anion is most likely due to the (obvious) increase of the electron-poor character of the pyridine rings upon coordination to copper(II), as reflected by the MEP representations in Figure 4A and D.

Similar calculations have been carried out to study the pyridine cage containing the bromide anion. The so-obtained data clearly show that the stability of the host–guest complex is higher than that of the chloride one (Table 2 and Figure 4C–F). For instance, the formation energy of the system [pyridine cage (CuBr)]···Br is –149.6 kcal mol^{-1}, whereas it is –91.2 kcal mol^{-1} for the chloride analogue (Table 2).

Table 2. Formation energies calculated for different host–halide systems (see Figure 4 and Figure 5).

Host–guest system	Formation energy [kcal mol^{-1}]
Pyridine cage + Cl	+7.8
[Pyridine cage (CuCl)] + Cl	–91.2
Pyridine cage + Br	–13.3
[Pyridine cage (CuBr)] + Br	–149.6
Triazine···Cl	–115.5
Triazine···Br	–240.2

In both cases the MEP representations are qualitatively comparable, providing no clear reason for the preference towards bromide ions. It also appears that the size of the anion cannot fully explain the differences observed in the molecular structures of compounds **1** and **2** (Figure 2). The solvation of the halide anions may play a role; for instance, the interaction energies ΔE_{int} for $\text{Cl}\cdots\text{H}_2\text{O}$ and $\text{Br}\cdots\text{H}_2\text{O}$ are –14.6 and –12.9 kcal mol^{-1}, respectively.[46,47] Moreover, the free energies of transfer ($\Delta G^0{}_{\text{tr}}$) of chloride and bromide from water to acetonitrile (an aprotic solvent like dichloromethane) are 10.0 and 7.5 kcal mol^{-1}, respectively.[48,49]

The weakening of solvation is evidenced by a larger positive $\Delta G^0{}_{\text{tr}}$ value. Such a phenomenon probably occurs between water and dichloromethane, but no investigations have been reported so far for this biphasic system, most likely because these two solvents are not miscible.

Next, *qualitative* theoretical kinetic studies have been carried out to appraise whether the transfer of the halide ion from the solvent into the host cage is less favoured for Br$^-$ than for Cl$^-$. For that purpose, starting from the supramolecular complexes where the halide is sitting inside the cage, the guest ion has been pulled out from the host by 0.4 Å steps, and the corresponding host–guest complex energies have been calculated. The results are illustrated in Figure 5.

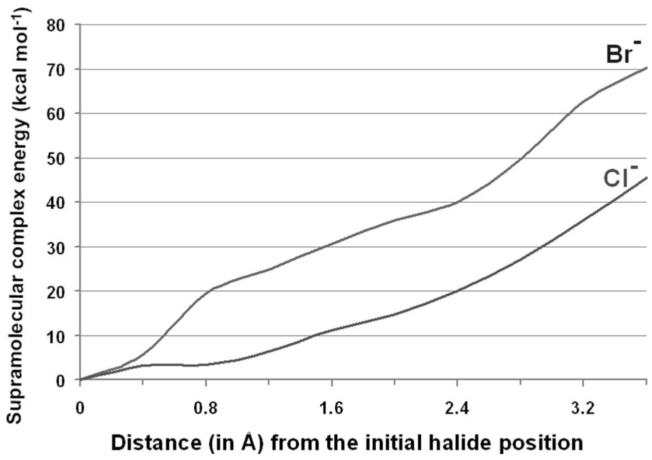

Figure 5. Formation energies [kcal mol^{-1}] as a function of the anion distance from the initial position inside the cage. Energies are reported as relative to the energy obtained by single-point calculations on the experimental structure (see Computational Studies).

These calculations suggest that the transfer of the halide guests into the host cavity may be dominated by diffusion, which is correlated to the size and/or solvation of the anion. Indeed, energy barriers reflecting the occurrence of transition states in the host–guest formation process should result in the observation of maxima in the curves depicted in Figure 5. The absence of maxima suggests that the halides tend to diffuse into the cage, which is realized slightly more gradually in the case of Br$^-$. Such higher affinities towards Cl$^-$ have been observed with polyamine host–guest systems,[50,51] and have been explained by the diffusion of hydrated halide species and by their dehydration (desolvation) before complexation with the guest molecule.[52–54]

An alternative explanation for the chloride/bromide selectivity of the pyridine-based host cage may be a different affinity of the π-acidic triazine ring (of the azadendtriz ligand) for chloride and bromide ions. It is well known that the electron-deficient s-triazine ring can favorably interact with halides through anion–π interactions.[55–58] The interaction energy of each halide···triazine(centroid) pair has been determined, which is –115.5 kcal mol^{-1} for Cl$^-$ and –240.2 kcal mol^{-1} for Br$^-$ (Table 2).[59] The energy difference between the Cl$^-$ ion in the cage and on top of the triazine ring amounts to only 24 kcal mol^{-1}, whereas it is 91 kcal mol^{-1} for Br$^-$. The Br···triazine pair appears to be significantly more stable than the Br···cage system.

Conclusions

Anion–π and lone-pair–π interactions are supramolecular contacts that have only recently been recognized as such by the scientific community. In the present study, the solid-state structures of coordination compounds bearing anion–host cavities based on such interactions reveal their apparent selectivity for chloride over bromide. DFT calculations suggest that this discrimination most likely arises from distinct diffusion transfer processes of the two halides, but further studies are required to confirm these observations. In addition, it appears that the affinity of the pyridine-based receptor for the bromide anion is lower than that of the π–acidic triazine ring, whereas it is the opposite for the chloride ion.

Experimental Section

General Procedures: All starting materials were commercially available and used as received. IR spectra were recorded with a Perkin–Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate diamond, and peaks are reported in cm^{-1}. C, H, and N analyses were performed with a Perkin–Elmer 2400 series. The ligand azadendtriz was prepared according to a procedure described earlier.[40] The preparation and molecular structure of compound **1** have been reported in a previous paper.[39]

Synthesis of Compound 2: The ligand azadendtriz (23.3 mg, 12.4 µmol) was dissolved in dichloromethane (3.5 mL) and layered with a solution of CuBr_2 (25.2 mg, 112.8 µmol) in water (3.5 mL). Blue needle-shaped single crystals of $[\text{Cu}_4(\text{azadendtriz})\text{Br}_4](\text{Br})_4(\text{H}_2\text{O})_{28}$, suitable for X-ray diffraction analysis, were obtained after 2 d by slow diffusion of the ligand into the aqueous phase (which turned from colorless to blue). The crystals were isolated by filtration and dried in air, which resulted in the loss of their crystallinity (most likely owing to the elimination of part of the lattice water molecules). Yield 16.6 mg (41 % based on the ligand). $\text{C}_{102}\text{H}_{84}\text{Br}_8\text{Cu}_4\text{N}_{40}\cdot 17\text{H}_2\text{O}$ (3069.75): calcd. C 39.91, H 3.87, N 18.25; found C 39.97, H 3.47, N 18.13. As mentioned above, compound **2** readily loses water upon exposure to air. IR: $\tilde{\nu}$ = 3420, 3068, 1604, 1558, 1464, 1374, 1266, 1026, 776, 668 cm^{-1}.

Crystallography: Crystallographic data for compound **2** are given in Table 3. The data collection was carried out at 173(2) K with a Nonius KappaCCD diffractometer. The single crystal was mounted onto a glass fiber by using the oil-drop method.[60] The intensity data were corrected for Lorentz and polarization effects and for absorption. The uncoordinated bromide ions and most of the water molecules were found to be disordered. The aromatic six rings were refined as rigid groups. The H atoms of the water molecules were not located. The voids between molecules of **2** are filled with crystallographically disordered water molecules (Figure 6), only part of which could be located. The non-hydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with a fixed geometry with regard to their carrier atoms. The programs SHELXS and SHELXL-97 were used for all the calculations.[61,62] It has to be mentioned that the high *R* value obtained is because of the numerous disordered water molecules present in the crystal lattice (Figure 6). However, the copper coordination part of the protein-like, solid-state structure of **2** is sufficiently accurate to discuss the supramolecular contacts observed. CCDC-709653 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data and structure refinement for compound **2**.

Empirical formula	$C_{204}H_{280}Br_{16}Cu_8N_{80}O_{56}$
M_r [g mol^{-1}]	6535.96
Temperature [K]	173(2)
Wavelength [Å]	0.71073
Crystal system, space group	monoclinic, *C2/m*
Unit cell dimensions	
a [Å]	32.069(6)
b [Å]	14.371(3)
c [Å]	19.999(4)
α [°]	90
β [°]	124.14(3)
γ [°]	90
Volume [Å^3]	7628(3)
Z, calculated density [mg m^{-3}]	1, 1.423
Absorption coefficient [mm^{-1}]	2.718 mm^{-1}
F(000)	3304
Crystal size [mm]	0.18 × 0.04 × 0.02
θ range for data collection [°]	2.45–20.81
Limiting indices	$-32 \le h \le 32$, $-14 \le k \le 14$, $-19 \le l \le 19$
Reflections collected/unique	26578/4083 [*R*(int) = 0.1632]
Completeness to θ = 20.81°	97.0%
Absorption correction	semi-empirical from equivalents
Max. and min. transmission	0.9476 and 0.6404
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	4083/139/433
Goodness-of-fit on F^2	2.041
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.1482$, $wR_2 = 0.3430$
R indices (all data)	$R_1 = 0.2327$, $wR_2 = 0.3831$
Largest diff. peak and hole [e Å^{-3}]	1.673 and –0.826

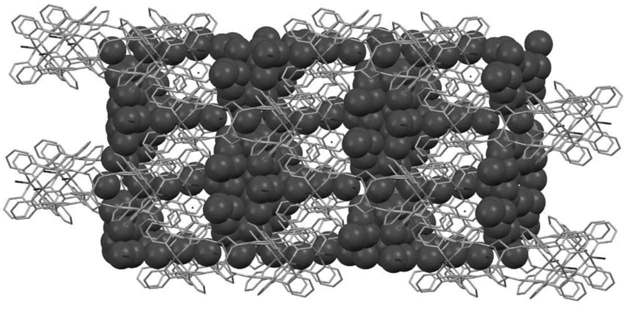

Figure 6. Representation of the crystal packing of compound **2**, showing the numerous water molecules filling the hollow space between the coordination molecules.

Computational Studies: All calculations were carried out by employing the Gaussian 03 suite of programs.[63] In order to estimate formation energies and the molecular electrostatic potential (MEP), single-point calculations at the BHandH/6-31+G(d) level were performed directly on the experimental (X-ray) structures. This approach has been recently applied to complexes featuring similar interactions to those studied here.[35,64] To evaluate the kinetics of the formation of the supramolecular complexes, BHandH/6-31G single-point calculations were performed on 10 structures per assembly as follows: starting from the experimental structure the anion was pulled out by 0.4 Å steps up to a maximum distance of 3.6 Å from the original position inside the cage. Then, the absolute energy was reported as relative to the formation energy of the minimum (calculated at the same level of theory, Figure 5).

Reliability of the DFT Calculations: The studied systems have a large size, with more than 100 atoms, including two copper centers. Thus, in line with previous studies,[35,64–66] the structures were not optimized, and single-point calculations were performed directly on the experimental structures obtained by single-crystal X-ray diffraction. The main issue about this procedure is that the DFT calculations (as all quantum-mechanics-based methods) may wrongly reproduce electronic structures that are away from the minimum. Despite the qualitative character of such an approach, many studies have been successfully proposed that are fully or partially based on experimental structures (obtained from NMR spectroscopic and/or X-ray data), where the molecular properties such as the electron density were calculated.[65–70] The 6-31+G(d) basis sets employed for the estimation of the formation energies and the MEPs are expected to provide a good description of the interactions.[71] Because of the large number of single-point calculations (20 in total), the (qualitative) kinetic studies were carried out by using the smaller 6-31G basis set. Because of the importance of this topic, test calculations have been performed on the experimental structures of the two main assemblies to evaluate the difference in the formation energies when using the smaller basis set. Importantly, these tests showed that the use of the smaller basis set leads to an overestimation of the formation energies of about 25 kcal mol^{-1} for both assemblies. Under the reasonable assumption that this error does not change significantly for all the steps of the kinetic studies, the trend observed in Figure 5 is not expected to significantly change when a larger basis set is employed. It has to be mentioned that the involvement of metal ions with unpaired electrons [like copper(II) ions in the present system] results in important difficulties for ab initio and DFT calculations.[72] In particular, the DFT calculations suffer from the so-called self-interaction error, which may lead to an unphysical delocalization of the spare electron over the entire ligand.[72–75] Nevertheless, a population analysis carried out in this work revealed that about 75% of the unpaired electrons were correctly localized on the metal center. Finally, dispersive forces may be difficult to evaluate by DFT calculations.[71,76–80] Importantly, previous theoretical studies on model systems featuring lone-pair–π and anion–π interactions have shown that even DFT calculations provide a fair description; however, it has also been found that post-Hartree–Fock calculations (in particular MP2) ensure the best performance.[56,71,81,82] Unfortunately, high-level ab initio methods, which correctly describe these forces, require a computational cost that is only affordable for relatively small molecules.[56,72] For complexes such as those investigated in the present study a valuable alternative is represented by the use of the hybrid BHandH functional, which has recently been shown to describe surprisingly well geometries and energies of a variety of systems for which dispersive forces are crucial.[71]

Supporting Information (see footnote on the first page of this article): Figure S1 showing the single-crystal X-ray structure of **2** with the atom-numbering scheme.

Acknowledgments

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[59] The formation energies of the triazine···Br(Cl) pairs are somewhat larger than those reported in previous studies on similar anion···π model systems (see for example ref.[31]). At least three explanations may be found for these discrepancies: (i) the complexes herein investigated contain two copper metal centers; therefore, the electrostatic contribution to the formation energy is possibly more significant than that of supramolecular complexes without metal ions, i.e., the present systems and those reported in ref.[31] feature similar interactions, but they are substantially different; (ii) in the geometries featuring Br (Cl) anions on top of a triazine ring, C–H···Br (Cl) interactions (involving pyridine rings) may also contribute to the formation energy; in such a case, the strength of these interactions may be (systematically) overestimated by the BHandH functional (see ref.[68]); (iii) finally, the models reported in ref.[31] are typically small complexes containing one aromatic ring and one halide, thus allowing a full optimization with a fine computational setup (often at the MP2 level). Because of the size of the

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