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Coordination Complexes Exhibiting Anion···π Interactions: Synthesis, Structure, and Theoretical Studies

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The polydentate ligand 2,4,6-tris(dipyridin-2-ylamino)-1,3,5-triazine (dpyatriz) in combination with the $Cu(ClO_4)_2$/CuX_2 salt mixtures ($X^- = Cl^-$, Br^-, or N_3^-) leads to the formation of molecular coordination aggregates with formulas $[Cu_3Cl_3(dpyatriz)_2](ClO_4)_3$ (**2**), $[Cu_3Br_3(dpyatriz)_2](ClO_4)_3$ (**3**), and $[Cu_4(N_3)_4(dpyatriz)_2(DMF)_4(ClO_4)_2](ClO_4)_2$ (**4**). These complexes consist of two dpyatriz ligands bridged via coordination to Cu^{II} and disposed either face-to-face in an eclipsed manner (**2** and **3**) or parallel and mutually shifted in one direction. The copper ions complete their coordination positions with Cl^- (**2**), Br^- (**3**), or N_3^-, ClO_4^-, and *N*,*N*-dimethylformamide (DMF) (**4**) ligands. All complexes crystallize together with noncoordinate ClO_4^- groups that display anion···π interactions with the triazine rings. These interactions have been studied by means of high level ab initio calculations and the MIPp partition scheme. These calculations have proven the $ClO_4^-\cdots[C_3N_3]$ interactions to be favorable and have revealed a synergistic effect from the combined occurrence of π−π stacking of triazine rings and the interaction of these moieties with perchlorate ions, as observed in the experimental systems.

Introduction

Anions are commonly found in living organisms, where they often play crucial structural and functional roles.[1] Therefore, it is essential to understand how anionic species interact with biomolecules because potential medicinal applications are expected from such investigations.[2] The design of synthetic anion receptors is a rapidly rising area of supramolecular chemistry.[3] The preparation of anion−host systems is particularly challenging because anions are large molecular species with low charge-to-radius ratios,[4] giving rise to less effective electrostatic binding interactions, compared to cations.[5] In addition, in aqueous solutions, many anions only exist in a narrow pH range and are usually coordinatively saturated, which brings in problems of binding affinity and stability of the host−guest pairs.[6]

Most of the anion receptors described in the literature[7] are based on hydrogen bonding,[8,9] electrostatic interac-

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tions,[10,11] and coordination bonds to metal ions.[12] However, recent detailed computational studies[13–16] clearly indicate that anions can bind to neutral π receptors,[17,18] with bonding energies comparable to those achieved in cation$-\pi$ complexations.[19] Since 2004, the field of anion recognition involving electron-deficient aromatic rings has thrived, and new remarkable examples are regularly reported in the literature.[20–29]

In the present study, experimental and theoretical investigations on triazine-based host systems for anion guests are reported. Especially, the binding selectivity toward different anions, namely, chloride, bromide, perchlorate, and azide, present in the different complexes prepared is investigated by theoretical calculations. Moreover, a bis(*s*-triazine) stacking motif revealed by the solid-state structures herein described interacts more efficiently with anions than a single *s*-triazine unit. This aspect suggests an increased anion-binding ability of the π-stacked *s*-triazine rings, compared to an isolated triazine unit. Such an effect has been recently reported for the binding interactions between 1,3,5-trifluorobenzene stacks and ions.[30]

Experimental Section

Synthesis. All reactions were conducted in an aerobic atmosphere. Solvents and reagents were used as received. The ligand 2,4,6-tris(dipyridin-2-ylamino)-1,3,5-triazine (dpyatriz) was prepared as described elsewhere.[31]

Caution! *Azido complexes and perchlorate salts are potentially explosive, especially in the presence of organic ligands. Therefore, these compounds must be handled with care and prepared only in small amounts.*

$[Cu_3Cl_3(dpyatriz)_3](ClO_4)_3$ (2). Solid $CuCl_2\cdot 2H_2O$ (21 mg, 0.13 mmol), $Cu(ClO_4)_2\cdot 6H_2O$ (46 mg, 0.13 mmol), and dpyatriz (100 mg, 0.17 mmol) were dissolved in MeOH (80 mL) and stirred for a few minutes. The blue solution was left undisturbed overnight for slow evaporation. After 24 h, large blue crystals had deposited, which were collected by filtration. The yield was 80%. Anal. Calcd (found) for **2**·3MeOH: C, 44.35 (42.80); H, 3.24 (2.84); N, 17.99 (18.33).

$[Cu_3Br_3(dpyatriz)_2](ClO_4)_3$ (3). Solid $CuBr_2$ (28 mg, 0.13 mmol), $Cu(ClO_4)_2\cdot 6H_2O$ (46 mg, 0.13 mmol), and dpyatriz (100 mg, 0.17 mmol) were dissolved in *N*,*N*-dimethylformamide (DMF; 10 mL), and the blue mixture was stirred for about 30 min. The solution was then layered with Et_2O, and the system was then left undisturbed for a few days, after which blue crystals had deposited on the walls of the tube. The yield was 70%. Anal. Calcd (found) for **3**·3DMF·H_2O: C, 39.21 (37.90); H, 3.11 (2.46); N, 16.46 (16.19).

$[Cu_4(N_3)_4(dpyatriz)_2(DMF)_4(ClO_4)_2](ClO_4)_2$ (4). Solid $Cu(ClO_4)_2\cdot 6H_2O$ (93 mg, 0.25 mmol), NaN_3 (8 mg, 0.12 mmol), and dpyatriz (100 mg, 0.17 mmol) were dissolved in DMF (10 mL), and the green mixture was stirred for about 30 min. The solution was layered with Et_2O, and the system was left undisturbed for a few days, after which green crystals had deposited on the walls of the tubes. The yield was 65%. Satisfactory microanalytical results could not be obtained, most likely because of the combined presence of ClO_4^- and N_3^- in this compound, together with its high content of nitrogen.

Physical Measurements. IR spectra were recorded as KBr pellet samples on a Nicolet 5700 FT-IR spectrometer. Elemental analyses were performed in-house on a Perkin-Elmer series II CHNS/O analyzer 2400, at the Servei de Microanàlisi of CSIC, Barcelona, Spain.

X-ray Crystallography. Data were collected at 150 K either (i) for compound $[Cu_3Cl_2(H_2O)(dpyatriz)_2](ClO_4)_4$ [**1**, where dpyatriz = 2,4,6-tris(dipyridin-2-ylamino)-1,3,5-triazine] using a Bruker APEX II CCD diffractometer on station 9.8 of the Synchrotron Radiation Source at CCLRC Daresbury Laboratory, at 0.6894 Å, from a silicon(111) monochromator, (ii) for compound **2** with a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å), (iii) for compound **3** using a Bruker APEX II CCD diffractometer on station 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory, at 0.7749 Å, from a silicon(111) monochromator, or (iv) using a Bruker APEX II CCD diffractometer on station 16.2SMX of the Synchrotron Radiation Source at CCLRC Daresbury Laboratory, at 0.8464 Å, from a silicon(111) monochromator. The structures were solved by direct methods, and the refinement and all further calculations were carried out using the *SHELX-TL* suite of programs.[32,33] Crystallographic and experimental details for the different structures are summarized in Table 1. Selected bond distances and angles are given throughout the text and as Supporting Information, while all details can be found in the supplementary crystallographic data for this paper in CIF format with CCDC numbers 676292−676295. These data can be obtained free of

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Table 1. Crystal Data for Compounds **1**−**4**

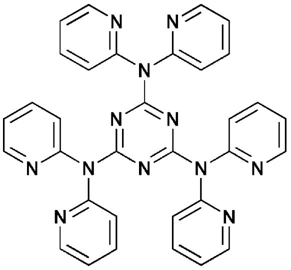
	1	**2**	**3**	**4**
formula	$C_{68.50}H_{55}Cl_6Cu_3N_{25}O_{17.50}$	$C_{69}H_{60}Cl_6Cu_3N_{24}O_{15}$	$C_{82.25}H_{88.95}Br_3Cl_3Cu_3N_{27.15}O_{17.80}$	$C_{82.25}H_{88.95}Br_3Cl_3Cu_2N_{21.50}O_{11.56}$
fw, g/mol	1911.69	1868.73	2279.36	1230.70
cryst syst	tetragonal	monoclinic	monoclinic	triclinic
space group	*P*4(1)2(1)2	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	15.5859(9)	16.227(3)	15.596(6)	13.460(3)
b, Å	15.5859(9)	23.272(5)	23.380(8)	14.548(3)
c, Å	43.359(3)	22.945(5)	27.543(9)	14.894(3)
α, deg	90	90	90	87.581(2)
β, deg	90	98.30(3)	90.028(6)	81.918(2)
γ, deg	90	90	90	78.461(2)
V, Å^3	10533(1)	8574(3)	10043(6)	2829(1)
Z	4	4	4	2
ρ_{calc}, g/cm^3	1.206	1.448	1.507	1.445
μ, mm^{-1}	0.816	0.998	2.462	0.921
T, K	150	150	150	150
transmn range	0.83−0.83	0.74−0.86	0.59−0.78	0.91−0.96
total/unique reflns	48 346/10 676	49 011/17 398	12 2482/23 080	15 857/7941
param/restraints	583/139	1080/60	1289/609	735/143
wR2 (all data)	0.2186	0.1885	0.1833	0.2649
R1 [$I > 2\sigma(I)$]	0.0668	0.0655	0.0629	0.0836
S (all data)	1.090	1.056	1.102	1.079

charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. The geometry of all complexes included in this study (see Figure 9) was fully optimized at the RI-MP2(full)/6-31++G** level of theory. The binding energies were calculated at the same level with and without correction for the basis set superposition error (BSSE), using the Boys−Bernardi counterpoise technique.[34] The calculations at the resolution of the identity MP2 (RI-MP2) level of theory were performed using the program *TURBOMOLE* version 5.7.[35] Because the *TURBOMOLE* program does not include an auxiliary basis set for 6-31++G**, we used Ahlrich's VDZ (SVP in *TURBOMOLE* notation) as the auxiliary basis set.[36]

The contributions to the total interaction energy have been computed using the Molecular Interaction Potential with polarization (MIPp),[37] which is an improved generalization of the MEP, where three terms contribute to the interaction energy: (i) an electrostatic term identical with the MEP,[38] (ii) a classical dispersion−repulsion term, and (iii) a polarization term derived from perturbational theory.[39] The calculation of the MIPp of *s*-triazine and its dimers was performed using the HF/6-31++G**//RI-MP2/6-31++G** wave functions by means of the *MOPETE-98* program.[40] The ionic van der Waals parameters for Cl^- were taken from the literature.[41] The results obtained for Cl^- in relation to the contributions to the total interaction energy and the analysis of the nature of the interaction and the synergistic effects were extrapolated to the case of the ClO_4^- anion because a limitation of the *MOPETE* program[40] prevents us from treating the ClO_4^- species as polyatomic. The quadrupole moments of the *s*-triazine dimers were computed using the *CADPAC* program[42] at the MP2/6-31G*//RI-MP2(full) level of theory because previous studies[43] have demonstrated that reliable results are obtained at this level of theory.

Scheme 1



Results and Discussion

Synthesis and Reactivity. The structure of the new complex $[Cu_3Cl_2(H_2O)(dpyatriz)_2](ClO_4)_4$ (**1**; dpyatriz = 2,4,6-tris-(di(pyridin-2-yl)amino)-1,3,5-triazine; see Scheme 1) was obtained accidentally using crystals from a reaction aimed at linking clusters of different nature into magnetic one-dimensional chains, namely, $Na[Cu_6(pro)_{12}](ClO_4)_4$ (Hpro = proline)[44] and $[Fe_2(dpyatriz)_2Cl_2](SO_3CF_3)_2$.[45] The formation of **1** underscores the lability of the above complexes, on the one hand, and the stability of the trinuclear assembly featured by **1**, on the other hand. Examination of the molecular structure of the latter unveiled the presence of interesting anion$\cdots\pi$ interactions between perchlorate ions and the triazine rings of dpyatriz (see below). In order to study this phenomenon in more detail, the preparation of **1** or similar compounds from simple components was attempted. Thus, the derivative $[Cu_3Cl_3(dpyatriz)_2](ClO_4)_3$ (**2**) was cleanly prepared in crystalline form and high yield from

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the appropriate mixture of Cu^{II} salts, as outlined in eq 1.

$$3Cu(ClO_4)_2 + 3CuCl_2 + 4dpyatriz \rightarrow 2[Cu_3Cl_3(dpyatriz)_2](ClO_4)_3 \quad (1)$$

Complex **2** shows three square-pyramidal Cu^{II} ions, all with Cl^- ions at the apical sites. A complex possessing the same $[Cu_3Cl_3(dpyatriz)_2]^{3+}$ cluster cation as **2** has been previously reported by another group, as obtained from a reaction similar to the above one but in the absence of ClO_4^-. The reported cluster has Cl^- and $[CuCl_4]^{2-}$ as counterions and also shows anion$\cdots\pi$ interactions.[28]

In order to study in more detail these unconventional supramolecular interactions, the preparation of new members of the above family with other ligands at the apical site of Cu^{II} was attempted through the use of different sources of the metal. Thus, the analogue of **2** with bromide, $[Cu_3Br_3(dpyatriz)_2](ClO_4)_3$ (**3**), was prepared successfully according to the reaction in eq 2. This reaction was conducted in DMF, and crystals were obtained by slowly diffusing Et_2O.

$$3Cu(ClO_4)_2 + 3CuBr_2 + 4dpyatriz \rightarrow 2[Cu_3Br_3(dpyatriz)_2](ClO_4)_3 \quad (2)$$

Complex **3** also exhibits interactions between ClO_4^- and the triazine rings.

Given the above synthetic successes, the analogous reactivity was attempted with N_3^- sources. The azide anion was now introduced in the form of NaN_3, as indicated in eq 3, and the reaction was performed in DMF. The nature of the product, with formula $[Cu_4(N_3)_4(dpyatriz)_2(DMF)_4(ClO_4)_2](ClO_4)_2$ (**4**), was, however, rather distinct, although many features of the above complexes were maintained (see the structure below).

$$4Cu(ClO_4)_2 + 4NaN_3 + 2dpya + 4DMF \rightarrow [Cu_4(N_3)_4(dpyatriz)_2(DMF)_4(ClO_4)_2](ClO_4)_2 + 4NaClO_4 \quad (3)$$

This is in line with the fact that the anion N_3^- is rarely seen as the apical ligand of a square-pyramidal Cu^{II} cation,[46] which possibly causes the cluster to organize differently in order to avoid this. Thus, in complex **4**, the azide ligands are not forced to be on axial sites. This system, nevertheless, also exhibits the kind of $ClO_4^-\cdots$triazine interactions that are observed on the trinuclear clusters described above.

Description of the Structures. Various aspects about the structures of complexes **1**−**4** are represented in Figures 1–8. Crystallographic data are collected in Table 1. Parameters related to anion$\cdots\pi$, $\pi\cdots\pi$, and hydrogen-bonding interactions are given in Tables 2–4, whereas the rest of the structural parameters are summarized in the Supporting Information.

$[Cu_3Cl_2(H_2O)(dpyatriz)_2](ClO_4)_4$ (1). Cluster **1** (Figure 1) can be described as the face-to-face assembly of two dpyatriz ligands mediated by coordination in a chelating fashion of their dipyridylamino moieties to three Cu^{II} ions. The latter are in square-pyramidal coordination geometry ($\tau = 0.02$, Cu1; 0.15, Cu2),[47] with the basal positions occupied by the nitrogen donors of dpyatriz and the axial sites pointing outward in a radial manner, occupied by either Cl^- ions (Cu1 and Cu1a) or a molecule of H_2O (Cu2). A crystallographic C_2 axis going through the Cu−O bond relates half of the molecule to the other. The multidentate ligands are, therefore, arranged in a perfectly eclipsed configuration, with a triazine centroid-to-centroid distance of 4.125 Å. The equatorial Cu−N distances range from 2.010(5) to 2.069(5) Å, whereas the apical coordination bonds are 2.379(3) Å (Cu−O) or 2.388(2) Å (Cu−Cl). The intermetallic distances are very similar [8.079(1)−8.262(1) Å]. The positive charge of the cluster is compensated for by four perchlorate ions. Two of them are located very close to each triazine ring (Figure 2), respectively, evidencing the presence of anion$\cdots\pi$ interactions (see below). The distance between this perchlorate's chlorine atom and the respective triazine's centroid is 3.742 Å. This distance might have been influenced by the close presence of the pyridyl rings of dpyatriz. In the space-filling diagram of Figure 2, one can observe that the ClO_4^- ions are, nevertheless, well accommodated close to the $[C_3N_3]$ ring.

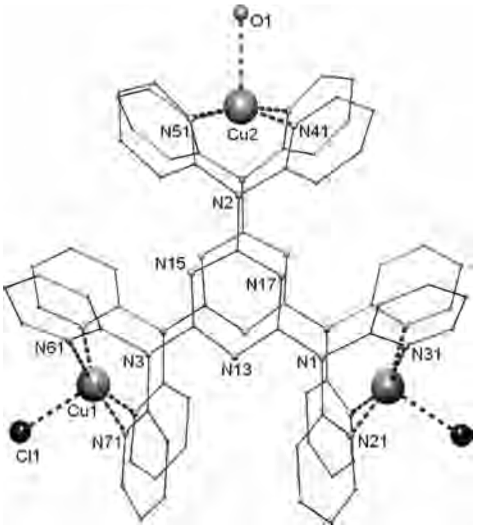

Figure 1. Representation of the crystal structure of the $[Cu_3Cl_2(H_2O)(dpyatriz)_2]^{4+}$ cation of **1**. Hydrogen atoms are not shown. Only unique heteroatoms and metals are labeled. Their symmetry equivalents are generated by applying a C_2 axis passing through Cu2 and O1.

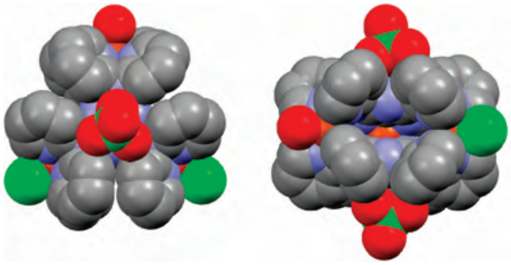

Figure 2. Space-filling diagrams of the $[Cu_3Cl_2(H_2O)(dpyatriz)_2]^{4+}$ cation of **1** showing two perpendicular perspectives and emphasizing the accommodation of perchlorate anions close to the triazine $[C_3N_3]$ rings. Hydrogen atoms are not shown.

$[Cu_3Cl_3(dpyatriz)_2](ClO_4)_3$ (2). This complex is very similar to **1**, although more regular (Figure 3) because the dpyatriz ligands play the same function as above but the axial

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positions of all Cu^{II} ions are now occupied by Cl^-. Thus, the cluster has only three negative charges, which are compensated for by three perchlorate anions. Two of these are again establishing anion···π interactions with the triazine rings on each side of the complex, exhibiting Cl-to-centroid distances of 3.695 and 3.784 Å. The triazine centroid-to-centroid separation is smaller at 3.965 Å. The Cu−Cl bond distances range from 2.387(2) to 2.413(2) Å, while the other metric parameters are very similar to these in **1**.

$[Cu_3Br_3(dpyatriz)_2](ClO_4)_2$ (3). Complex **3** is the analogue of **2** but with Br^- apical ligands instead of Cl^-. Again, the three positive charges of the cluster are compensated for by three perchlorate anions. As for the above complexes, compound **3** exhibits interactions among the triazine rings (triazine centroid-to-centroid separation of 3.949 Å) and between the triazine rings and some of the counterions (Figure 4), in particular with perchlorate ions on both sides of the complex (Cl-to-centroid distance of 3.639 and 3.623 Å). The Cu−Br bond distances are in the range 2.527(2)−2.560(1) Å.

$[Cu_4(N_3)_4(dpyatriz)_2(DMF)_4(ClO_4)_2](ClO_4)_2$ (4). Complex **4** is related to complexes **1**−**3** in that it consists of two centrosymmetrically related dpyatriz ligands linked opposite to each other by Cu^{II} ions through coordination to the dipyridylamino (dpya) chelating fragments (Figure 5). In this case, however, both dpyatriz ligands are mutually shifted instead of superimposed, and the link is thus made only by two metals rather than by three. Therefore, only two dpya moieties per ligand are engaged in the bridging function, while the third dpya of each ligand coordinates to another metal that does not bridge. The bridging ions are hexacoordinate, with four nitrogen donors from dpya disposed in a cis configuration and the other sites occupied by one N_3^- ligand and one ClO_4^-, respectively. The bond distances are as follows: $Cu-N_{dpya}$, 2.016(6)−2.269(6) Å; $Cu-N_{az}$, 2.003(6) Å; Cu−O, 2.777(6) Å. The nonbridging Cu^{II} ions are square-pyramidal ($\tau = 0.05$), with two equatorial nitrogen donors from one dpya [Cu−N, 2.016(6) and 2.041(6) Å], one equatorial site occupied by N_3^- [Cu−N, 1.965(8) Å], and the other positions saturated by solvate DMF ligands through the oxygen atoms [$Cu-O_{eq}$, 1.992(6) Å; $Cu-O_{ax}$, 2.173(7) Å]. The intermetallic distances within the molecule are as follows: Cu1···Cu1a, 13.163(3) Å; Cu2···Cu1, 7.811(2) Å; Cu2···Cu2a, 8.949(2) Å. The positive charges of the cationic cluster are compensated for by two perchlorate ions. These, as seen for all of the above complexes, are interacting with the triazine rings of the dpyatriz ligands (Figure 6), with a Cl-to-centroid distance of 3.794 Å.

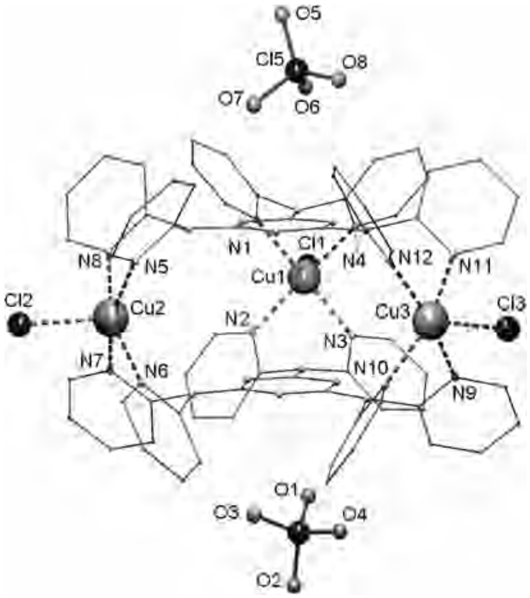

Figure 3. Representation of the crystal structure of the $[Cu_3Cl_3(dpyatriz)_2]^{3+}$ cation of **2** showing the perchlorate ions interacting with the triazine rings. Only the metals and the atoms bound to them are labeled. The smallest balls represent carbon atoms. Hydrogen atoms are not shown.

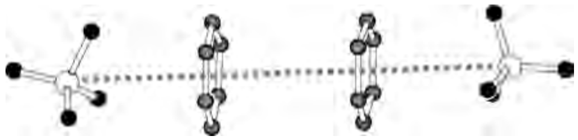

Figure 4. Representation of the moiety involved in the sequence of interactions $ClO_4^-\cdots[C_3N_3]\cdots[C_3N_3]\cdots ClO_4^-$, found in complex **3**. Similar motifs are found in complexes **1** and **2**.

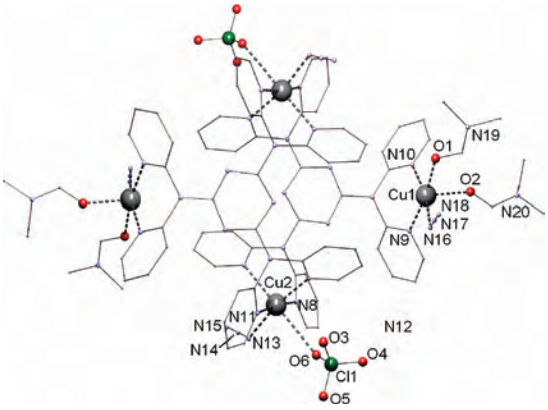

Figure 5. Representation of the crystal structure of the $[Cu_4(N_3)_4(dpyatriz)_2(DMF)_4(ClO_4)_2]^{2+}$ cation of **4** emphasizing how both dpyatriz ligands are mutually shifted. Unique metal atoms, donor atoms from dpyatriz, and heteroatoms from the other ligands are labeled. Hydrogen atoms are not shown.

Structural Analysis of the Anion···π Interaction. Complexes **1**−**4** exhibit anion···π interactions in the solid state, all as close contacts between ClO_4^- anions and the triazine ring of one dpyatriz ligand. We discuss here the nature of this interaction by analyzing various structural parameters, in the context of the previously observed systems of this nature. For this purpose, we take as a representative example the perchlorate anion [Cl1, O1, O2, O3, O4] of complex **2**. Of this ClO_4^- ion, the oxygen atoms O1 and O3 are most significantly interacting with the corresponding triazine ring (Figure 7). Thus, O1 exhibits a very short contact distance with atom C61 (Table 3); this separation, 3.021(6) Å, is below the sum of the van der Waals radii of both atoms (vdW C + vdW O = 3.22 Å).[48] In turn, O1 is in close contact as well with the triazine nitrogen atom N70 [O1···N70, 3.163(6) Å; Table 3]. However, this distance

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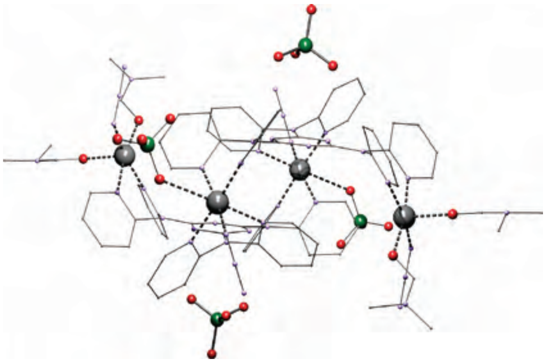

Figure 6. Representation of the crystal structure of **4** emphasizing the interaction between the perchlorate ions and the triazine rings. Hydrogen atoms are not shown.

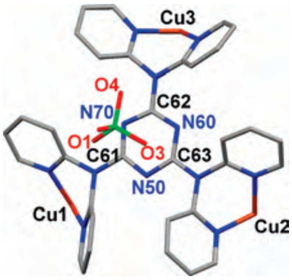

Figure 7. Illustration of the $ClO_4^-\cdots$triazine interactions present in complex **2**.

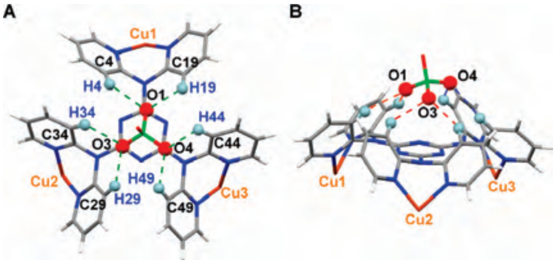

Figure 8. Representations of the $C_{arene}-H\cdots O_{perchlorate}$ bonding interactions, which strengthen the $ClO_4^-\cdots$triazine supramolecular pairing.

denotes a moderate interaction because it is just above the sum of the van der Waals radii of both atoms (vdW C + vdW N = 3.07 Å).[49] These interactions result in a distance $O1\cdots centroid_{triazine}$ of 3.248 Å, which reflects a moderate interaction of the atom with the π cloud (indeed a strong interaction is characterized by a separation distance below 3.03 Å), but it is within the range of the $ClO_4^-\cdots$triazine contacts found in the Crystal Structure Database, CSD (mean perchlorate−centroid distance, 3.141 Å).[49] The perchlorate atom O3 (Figure 7 and Table 3) experiences comparable interactions with the same triazine ring. Thus, the distances O3···C63 and O3···N60 are 3.121(6) and 3.275(6) Å, respectively. The ensuing O3···centroid distance of 3.310 Å is also just above the average distance found in the CSD for such interactions.[49] The combined interactions of O1 and O3 with the π-acidic ring should increase the stability of the supramolecular pair. In addition to the anion$\cdots\pi$ interactions, one has also to consider the involvement of $C_{arene}-H\cdots$anion hydrogen bonds when examining the interaction between anions and electron-deficient π rings.[50] Indeed, such hydrogen bonds play a significant role in the formation of certain supramolecular adducts.[28] Moreover, a recent search in the CSD has revealed that anion$\cdots\pi$ interactions are very often associated with hydrogen-bonding interactions.[49] In the present case, hydrogen bonds between the perchlorate and C−H groups from six pyridine rings are observed as well (Figure 8). The $C_{pyridine}-H\cdots O_{perchlorate}$ separation distances range from 3.203(9) to 3.452(7) Å (Table 4), indicative of weak-to-moderate hydrogen bonds.[51] This cooperativity between anion$\cdots\pi$ and $C_{arene}-H\cdots$anion interactions obviously enhances the bonding association and, therefore, the anion binding properties of the system. We have studied both effects at the theoretical level (see below). Such a combination of noncovalent bonds should be taken into account by the supramolecular chemist to design anion receptors.

Theoretical Studies. Table 5 reports the energies and equilibrium distances corresponding to the interaction of the *s*-triazine ring (**5**) with various anions and to the formation of two *s*-triazine dimers (eclipsed and staggered, with D_{3h} and D_{3d} symmetries, respectively). The interactions involving various anions other than ClO_4^-, which also appear in the X-ray structures, have also been studied for comparison purposes, even if they do not participate in anion$\cdots\pi$ interactions. For all complexes (**6**−**15**), the interaction energies (E_{BSSE}) are negative, indicating that the complexation process is favorable. The interaction energies of **5** with Cl^-, Br^-, ClO_4^-, and N_3^- (21−26 kJ/mol) are very similar and indicate a modest selectivity for the azide anion. As for the pairs of triazine rings, the dimer **7** is 8 kJ/mol more favorable than **6**; however, it should be mentioned that in the X-ray structures reported in the present study, because of the spatial orientation imposed by coordination to the copper atom, the stacked *s*-triazine rings adopt the D_{3h} geometry. We have also computed the interaction of **5** with a perchlorate anion, exploring several orientations (see Figure 9; complexes **11a**−**d**). The most stable orientation is **11b**, where three oxygen atoms of the anion interact with the aromatic ring, pointing to the three carbon atoms of the *s*-triazine unit, in agreement with the X-ray structure depicted in Figure 2. Energetically, the conformations **11c** and **11d** are comparable, with only one oxygen atom of the anion interacting with the aromatic ring, while the other three oxygen atoms are either over the three nitrogen atoms of the ring (**11c**) or over the three carbon atoms of the ring (**11d**). The equilibrium distances of both complexes are identical. Finally, the less stable conformation is **11a**, where three oxygen atoms of the anion interact with the aromatic ring, pointing to the three nitrogen atoms of the latter. In Table 5, the interaction energies and equilibrium distances of the ternary complexes **12**−**15** are also summarized. Some very interesting features can be extracted from the geometrical and energetic results. First, the equilibrium distances

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Table 2. Distances and Angles Characterizing the Anion···π and π−π Interactions in Compounds **1**−**4**[a]

distances and angles	1	2	3	4
centroid−centroid (Å)	4.125	3.965	3.949	
O_3−centroid (Å)	3.218	3.211	3.151	3.294
		3.311	3.175	
Cl−centroid (Å)	3.742	3.695	3.639	3.794
		3.784	3.623	
O_3−centroid−centroid (deg)	174.91	171.63	174.89	
		174.22	173.94	
Cl−centroid−centroid (deg)	176.54	176.44	176.48	
		173.54	176.96	
O_3−centroid−centroid−O_3 torsion (deg)	6.96	34.29	21.83	
Cl−centroid−centroid−Cl torsion (deg)	21.81	34.73	26.81	

[a] "centroid" represents the triazine ring centroid, while "O_3" represents the center of the plane made by the three oxygen atoms of the perchlorate anion situated toward the triazine ring.

Table 3. Contact Distances (Å) for Perchlorate···π Interactions Observed in the Crystal Structure of **2** (See Figure 4)[a]

O1···C61	*3.021(6)*	O1···N50	3.429(6)
O1···C62	3.583(7)	O1···N60	3.969(6)
O1···C63	3.801(7)	O1···N70	**3.163(6)**
O3···C61	3.827(6)	O3···N50	3.487(7)
O3···C62	3.636(7)	O3···N60	**3.275(6)**
O3···C63	*3.121(6)*	O3···N70	3.987(8)
O4···C61	4.309(7)	O4···N50	4.638(7)
O4···C62	3.460(6)	O4···N60	3.810(6)
O4···C63	4.315(7)	O4···N70	3.783(5)

[a] In italics: strong interaction. In bold: moderate interaction. In regular font: very weak interaction.

Table 4. C−H···ClO_4 Hydrogen Bonds for a (Representative) Triazine−Perchlorate Adduct in Complex **2** (See Figure 5)

	C−H···O (Å)	D−H−A (deg)
C4−H4···O1	3.452(7)	146
C19−H19···O1	3.293(7)	136
C29−H29···O3	3.250(7)	148
C34−H34···O3	3.405(7)	143
C44−H44···O4	3.203(9)	135
C49−H49···O4	3.329(7)	140

in the ternary complexes are shorter than those of the corresponding 1:1 complexes, indicating that the occurrence of π−π binding contacts between the triazine rings strengthens the anion−π interaction. This effect is clearly evidenced with the complexes between **7** (D_{3d} dimer) and anions. For instance, in complex **15**, the equilibrium anion-to-ring distance shortens by 0.03 Å with respect to the binary complex **8**, and the equilibrium distance between the stacked *s*-triazine ring shortens by 0.17 Å with respect to the binary complex **7**. Second, the synergetic energies (E_{syn}) have been included in Table 5 (values in parentheses), corresponding to the difference between the interaction energies of the ternary 1:1:1 complexes and the interaction energies of the two related binary 1:1 complexes. For instance, the synergetic energy of complex **12** (**5**···**5**···ClO_4^-) is computed by subtracting the interaction energies of **11b** (**5**···ClO_4^-) and **6** (**5**···**5**, D_{3h}) from the interaction energy of **12**. This value gives valuable information about the interplay between the anion−π and π−π noncovalent interactions. It is worth mentioning that E_{syn} is negative for all complexes, therefore suggesting that either the anion−π binding interaction influences the formation of the π−π stack or vice versa. It appears that the simultaneous formation of both types of interactions is more favorable than their separate occurrences. These results are in agreement with a recently reported theoretical study of cooperative effects between anion−π and π−π interactions that regulate the self-assembly of nitrate−triazine−triazine complexes.[52]

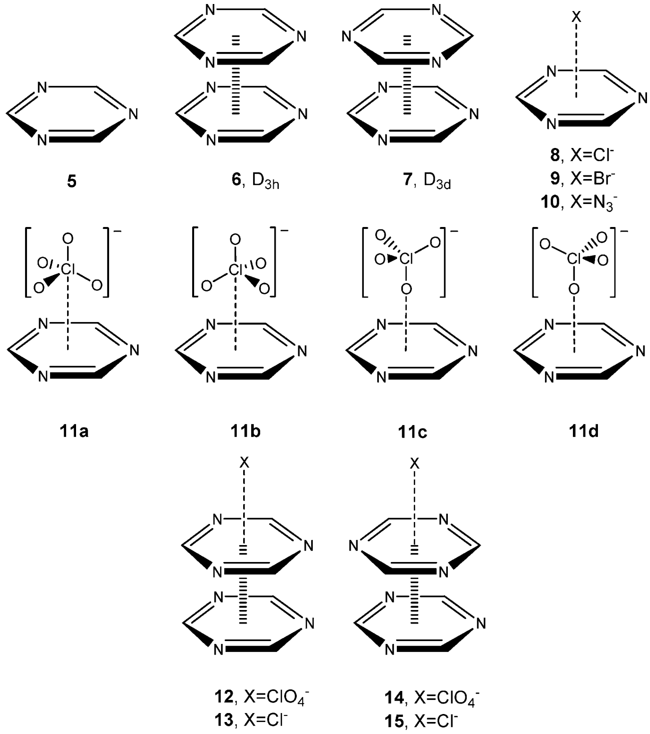

Figure 9. Schematic representation of the entities studied during theoretical calculation of $[C_3N_3]$···anion and $[C_3N_3]$···$[C_3N_3]$ interaction energies.

The equilibrium distances extracted from these calculations (Table 5) are to be compared with the corresponding parameters as observed on the crystal structures of compounds **1**−**4** (Table 2). The experimental ring-to-ring distances are between 0.58 and 0.40 Å larger than those obtained theoretically. The reasons for these differences are certainly the constraints imposed by the overall structure of the coordination architecture where these rings are imbedded. This argument does not apply for explanation of the disparities concerning the perchlorate-to-triazine distances because the anions are free. This separation is taken as the distance between the chlorine atom of the anion and the centroid of the $[C_3N_3]$ ring. In the crystal structures, this parameter ranges from 3.623 to 3.794 Å (Table 2) and is thus 0.10−0.27 Å longer than the calculated one for the most comparable moiety (i.e., complex **11b**). Thus, the calculated and experimental values are remarkably close, even more so if the observed experimental variability is taken into consideration.

Table 5. Interaction Energies at the RI-MP2(full)/6-31++G** Level of Theory without and with the BSSE Corrections (E and E_{BSSE}, kJ/mol), Synergetic Energy[c] (E_{syn}, kJ/mol), and Equilibrium Distances (R_e, Å) for Complexes **6**−**15**

compound	E	E_{BSSE} (E_{syn})	R_e
5···**5** (**6**, D_{3h})	−17.6	−4.6	3.55
5···**5** (**7**, D_{3d})	−25.5	−12.6	3.54
5···Cl^- (**8**)	−37.7	−22.2	3.22
5···Br^- (**9**)	−35.2	−20.9	3.34
5···N_3^- (**10**)	−39.4	−26.4	2.80
5···ClO_4^- (**11a**)	−30.1	−15.5	3.70[a]
5···ClO_4^- (**11b**)	−37.7	−20.9	3.54[a]
5···ClO_4^- (**11c**)	−33.5	−17.2	3.69
5···ClO_4^- (**11d**)	−34.8	−18.0	3.69
6···ClO_4^- (**12**)	−61.5	−28.5 (−2.9)	3.52/3.51[b]
6···Cl^- (**13**)	−62.4	−30.1 (−3.3)	3.20/3.52[b]
7···ClO_4^- (**14**)	−70.3	−35.6 (−2.1)	3.50[a]/3.38[b]
7···Cl^- (**15**)	−71.6	−37.3 (−2.5)	3.19/3.38[b]

[a] Chlorine atom to ring centroid distance. [b] Ring centroid to ring centroid distance of both *s*-triazine rings. [c] Synergetic contribution of the association.

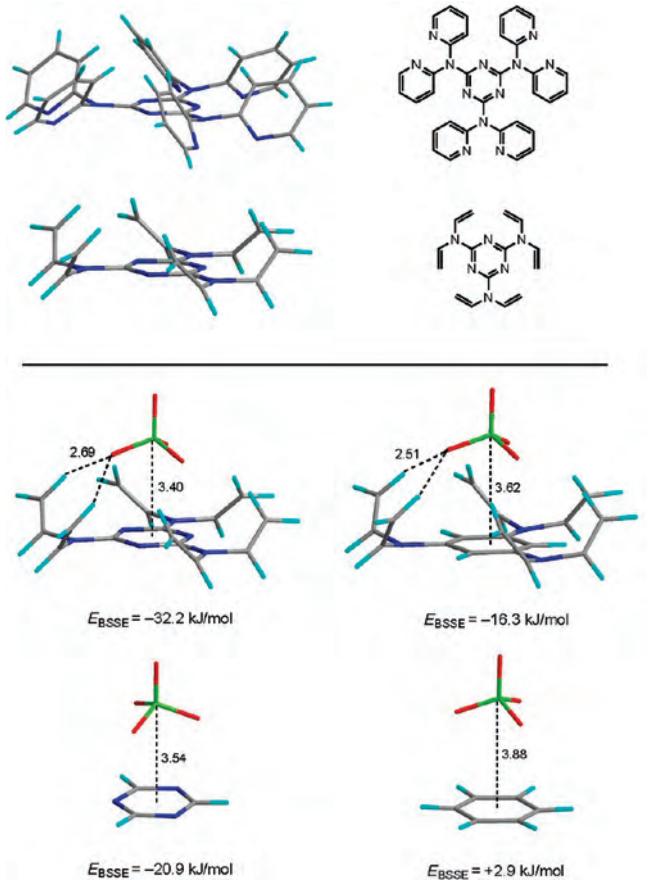

Figure 10. Top: Three- and two-dimensional representations of the dpyatriz ligand and the model used for calculations. Bottom: RI-MP2/6-31++G**-optimized complexes of ClO_4^- with the model ligand featuring a central *s*-triazine (left) and the same complex where the model ligand displays a phenyl ring instead of an *s*-triazine ring (right). The equilibrium distances are in angstroms.

We have also used a more elaborated model in order to evaluate the importance of unconventional hydrogen bonds (C−H···O) that can be established between the ClO_4^- anion and the hydrogen atoms of the pyridine ring. In Figure 10, we depict the model system that we have used to study the effect of these hydrogen bonds. This model allows us to keep the size of the system reasonably small and thus perform calculations at the RI-MP2/6-31++G** level of theory. Moreover, this system is adequate to study the additional effect of the three amino substituents of the *s*-triazine ring because they can affect the π-binding ability of the aromatic ring. We have also calculated the analogous system where the *s*-triazine moiety has been replaced by a phenyl ring. Their optimized complexes with the ClO_4^- anion and some energetic and geometric features are also included in Figure 10. The complexes of the ClO_4^- anion with *s*-triazine and benzene alone have also been included for comparison purposes. Inspection of the results raises several interesting points. First, the binding energy is considerably higher and the equilibrium distance significantly shorter in the complex of ClO_4^- with the model ligand made with *s*-triazine than with that with a phenyl ring. This result underscores the importance of the anion−π interaction in the binding mechanism. Second, the six weak C−H···O interactions also contribute to the binding of the anion; however, the C−H···O equilibrium distances are shorter for the model ligand with the phenyl ring. This indicates that the importance of this interaction is less significant in the system with *s*-triazine, probably because of the charge transfer from the anion to the electron-deficient ring, which weakens the C−H···O interaction. Third, the equilibrium distance of the anion to the ring centroid is shorter in the model ligand with *s*-triazine than in that with *s*-triazine alone. Therefore, the three R_2N− substituents of *s*-triazine have an overall favorable effect on the anion−π interaction.

The MIPp partition scheme[37] has been used to analyze the physical nature of the interaction involved in the binary and ternary complexes and to determine the bonding mechanism and estimate the synergetic energies. The MIPp of **5** and the dimers of **5** (**6** and **7**) associated with a chloride anion have been computed to evaluate the interactions taking place in the binary and ternary complexes. The results are summarized in Table 6, together with the interaction energies of the corresponding complexes at the RI-MP2(full)/6-31++G** level. For the ternary complexes **13** and **15**, the interaction energies have been computed by treatment of the complexation as two component systems, i.e. **6** + Cl^- → **13** and **7** + Cl^- → **15**. This approach allows a direct comparison with the interaction energy computed using the partition scheme of MIPp because it is computed using **6** and **7** as single quantum molecules and Cl^- as the interacting classical particle. The results presented in Table 6 reveal some important aspects. First, the interaction energies computed using the MIPp and RI-MP2 methodologies are in good agreement because they both lead to the same trend, thus giving reliability to the MIPp partition scheme. Second, as previously reported,[53] the interaction of the *s*-triazine ring with an anion is mainly dominated by polarization effects because the electrostatic term is moderate, in line with the small quadrupole moment of the *s*-triazine moiety (Q_{zz} =

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Table 6. Contributions to the Total Interaction Energy (E_t, kJ/mol) Calculated with MIPp for **5**−**7** Interacting with Cl^- at Several Distances (d, Å) from the Center of the Ring and Perpendicular to It along the C_3 Symmetry Axis[a]

d	E_e	E_p	E_{vw}	E_t	$E_{RI\text{-}MP2}$	R_e
			Complex **8**			
2.0	−55.3	−83.7	925.3	786.3		
2.5	−29.7	−45.6	92.5	17.2		
3.0[b]	−12.6	−18.8	−4.2	−35.6	−37.7	3.2
3.5	−8.8	−13.0	−5.0	−26.8		
4.0	−5.4	−7.5	−2.9	−15.9		
			Complex **13**			
2.0	−45.6	−90.9	866.2	729.8		
2.5	−23.0	−50.7	87.1	13.4		
3.0[b]	−12.6	−29.3	1.7	−40.2	−44.8[c]	3.2
3.5	−7.1	−17.6	−5.4	−30.1		
4.0	−4.6	−11.3	−4.2	−20.1		
			Complex **15**			
2.0	−46.1	−90.0	847.4	711.3		
2.5	−23.0	−50.2	85.0	11.7		
3.0[b]	−12.6	−29.3	1.3	−40.6	−46.1[c]	3.2
3.5	−7.5	−17.6	−5.4	−30.6		
4.0	−4.6	−11.3	−4.2	−19.7		

[a] For comparison purposes, the binding energies and the equilibrium distances of complexes **8**, **13**, and **15** at the RI-MP2/6-31++G** basis set are included. E_e = electrostatic energy, E_p = polarization energy, and E_{vw} = van der Waals energy. [b] Distance where the MIPp is minimum. [c] To be comparable with the MIPp energy, the RI-MP2 energy has been computed as a two-component system, i.e., *s*-triazine dimer + Cl^-.

0.90 B). Third, the interaction of the *s*-triazine dimers **6** and **7** with Cl^- is also dominated by polarization effects, and the electrostatic and dispersion−repulsion terms are small in both cases. The calculated values of the quadrupole moments of the dimers **6** and **7** are small (2.17 and 1.51 B, respectively), in agreement with the electrostatic term (E_e) of MIPp. Fourth, the higher anion-binding ability of the *s*-triazine π stacks, compared to only one electron-deficient ring, is most likely due to anion-induced polarization effects, as deduced from the values of the polarization terms reported in Table 6 (E_p), which are 10.5 kJ/mol more favorable for the dimers **6** and **7**than for **5**.

Concluding Remarks

In the present manuscript, the synthesis and X-ray characterization of several Cu^{II} coordination clusters, constituting *s*-triazine-based host systems, have been described. The solid-state structures show the presence of π−π stacks formed by two *s*-triazine units. These bis(triazine) units represent improved anion receptors, able to interact more favorably with anions than a single *s*-triazine ring. These units also provide the possibility of establishing an array of $C_{arene}-H\cdots$anion hydrogen bonds that reinforce the noncovalent interaction. High-level ab initio calculations and the MIPp partition scheme have been used to explain this behavior. It appears that the simultaneous occurrence of π−π and anion−π interactions has a synergetic effect that mutually reinforces both noncovalent interactions. From the MIPp partition scheme, it has been demonstrated that the physical nature of this cooperativity originates from ion-induced polarization effects.

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Supporting Information Available: Bond distances and angles for the coordination spheres of copper ions in compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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