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Crystallographic evidence of theoretically novel anion– π interactions†‡

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The reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with the multidentate ligand N,N',N'',N''' -tetrakis{2,4-bis(di-2-pyridylamino)-1,3,5-triazin-6-yl} triethylenetetramine (dpatta) in acetonitrile at high temperature and pressure results in the formation of the tetranuclear coordination compound $[\text{Cu}_4(\text{dpatta})(\text{NO}_3)_4](\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$ (**1**), whose crystal structure exhibits remarkable anion– π interactions which have been calculated, considering the unexpected position of the anion toward the aromatic ring.

1. Introduction

Non-covalent interactions between molecules are weak intermolecular contacts that play a central structural and functional role in biomolecules,¹ and govern the physicochemical properties of molecular systems in the condensed phase.² Thus, the preparation of supramolecular networks by means of non-covalent forces is a topical area of interest.^{3–7} Non-covalent interactions have been widely exemplified by hydrogen bonding^{8,9} and aromatic–aromatic (π – π) interactions.¹⁰ This family was recently extended to anion–aromatic (anion– π) interactions.^{11–13} These interactions would be expected to be repulsive however, theoretical studies have demonstrated that they are energetically favourable.¹² In these analyses, the usual electron deficient π systems investigated are hexafluorobenzene, 1,3,5-triazine and 2,4,6-trifluoro-1,3,5-triazine; and the anions are Cl^- , F^- , N_3^- , and NO_3^- .^{13–29} These theoretical investigations have highlighted that interactions between an anion and one,^{19,24} and even two or three,¹⁶ electron-deficient aromatic rings are possible.

These theoretical results have greatly encouraged the exploration of anion molecular recognition due to the importance of the phenomenon in biology, medicine, catalysis and environment, for instance.^{30–34} However the design of anion receptors remains challenging and only a few examples of unambiguous crystallographic evidence of anion– π bonding have been reported so far. The first examples describe receptors based on triazine and pyridine moieties encapsulating chloride anions.^{35,36} Examples of halide (Br^- , Cl^- , I^-) recognition by olefinic (tetracyanoethylene) and aromatic (tetracyanopyrazine and chloranil) π receptors have also been recently reported.³⁷

Our interest in the preparation of supramolecular coordination compounds with relevant inter- and intramolecular non-covalent forces prompted us to synthesise a flexible organic ligand based on triazine moieties because of the well-demonstrated ability of the triazine moiety to promote anion– π interactions.³⁸ N,N',N'',N''' -Tetrakis{2,4-bis(di-2-pyridylamino)-1,3,5-triazin-6-yl} triethylenetetramine (dpatta, **L**, Fig. 1) was obtained by reaction of the N-multidentate building block 2-chloro-4,6-bis(dipyridin-2-ylamino)-1,3,5-triazine with triethylenetetramine.

2. Experimental

2.1. General procedures and materials

Elemental analyses (C, H, N) were performed using a Perkin Elmer 2400 analyser. FTIR spectra were recorded with a Perkin-Elmer Paragon 1000 FTIR spectrophotometer, equipped with a Golden Gate ATR device, using the reflectance technique (4000 – 300 cm^{-1}). Ligand-field spectra were obtained on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference, over the range 2000 – 200 nm at room temperature. X-band powder EPR spectra were recorded on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. Magnetic susceptibility measurements were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer at 1000 Oe in the temperature range 2 – 300 K. Data were corrected for the diamagnetic contributions estimated from the Pascal constants.³⁹ All commercially available reagents were used without further purification.

2.2. Synthesis of N,N',N'',N''' -tetrakis{2,4-bis(di-2-pyridylamino)-1,3,5-triazin-6-yl} triethylenetetramine (dpatta, **L**)

The building block 2-chloro-4,6-bis(dipyridin-2-ylamino)-1,3,5-triazine was prepared according to a reported procedure.⁴⁰

A solution of triethylenetetramine dihydrochloride (0.36 g, 1.65×10^{-3} mmol) and *N*-ethyl-diisopropylamine (0.43 g, 3.30×10^{-3} mmol) was added to a solution of 2-chloro-4,6-bis(dipyridin-2-ylamino)-1,3,5-triazine (3 g, 6.62×10^{-3}

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† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Crystal packing figures for compound **1**. See DOI: 10.1039/b608172j

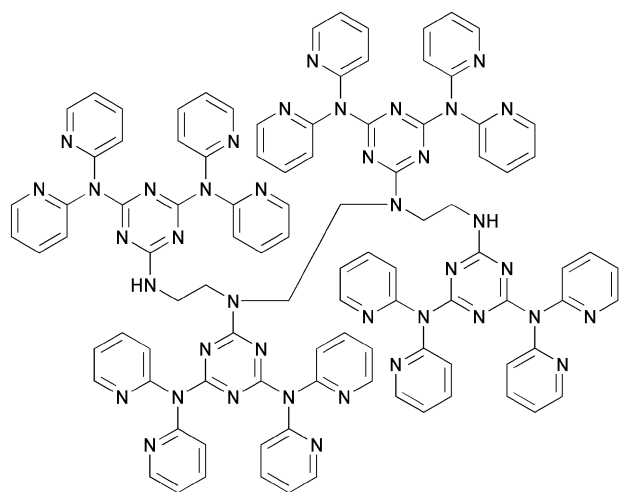


Fig. 1 Multidentate ligand N,N',N'',N''' -tetrakis{2,4-bis(di-2-pyridylamino)-1,3,5-triazin-6-yl} triethylenetetramine (dpatta).

mmol) and N -ethyl-diisopropylamine (0.86 g, 6.62×10^{-3} mmol) in acetonitrile (150 mL). The resulting reaction mixture was heated to 90 °C for 2 days. A white precipitate appeared which was filtered off and washed with ethanol.

Yield = 66%. $^1\text{H NMR}$ (DMSO- d_6 , 300 MHz) δ 8.20 (d, 16H, 6-py-H), 7.59 (dd, 16H, 4-py-H), 7.34 (dd, 16H, 5-py-H), 7.08 (d, 16H, 3-py-H), 3.02 (t, 4H, CH₂), 2.97 (t, 4H, CH₂), 2.89 (s, 4H, CH₂) ppm. $^{13}\text{C NMR}$ (DMSO- d_6 , 300 MHz) δ 155.4, 147.9, 137.0, 133.6, 120.5, 45.4, 44.6 ppm. IR (neat) 3271(w), 3055(w), 1558(s), 1542(s), 1526(s), 1461(s), 1367(s), 1265(s), 1145(m), 996(m), 806(s), 773(s), 667(s), 410(m) cm^{-1} . Anal. calc. for $\text{C}_{98}\text{H}_{78}\text{N}_{40}$: C, 64.82; H, 4.33; N, 30.85. Found: C, 64.15; H, 4.45; N, 31.20%.

2.3. Synthesis of $[\text{Cu}_4\text{L}(\text{NO}_3)_4](\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$ (**1**)

The complex was prepared by solvothermal reaction. To a suspension of dpatta (15 mg, 8.26×10^{-3} mmol) in acetonitrile, was added copper(II) nitrate trihydrate (8 mg, 33×10^{-3} mmol). The resulting blue solution was kept at 100 °C under autogenous pressure in a sealed Pyrex tube. Blue needles, suitable for X-ray single crystal diffraction, readily appear within 12 hours.

Yield: 52%. $\text{Cu}_4\text{C}_{98}\text{H}_{102}\text{N}_{48}\text{O}_{36}$: calc. C, 42.30; H, 3.69; N, 24.16. Found C, 43.03; H, 3.64; N, 23.87%. Main IR absorption bands (cm^{-1}) 3369(w), 3083(w), 1604(s), 1557(s), 1540(s), 1484(s), 1468(s), 1370(s, large), 1158(m), 1023(m), 802(m), 774(m), 669(m). UV-Vis (reflectance, nm) 290(s), 325(shoulder), 385(shoulder), 698(s, broad). Solid state EPR: broad singlet with $g = 2.1$. Magnetic behaviour: weak anti-ferromagnetic interactions at low temperature showing that the copper(II) magnetic centres are far apart.

2.4. X-Ray crystallographic analysis and data collection

The molecular structure of compound **1** was determined by single-crystal X-ray diffraction methods. Crystallographic and experimental details are summarized in Table 1. Intensity data were collected using Mo K α radiation ($\lambda = 0.71069$ Å) on a Bruker AXS Smart 1000 single-crystal diffractometer,

Table 1 Crystallographic data and refinement details for **1**

Formula	$\text{C}_{98}\text{H}_{102}\text{Cu}_4\text{N}_{48}\text{O}_{36}$
$F_w/\text{g mol}^{-1}$	2782.44
Crystal system	Triclinic
Space group	$P\bar{1}$
$a/\text{Å}$	13.170(2)
$b/\text{Å}$	14.881(3)
$c/\text{Å}$	16.134(3)
$\alpha/^\circ$	88.648(3)
$\beta/^\circ$	76.965(3)
$\gamma/^\circ$	69.770(3)
$V/\text{Å}^3$	2885.4(9)
Z	1
μ/mm^{-1}	0.833
$D_{\text{calc}}/\text{g cm}^{-3}$	1.601
T/K	293(2)
$\lambda/\text{Å}$	Mo K α 0.71069
$F(000)$	1430
Final R indices [$F_o > 4\sigma(F_o)$] ^a	$R_1 = 0.0598$, $wR_2 = 0.1435$
R indices (all data)	$R_1 = 0.1216$, $wR_2 = 0.1677$
Goodness-of-fit ^b	1.009

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$. ^b Goodness-of-fit $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

equipped with a CCD area detector at 293(2) K. The structure was solved by direct methods using the SIR97 program⁴¹ and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program.⁴² The data reduction was performed using the SAINT⁴³ and SADABS⁴⁴ programs. All the non-hydrogen atoms were refined with anisotropic atomic displacements, with the exclusion of the nitrogen atom N23 of one nitrate group. The hydrogen atoms were included in the refinement at idealized geometries (C–H 0.95 Å) and refined “riding” on the corresponding parent atoms, with the exception of H11N, which was located in the difference Fourier map. The weighting scheme used in the last cycle of refinement was $w = 1 / [\sigma^2(F_o^2) + (0.085P)^2]$, (where $P = (F_o^2 + 2F_c^2)/3$). All calculations were performed with a DIGITAL Alpha Station 255 computer. CCDC reference number 615306. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608172j. Geometric calculations and molecular graphics were performed with the PARST97 program⁴⁵ and the PLATON package.⁴⁶

3. Results and discussion

The solvothermal reaction of dpatta with copper(II) nitrate led to the tetranuclear complex $[\text{Cu}_4\text{L}(\text{NO}_3)_4](\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$ (**1**). **1** crystallises in the triclinic $P\bar{1}$ space group; the symmetry operator is located at the centre of the tetramine ligand, *i.e.* between the carbon atoms C26 and C26', the amine fragment being composed of the N11, C25, C24, N10, C26, C26', N10', N11', C24' and C25' atoms (the prime indicates the atoms generated by symmetry). Fig. 2 shows the tetranuclear complex **1**, together with the atomic labelling scheme. Selected bond distances and angles are listed in Table 2.

The two Cu^{II} ions in the asymmetric unit show a distorted geometry, intermediate between a square pyramid in which the metal centre deviates from the square plane by 0.389(1) Å (Cu1) and 0.335(7) Å (Cu2) and a trigonal pyramid ($\tau = 0.46$ and 0.45 for Cu1 and Cu2, respectively).⁴⁷ Their coordination

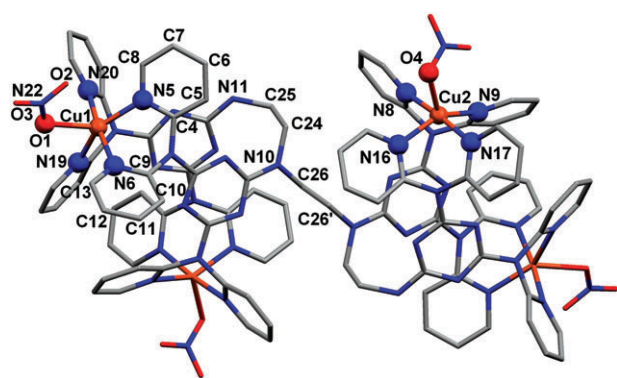


Fig. 2 Partial stick view of the two symmetry-related units forming the tetranuclear complex $[\text{Cu}_4\text{L}(\text{NO}_3)_4](\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$ (**1**). Hydrogen atoms, non-coordinated nitrate anions, and lattice molecules are omitted for clarity.

spheres include two N-bidentate dipyridylamine moieties, belonging to two different building blocks, and one monodentate coordinated nitrate anion. As a result of the synclinal N11-C25-C24-N10 torsion angle $[80.1(6)^\circ]$ in the asymmetric unit, the two triazine rings N1 C1 N2 C2 N3 C3 (ring **A**) and $\text{N12 C27 N13 C28 N14 C29}$ (ring **B**) are π - π stacked with a dihedral angle between the triazine planes of $15.42(1)^\circ$. The centroid-to-centroid ($\mathbf{A} \cdots \mathbf{B}$, Fig. 3) distance between the triazine planes of $3.45(9) \text{ \AA}$ is consistent with the usual value reported for aromatic stacking (around 3.5 \AA)¹⁰ but is slightly shorter than the distance found for 1,3,5-triazine ring stacking (about 3.6 to 3.9 \AA for perfect faced triazine moieties).^{35,36} The shrinking of the distance can be explained by the fact that the two rings are staggered, *i.e.* the nitrogen atoms of one triazine ring are not located over the nitrogen atoms of the second ring (for example, N3 is facing C27 ; Fig. 3). In addition, the two aromatic rings are slipped (*i.e.*, they are not directly on top of each other). Interestingly, and as anticipated, triazine **A** and **B** are also alternatively involved in an anion- π interaction with a lattice NO_3^- , namely with N23 O7 O8 O9 in position $-x, -y, 1-z$ (if the interaction regards triazine **A**, see Fig. 3) or with N24 O10 O11 O12 (in the case of triazine **B**). This phenomenon is most likely favoured by the strong electron-deficient character of the triazine ring together with its involvement in the π - π stacking interactions described above. As a result, in complex **1**, both the $\mathbf{A} \cdots \mathbf{B} \cdots$ nitrate and $\mathbf{B} \cdots \mathbf{A} \cdots$ nitrate interactions occur, one for each of the two symmetry-related units forming the tetramer. It is worth mentioning that this complex represents one of the first crystallographic evidences of such anion- π - π interactions.¹¹

Table 2 Selected bond lengths (\AA) and angles ($^\circ$) for **1**

Cu1-N5	2.038(5)	Cu2-N8	1.997(5)
Cu1-N6	1.982(5)	Cu2-N9	2.076(4)
Cu1-N19	2.061(5)	Cu2-N16	2.036(5)
Cu1-N20	1.985(5)	Cu2-N17	1.987(5)
Cu1-O1	2.201(5)	Cu2-O4	2.226(5)
N5-Cu1-N19	144.1(2)	N8-Cu2-N17	173.6(2)
N6-Cu1-N20	171.7(2)	N16-Cu2-N9	146.4(2)

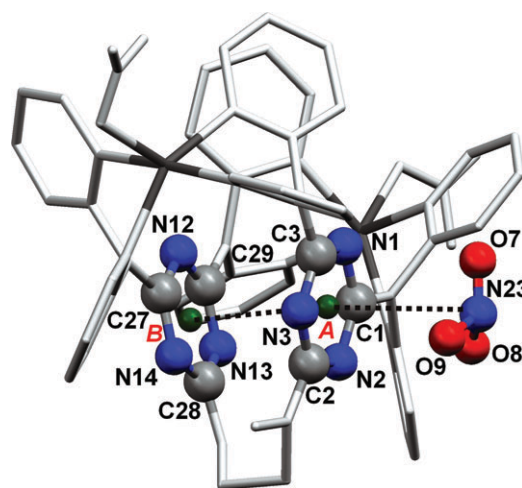


Fig. 3 Partial stick view of the asymmetric unit of **1** showing (i) the anion- π interaction between NO_3^- and the triazine ring **A** and (ii) the π - π stacking of **A** with the triazine **B** (the centroids of the rings are in dark green).

In particular, in the case of ring **A**, two oxygen atoms of the nitrate anion (O7 and O8) are both interacting with the triazine moiety. Remarkably, the oxygen atom O8 is found above the nitrogen N2 and not above a carbon atom as could be expected, while O7 and O9 lie between the carbon and nitrogen atoms (Fig. 4). Also the nitrate anion N22 O1 O2 O3 , which is coordinated to the copper centre Cu1 , is involved in short contacts⁴⁸ with the two pyridyl rings N5 C4 C5 C6 C7 C8 and $\text{N6 C9 C10 C11 C12 C13}$ in position $-1-x, 1-y, 2-z$, further stabilizing the crystal lattice. A network of hydrogen bonds also contributes to the stabilisation of the structure, involving mainly the water molecules of crystallization and the lattice nitrate ions. Also the hydrogen atom H11N of the tetramine moiety is involved in a hydrogen bond with the N24 O11 O12 O13 nitrate ion in position $-x, 1-y, 1-z$ [$\text{N11} \cdots \text{O12}$ $2.976(9) \text{ \AA}$, $\text{N11-H11} \cdots \text{O12}$ $150(6)^\circ$].

The crystal packing comprises channels running along the direction a , which are occupied by crystallization water molecules and nitrate anions (See ESI, Fig. S1-S3†). The fact that the water molecules are found in these cavities explain their relatively high thermal parameters.

The nitrate-triazine interaction has been investigated theoretically.¹⁹ Fig. 5 shows the calculated structure where the oxygen atoms of the nitrate anion are located logically on top

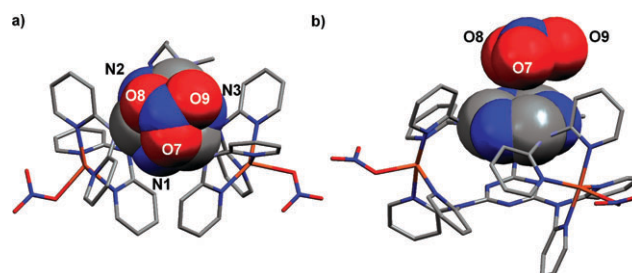


Fig. 4 Nitrate-triazine interaction observed in **1**; (a) top view; (b) side view.

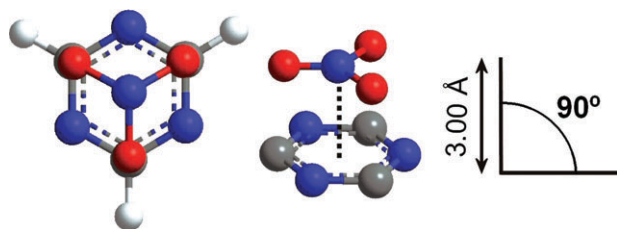


Fig. 5 Optimized structure of the NO_3^- complex with the 1,3,5-triazine ring calculated by Kim *et al.*¹⁹

of the electropositive carbon atoms of the aromatic ring. In the present study, the oxygen atoms surprisingly are facing the electronegative nitrogen atoms of 1,3,5-triazine (Fig. 4). Since repulsive interactions between the O and the N atoms are expected, computational studies have been carried out on this system. Density functional theory (DFT) calculations were therefore performed to analyze the anion- π interaction between the NO_3^- anion and the triazine ring. In particular, the question of the preference for the somehow unexpected coordination of the nitrate anion observed in the X-ray structure with one oxygen pointing to one nitrogen of the triazine ring and not to one carbon atom has been addressed. The nitrate-triazine system has thus been analysed, comparing the energies of two models of geometry A and B, respectively (see Fig. 6). The spatial orientation of A was derived directly from the X-ray structure, while in B the nitrate anion is kept parallel to the heterocycle with its oxygen atoms above the carbon atoms of the ring. This latter configuration has been previously predicted and discussed in a recent theoretical calculation carried out at the second-order Møller-Plesset (MP2) level of theory.¹⁹ Moreover, a second model including two triazine rings plus the nitrate ion has been considered as well, starting from the observed stacking of the rings in the X-ray data, in order to verify if this π - π stacking further stabilizes this supermolecular complex (Fig. 7).

The DFT calculations have been carried out using the Amsterdam density functional (ADF) code.^{49,50} We used the BLYP generalized gradient approximations for the exchange

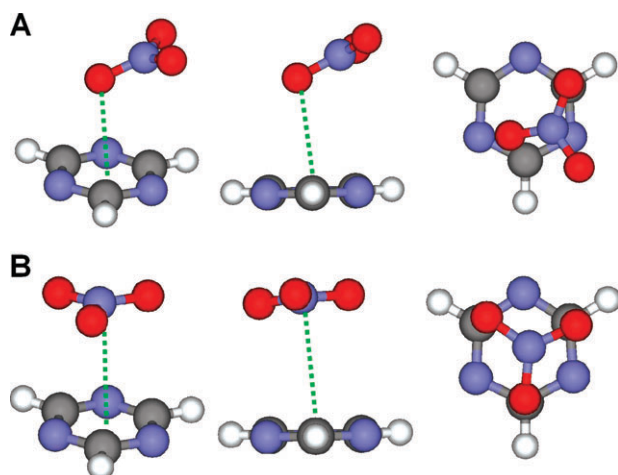


Fig. 6 (A) Optimization based on the crystal structure of **1**. (B) DFT calculation on the model proposed by Kim *et al.*¹⁹

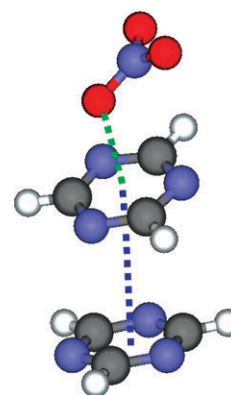


Fig. 7 Optimized structure for the nitrate-triazine-triazine interaction.

and correlation functional.^{51,52} It has been shown recently that the BLYP functional is able to properly describe anion- π and cation- π complexes.⁵³ We used a large Slater-type orbital (STO) basis set of quadruple- ζ quality (named ET-pVQZ in the ADF program). The geometries of the various complexes were fully optimized without imposing any symmetry constraints.

The DFT-BLYP geometry optimization for the model A (Fig. 6) shows that indeed a local minimum exists with a geometry very similar to that observed in the crystalline structure (Fig. 3 and 6A). In particular, the plane of the nitrate anion is not parallel to the plane of the triazine ring and one of the oxygen atom points in the direction of one of the N atoms of the ring. The shortest O-N distance is 3.15 Å, while the experimental value is 3.47(1) Å. In Table 3, we show some relevant predicted bond lengths and angles for model A. The comparison between calculated and experimental data in the crystalline structure shows a fair agreement. The distance from the centroid of the triazine ring to the nitrogen of the anion is 3.67 Å, which is very close to the experimental value 3.67(7) Å.

In order to study the relative stability, the model B¹⁹ (Fig. 6) has also been optimized by DFT calculations, starting from an initial structure with the plane of the anion parallel to the plane of the π ring. The geometry determined with this method is very similar to the one achieved by Kim *et al.* using MP2.¹⁹

Table 3 Selected experimental and calculated distances (Å) reflecting the nitrate-triazine interactions

Atom1...Atom2 ^a	Experimental	Calculated
N1...O7 ⁱ	3.74(1)	4.050
N2...O8 ⁱ	3.47(1)	3.151
N3...O9 ⁱ	3.57(1)	3.928
C1...O8 ⁱ	3.51(1)	3.139
C1...O9 ⁱ	3.58(1)	3.280
C2...O9 ⁱ	3.91(1)	4.396
C3...O7 ⁱ	3.57(1)	4.416
C3...O8 ⁱ	3.86(1)	3.503
C3...O9 ⁱ	3.98(1)	3.728
O8 ⁱ ...centroid A	3.42(7)	3.051
N23 ⁱ ...centroid A	3.67(7)	3.673
N24...centroid B	3.86(7)	3.673

^a Symmetry equivalent $i = -x, -y, 1 - z$.

However, the nitrogen of the anion is slightly displaced with respect to the normal to the centroid of the triazine ring. The distance between the centroid of the triazine ring to the nitrogen atom of the anion is 3.4 Å, which is about 13% longer than the MP2 value.¹⁹ The bonding energy is found to be higher in model A than in model B by about 0.5 kcal mol⁻¹ (-3.23 and -2.67 kcal mol⁻¹ for model A and model B in Fig. 6, respectively). This energy difference is quite small and within the experimental error for this type of calculation. Nevertheless, it can be assumed that the structure observed in the crystal data, though unexpected from purely electrostatic arguments, is energetically comparable to the structure predicted previously by MP2 calculations.¹⁹

Since the crystal structure of **1** exhibits π - π stacking interactions between two s-triazine rings (Fig. 3, **A**·**B**), the optimized structure of the complex, including two triazine rings and the nitrate anion, has been computed, and a bonding energy of -3.69 kcal mol⁻¹ is obtained, which is only 0.46 kcal mol⁻¹ higher than the complex including only one ring. Given this small difference in bonding energy, it is difficult to draw a conclusion on the stabilization induced by the π - π stacking on the supramolecular complex **1**. It has to be pointed out that the calculated distance between the centroid of the two rings is 4.16 Å, which is significantly longer than the one observed in the X-ray structure (**A**·**B**, 3.45(9) Å). This finding is in line with the generally still poor description of π - π interactions within the currently available functionals. In addition, it has to be mentioned that the two triazine rings are forced to stack closely, as a result of the coordination of their dipyridylamine units to the Cu1 and Cu2 ions (Fig. 2). These strong coordination forces, which go against the repulsive interactions between the nearly face-to-face triazine rings, have not been taken into account in the present study.

4. Conclusions

Anion coordination chemistry is a rapidly increasing and challenging topic of supramolecular chemistry,^{11,14} since the design of efficient anion-sensing receptors would be paramount for the discovery of new drugs. A number of computational studies have clearly shown that receptors based on anion- π interactions are promising candidates for the preparation of host-anion systems. These theoretical investigations have also suggested that the electron-deficient 1,3,5-triazine ring is a potentially effective anion host. The present study clearly confirms these first computational predictions, both crystallographically and theoretically. These important experimental results thus support the anion- π approach to synthesizing neutral anion host-guest systems, and other triazine-based receptors are currently being designed and prepared. In particular, the design and synthesis of compounds involving multi anion- π interactions (π -anion- π for example), as well as the selectivities of the host molecules towards different anions are now being examined.

Acknowledgements

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