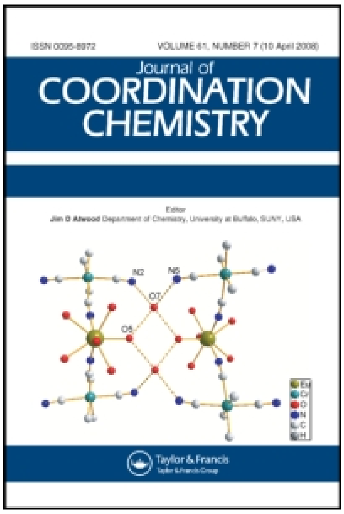

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Anion-π interaction stitching 2-D layers formed by self-assembly of cations of a mononuclear copper(II) complex: synthesis, crystal structure and magnetism of $[Cu(OAc)(2,2'\text{-dypam})_2](ClO_4)$ [HOAc = acetic acid, 2,2'-dypam = 2,2'-dipyridylamine]

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Anion-π interaction stitching 2-D layers formed by self-assembly of cations of a mononuclear copper(II) complex: synthesis, crystal structure and magnetism of $[Cu(OAc)(2,2'\text{-dypam})_2](ClO_4)$ [HOAc = acetic acid, 2,2′-dypam = 2,2′-dipyridylamine]

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A mononuclear Cu(II) compound $[Cu(OAc)(2,2'\text{-dypam})_2](ClO_4)$ (**1**), where HOAc and 2,2′-dypam are, respectively, acetic acid and 2,2′-dipyridylamine, has been synthesized and characterized by single crystal X-ray diffraction analysis. The cations of **1** link by N–H $\cdots$ O hydrogen bonds to form infinite 1-D zig-zag chains, which run along the *b* axis. Two adjacent chains along the *c* axis are joined by C–H $\cdots$ O hydrogen bonds to form a 2-D network. These 2-D layers are further bridged by perchlorate anions *via* weak anion-π interactions that act as a supramolecular glue to build the 3-D supramolecular network. Variable temperature (1.7–300 K) magnetic measurements revealed very weak intermolecular antiferromagnetic interactions at temperatures below 20 K between Cu(II) ions mediated by hydrogen bonds, C–H $\cdots$ π and $\pi \cdots \pi$ interactions. At temperatures $\geq$20 K, susceptibility data corresponds to isolated Cu(II) ions, indicating that the weak interactions affect the magnetism of **1** only at very low temperatures.

Keywords: Anion-π interaction; Self-assembly; 2,2′-Dipyridylamine; Cu(II) complex; Supramolecule; Magnetism

1. Introduction

Non-covalent supramolecular interactions with π aromatic clouds such as $\pi \cdots \pi$ stacking, C–H $\cdots$ π and cation $\cdots$ π interactions play roles in chemical and biological recognition [1]. Different approaches to study intermolecular interactions involving aromatic rings have recently been reviewed by Meyer *et al.* [2a] and by Reedijk *et al.* [2b].

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Numerous examples of cation $\cdots\pi$ interactions are found in Nature, where they have significant contributions to the structure and function of biomolecules [1, 3]. While cation $\cdots\pi$ interaction of aromatics is ubiquitous, non-covalent interactions of anions have been much less appreciated despite examples of encapsulated (host-guest) anion systems described by Park and Simmons [4] and Lehn [5] during the nascence of supramolecular chemistry. Electron-donating character of anions and the expected repulsive interactions with aromatic π-systems can be considered a main constraint for the poor development of non-covalent anion-π interaction chemistry. Motivated by the pioneering works of Park and Simmons [4] and Lehn [5], the scientific community became interested in the field of anion recognition [6], and in 1997 Alkorta *et al.* put forward the first DFT calculations to show the possibility of favorable binding interaction between an electron-rich species with electron-deficient aromatic rings [7]. In 2002, a series of computational studies [8] further confirmed the existence of favorable non-covalent binding interactions between several anions and aryl centroids of π-acidic aromatic rings; Frontera *et al.* coined a new term "anion-π interaction" to define these interactions while performing theoretical calculations on results derived from crystallographic structures [9]. Finally in 2004, the first crystallographic evidence of anion recognition by aromatic receptors was described [10, 11]. Since then, anion-π complexes have been found experimentally [2b], supporting theoretical predictions [7–9, 12], which suggest energetically favorable interactions between electron deficient π systems and anions and potential of synthetic anionic receptors based on anion-π interactions for medicinal and biological applications [8, 11, 12k, 12l].

Functions of anions in self-assembly reactions include template (host-guest) effects, coordination abilities and hydrogen-bonding interactions with receptor units [2b, 6, 13] and are exploited in designing functional molecular receptors and coordination polymers [2b, 14]. However, it is rarely observed that the feeble anion-π interactions are a controlling factor to direct the self-assembly of metal complexes into a supramolecular network [15]. For the first time, we present here crystallographic evidence of $ClO_4^- \cdots \pi$ interactions which act as a supramolecular glue to bind 2-D layers formed by a Cu(II) complex cation into a 3-D network.

2. Experimental

2.1. *Materials*

Safety note! Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution. All materials were purchased from commercial sources and used as received. Doubly distilled and then deionized water was used throughout.

2.2. *Physical measurements*

IR spectrum of **1** was recorded on a Perkin–Elmer RXI FT-IR spectrophotometer with a KBr pellet in the range 4000–600 cm^{-1}. Elemental analyses (C, H, N) were performed on a Perkin–Elmer 240C elemental analyzer. The electronic spectrum was measured at 25.0°C with a JASCO V-750 spectrophotometer equipped with thermostated cell compartments. Magnetization and variable-temperature (1.7–300 K) magnetic susceptibility measurements were carried out with a Quantum Design SQUID operating at different magnetic fields. Experimental susceptibilities were corrected for diamagnetism, temperature-independent paramagnetism, and the magnetization of sample holder.

2.3. *Synthesis of [Cu(OAc)(2,2′-dypam)$_2$](ClO$_4$) (1)*

Copper(II) acetate monohydrate (0.398 g, 2.0 mmol) was dissolved in 25 cm^3 water which, on warming, gave a clear blue solution. To this solution, 2,2′-dipyridylamine (0.340 g, 2.0 mmol) dissolved in 20 cm^3 methanol was added. The resulting green solution was heated at 50°C for an hour with continuous stirring and then allowed to cool. To this solution sodium perchlorate (0.122 g, 1.0 mmol) dissolved in minimum water was added, stirred and kept for crystallization. After a few days, greenish plate-like crystals suitable for X-ray analysis were formed from the mother liquor by slow evaporation at room temperature. The crystals were filtered off, washed with cold water and air-dried. The yield was 42%. Anal. Calcd for $C_{22}H_{21}N_6O_6ClCu$: C, 46.81; H, 3.75; N, 14.88%. Found: C, 46.34; H, 3.61; N, 14.53%.

2.4. *X-ray diffraction data collection and refinement*

A crystal having dimensions $0.08 \times 0.16 \times 0.26\,\mathrm{mm}^3$ for **1** was used for data collection on a Bruker SMART APEX II diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. Theta range for data collection was 1.8 to 26.5°. A total of 12543 reflections were measured to give 5054 independent reflections ($R_{\mathrm{int}} = 0.123$). The 2130 data [$I > 2\sigma(I)$] were used for solution and refinement by full-matrix least squares on F^2 using SHELX-97 [16]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at their geometrically idealized positions and constrained to ride on their parent atoms. Final R and Rw values were 0.0716 and 0.1328, respectively. Maximum and minimum residual electron densities were 0.45 (near heavy atom) and $-0.63\,\mathrm{e}\,\text{Å}^{-3}$, respectively. Information concerning crystallographic data collection and refinement is summarized in table 1.

3. Results and discussion

3.1. *Crystal structure of [Cu(OAc)(2,2′-dypam)$_2$](ClO$_4$) (1)*

X-ray structure analysis reveals that the asymmetric unit of **1** consists of a discrete [Cu(OAc)(2,2′-dypam)$_2$]$^+$ cation and a disordered perchlorate. An ORTEP diagram is shown in figure 1 and selected bond length, bond angles and supramolecular interactions are listed in tables 2–4. The central copper is coordinated by four nitrogens from two dypam ligands and two oxygens from acetate forming a *cis*, distorted octahedral CuN_4O_2 chromophore. The perchlorate in the asymmetric unit is rotationally disordered with the set of four oxygen atoms having an alternative orientation. The copper in [Cu(OAc)(2,2′-dypam)$_2$]$^+$ is basically five-coordinate, but a second oxygen atom (O2) from the acetate occupies the sixth position at a distance

Table 1. Crystallographic data for **1**.

Compound	**1**
Formula	$C_{22}H_{21}N_6O_6ClCu$
M	564.44
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cells and dimensions (Å, °)	
a	13.928(4)
b	7.965(3)
c	22.232(7)
α	90
β	92.75(2)
γ	90
$F(000)$	1156
V (Å^3)	2463.5(14)
Z	4
T (K)	150(2)
D_{Calcd} (Mg m^{-3})	1.522
λ (Mo-Kα) (Å)	0.71073
μ (Mo-Kα) (mm^{-1})	1.045
R_1 [$I > 2\sigma(I)$] (all)	0.0716
wR_2 [$I > 2\sigma(I)$] (all)	0.1328
Total reflections	12543
Unique data	5054 [$R_{\mathrm{int}} = 0.123$]
Observed data [$I > 2\sigma(I)$]	2130

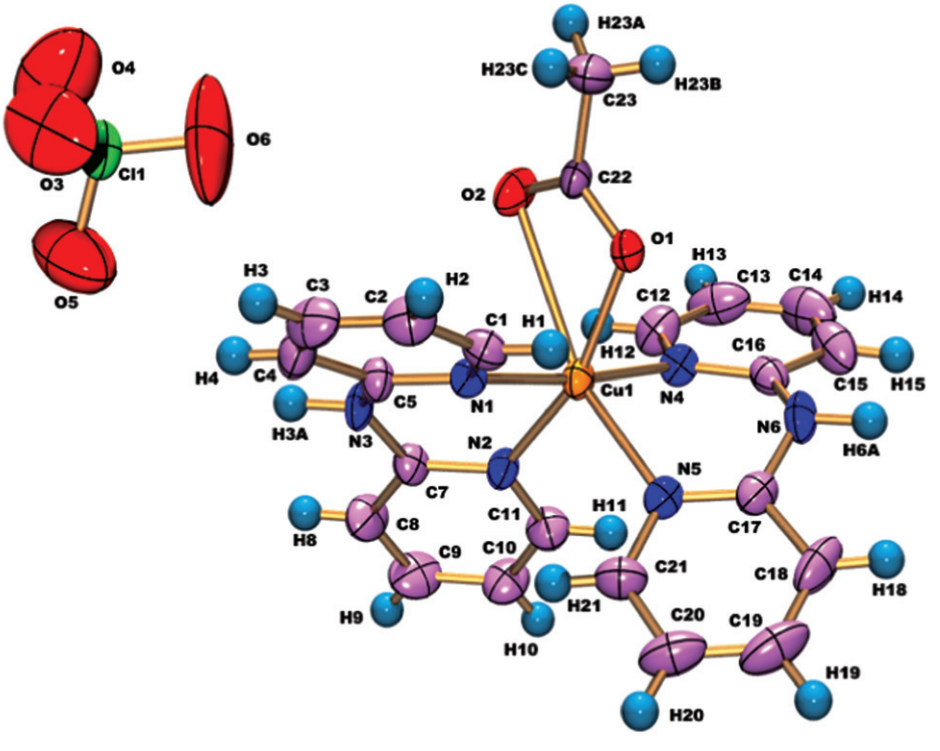

Figure 1. ORTEP diagram of **1** with atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Only one set of oxygens for the disordered perchlorate anion is shown.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–O(2)	2.710(4)	Cu(1)–N(4)	1.999(4)
Cu(1)–O(1)	2.016(3)	Cu(1)–N(5)	2.158(5)
Cu(1)–N(2)	2.020(4)	C(22)–O(1)	1.273(7)
Cu(1)–N(1)	1.997(4)	C(22)–O(2)	1.234(7)
N(1)–Cu(1)–N(2)	88.31(17)	N(2)–Cu(1)–N(5)	96.57(17)
N(1)–Cu(1)–N(4)	173.51(17)	N(4)–Cu(1)–N(5)	87.44(17)
N(1)–Cu(1)–N(5)	98.33(17)	N(2)–Cu(1)–O(1)	160.41(15)
N(2)–Cu(1)–N(4)	94.01(17)	O(1)–Cu(1)–O(2)	52.88(12)
N(4)–Cu(1)–O(2)	93.51(15)	O(1)–C(22)–O(2)	122.1(5)

Table 3. Relevant hydrogen bonds in **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N3–H3A···O2$^{\text{i}}$	0.86	2.04	2.816(6)	149
N6–H6A···O6$^{\text{ii}}$	0.86	2.02	2.846(10)	161
C3–H3···O6	0.93	2.58	3.305(11)	135
C4–H4···O2$^{\text{i}}$	0.93	2.57	3.294(8)	136
C11–H11···N4	0.93	2.62	3.060(7)	110
C14–H14···O5$^{\text{iii}}$	0.93	2.57	3.481(11)	165

Symmetry codes: (i) $1-x$, $1/2+y$, $1/2-z$; (ii) $1-x$, $-y$, $1-z$; (iii) $-1+x$, y, z.

Table 4. $\pi\cdots\pi$, C–H···π and anion-π interactions in **1**.

Cg(I)$^{\text{a}}$ → Cg(J)	Cg–Cg (Å)	Dihedral angle (°)	C/Cl–Cg (Å)
π–π interaction			
Cg(6) → Cg(7)$^{\text{I}}$	4.666(4)	30.76	
C–H···π interaction	H···Cg	<C–H···Cg	C···Cg
C(23)–H(23A) → Cg(4)$^{\text{ii}}$	2.93	158	3.839(6)
ClO_4^-···π interaction	O···Cg	<Cl–O···Cg	Cl···Cg
Cl(1)–O(3) → Cg(7)$^{\text{iii}}$	3.304(14)	164.5(9)	4.636(4)
Cl(1)–O(4) → Cg(6)$^{\text{iii}}$	3.476(9)	118.8(5)	4.339(4)

Symmetry code: (i) x, $-1+y$, z; (ii) x, $-1+y$, z; (iii) $1+x$, y, z.

[a] Cg(I) denotes centroid of Ith ring; Ring (4) N(1)/C(1)/C(2)/C(3)/C(4)/C(5); Ring (6) N(4)/C(12)/C(13)/C(14)/C(15)/C(16); Ring (7) N(5)/C(17)/C(18)/C(19)/C(20)/C(21).

of 2.710(4) Å. The structure of **1** can be best considered as the intermediate between a distorted square based pyramid, with an additional long bonded sixth O(2) ligand that generates an asymmetric *cis*-distorted octahedron giving a $(4+1+1^*)$ type coordination. The dypam bite angles are 88.3(2)° for the ligand defined by N1/N2 and 87.4(2)° for the ligand defined by N4/N5. The individual pyridine rings in the dypam ligands are planar. The dypam ligands, however, as a whole, are non-planar and are slightly twisted about the amine N–C bonds. The acetate in **1** is planar and nearly coplanar (dihedral angle being 9.92°) with the Cu, N2, N5 plane and, due to the small O1–Cu1–O2 bite angle [52.88(12)°], O2 lies well off the *z* axis of the CuN_3ON' square pyramid at a distance 2.710(4) Å, but close enough to be involved in off-the-*z*-axis bonding to Cu(II). There are no unusual bond lengths and angles observed when the structure of **1** was compared with similar types of compounds having *cis*-distorted CuN_4O_2 chromophore [17].

Each monomeric $[Cu(OAc)(2,2'\text{-dypam})_2]^+$ links another by a N3–H3A $\cdots$ O2 [2.816(6) Å, symmetry code: $1-x, 1/2+y, 1/2-z$] hydrogen bond to form infinite 1-D zig-zag chains which run parallel to the *b* axis (figure 2). Each monomeric unit also links one dangling perchlorate anion by a N6–H6A $\cdots$ O6 [2.846(10) Å, symmetry code: $1-x, -y, 1-z$] hydrogen bond. Disposition of the monomeric units in a chain also gives weak edge-to-face C(23)–H(23A) $\cdots \pi$ [C $\cdots$ Cg(4) = 3.839(6) Å, symmetry code: $x, -1+y, z$] and face-to-face $\pi \cdots \pi$ [Cg(6) $\cdots$ Cg(7) = 4.666(4) Å, symmetry code: $x, -1+y, z$] interactions between the centroid of the aryl ring and with the nearest carbon atom C23 and/or with another aryl ring of dypam (figure 3). Two such adjacent chains along the *c* axis are joined by a C3–H3 $\cdots$ O6 [3.305(11) Å] hydrogen bond to form a 2-D network (figure 4). These 2-D layers are interlinked along the a axis by ClO_4^- through Cl(1)–O3 $\cdots \pi$, Cl(1)–O4 $\cdots \pi$ (table 4) interactions. This $ClO_4^- \cdots \pi$ interaction is further supplemented by a C14–H14 $\cdots$ O5 [3.481(11) Å, symmetry code: $1+x, y, z$] hydrogen bond resulting in 3-D assembly of the 2-D layers.

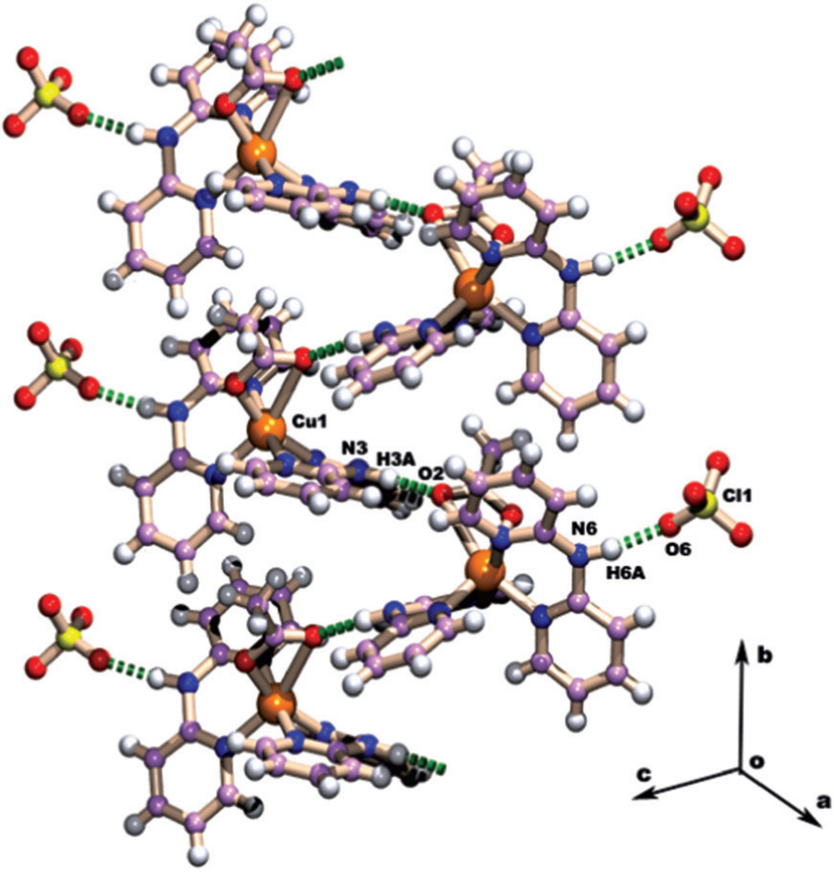

Figure 2. Zig-zag 1-D chain of monomeric units formed through N3–H3A $\cdots$ O2 hydrogen bonds and runs along the *b* axis. Perchlorate anions are attached with the chain via N6–H6A $\cdots$ O6 hydrogen bonds.

Perchlorate oxygens (O3 and O4) are involved in π-interactions with the centroids of aryl rings of the dypam ligands (figure 5). The distances between the O atoms of ClO_4^- and the centroids of the phenyl rings of the dypam ligands are 3.304(14) [Cl(1)–O(3) to Cg(7)] and 3.476(9) [Cl(1)–O(4) to Cg(6)], indicating anion-π interaction. Various contact distances between perchlorate oxygen to centroid of the aromatic ring have been reported in the literature (ranging 2.99–3.86 Å) in Co(II), Ag(I) and Cu(II) complexes. The strength of this interaction depends on the electron deficiency of the interacting aromatic rings [15b, 18] with higher electron deficiency of the aromatic ring giving stronger interaction. Zhou *et al.* [15b] found that multiatomic anions (ClO_4^-, BF_4^-, and PF_6^-) determine the self-assembly of Ag-tpt [tpt = 2, 4, 6-tri(2-pyridyl)-1, 3, 5-trazine, O $\cdots$ π contact distances are 3.157 and 3.821 Å] 1-D coordination polymers through anion-π interactions.

Favorable anion-π interactions exist between anions and tetrazine rings in 1-D polymers of [Ag(μ-bptz)(bptz)][BF_4] [19] and [Cd(μ-bptz)(NO_3)$_2$] [20], but were not explored in detail. Dunbar *et al.* [15a] establish anion-π interactions play decisive roles in 1-D self-assembly processes. In their observations, Dunbar *et al.* found that when

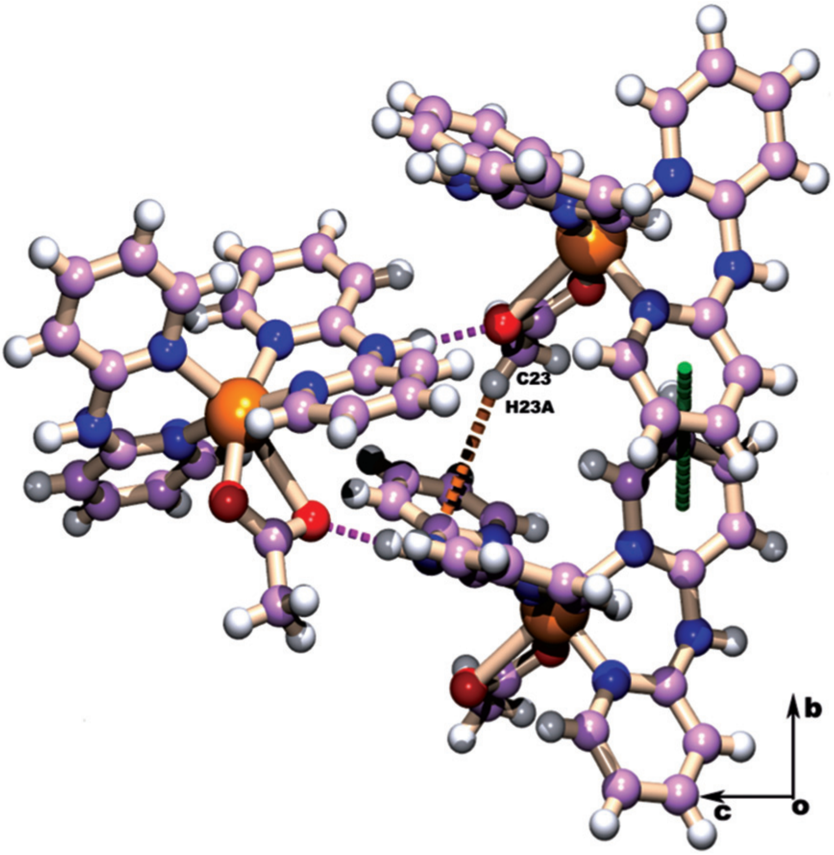

Figure 3. Intra chain C23–H23A $\cdots$ π (shown by coral; color online only) and weak $\pi \cdots \pi$ stacking (shown by green) interactions. Perchlorate anions are omitted for clarity.

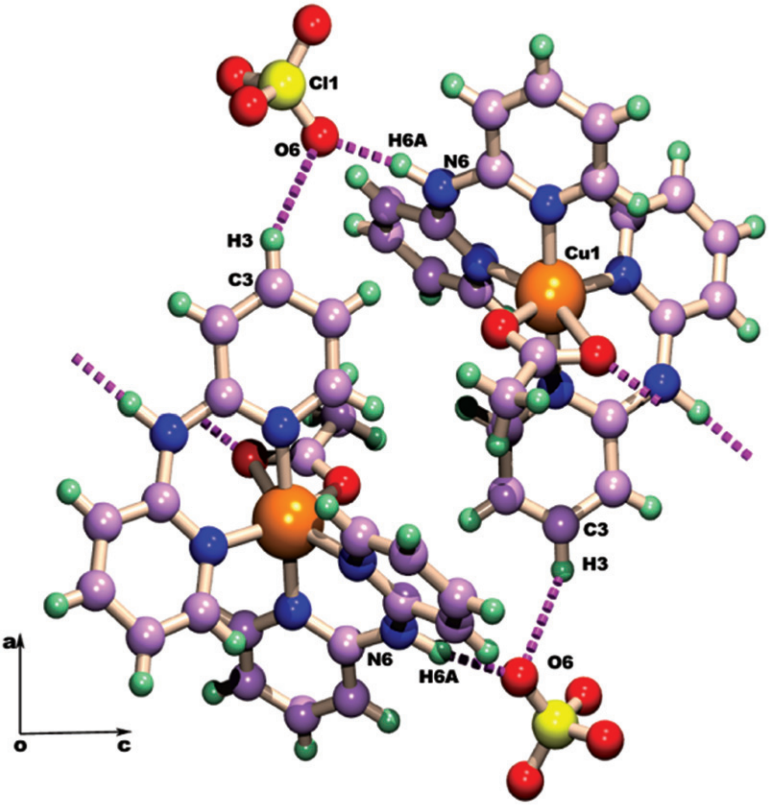

Figure 4. 2-D assembly of monomeric units by C3–H3 ⋯ O6 hydrogen bonds. Viewed along the *b* axis.

AgX salts (X = $[PF_6]^-$, $[AsF_6]^-$, $[SbF_6]^-$ and $[BF_4]^-$) are reacted with bptz and bppn, complexes of different structural motifs result depending on the π-acidity of the ligand central ring and the outer-sphere anion (bptz = 3, 6-*bis*(2′-pyridyl)-1,2,4,5-tetrazine, bppn = 3,6-*bis*(2′-pyridyl)-1,2-pyridazine). Reactions of bppn with AgX produced grid-like structures regardless of the anions present. In these structures, $\pi \cdots \pi$ stacking interactions were maximized at the expense of anion-π interactions. In contrast, multiple and strong anion–π interactions were seen between the anions and the tetrazine rings that reflect more electron-rich character of the bppn pyridazine ring as compared to the bptz tetrazine ring [15a]. In **1**, we find that the $ClO_4^- \cdots \pi$ interaction is weak as the aromatic rings of the dypam ligands are electron rich. This is because in dypam, the two pyridine rings contain only one electron-withdrawing sp^2 hybridized nitrogen atom per ring intervened by an ortho –NH– spacer which must increase the electron density on either pyridine ring by conjugation with the π-electrons of the pyridine rings. Still, this weak interaction has increased the dimensionality of **1** from 2-D to 3-D. We thus provide an example where anion-π interaction controls the self-organization of the metal complex even when the π-system of the aromatic ring is not electron-poor. It may be possible that Cu(II), bonded with pyridine nitrogens, withdraws electron density to some extent by polarizing the π-electron density of the ring [21], increasing perchlorate interaction with the π-face of the aromatic rings and thereby facilitating the 3-D

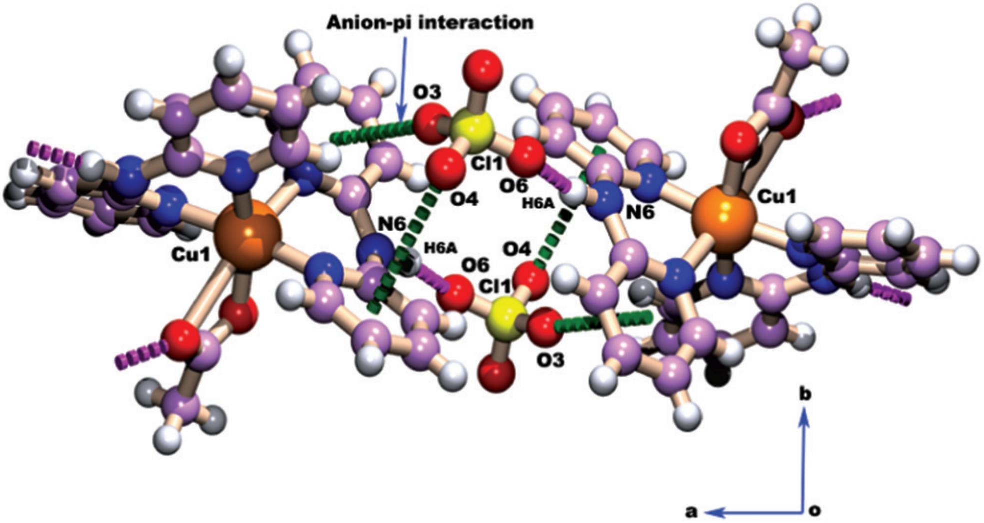

Figure 5. 3-D assembly of monomeric units dominated by anion-π interactions. A supramolecular synthon is formed involving anion-π interactions. Viewed along the *c* axis.

supramolecular network. We show, for the first time, the π-system of 2,2′-dipyridylamine can be used as an anion acceptor. In the literature, two isomorphous analogues of **1**, namely [Cu(OAc)(2,2′-DPA)$_2$](NO$_3$) (DPA = 2,2′-dipyridylamine) [22a] and [Cu(OAc)(2,2′-DPA)$_2$](BF$_4$) [22b] have been reported. In these two complexes, we uncover $NO_3^- \cdots \pi$ and $BF_4^- \cdots \pi$ interactions between the O/F atoms of the nitrate/tetrafluoroborate group with the centroid of the aromatic rings of the dypam ligand, which were ignored by the authors [22a, 22b] at that time as anion-pi interaction phenomenon is a very recent addition to supramolecular chemistry [9–11]. We calculate the distances N(7)–O(4) to Cg = 3.351 Å, where Cg is the centroid of the ring N(4)–C(11)–C(12)–C(13)–C(14)–C(15) for the nitrate complex [22a] and B1-F1A to Cg = 3.199 Å, where Cg is the centroid of the ring comprising N(5)–C(16)–C(17)–C(18)–C(19)–C(20) for the tetrafluoroborate complex [22b]. These interactions help to build the 3-D supramolecular networks in [Cu(OAc)(2,2′-DPA)$_2$](NO$_3$) and [Cu(OAc)(2,2′-DPA)$_2$](BF$_4$).

3.2. *Spectroscopic properties*

The electronic spectrum of 1 exhibits a broad featureless band at 668 nm ($\varepsilon = 107\,\mathrm{M^{-1}\,cm^{-1}}$) in acetonitrile. The band at 3309 cm^{-1} in the IR spectra of the title complex can be assigned to υ(N–H). The band at 1085 cm^{-1} is due to ClO_4^- anion. The υ_{as}(COO) and υ_s(COO) bands of **1** are observed, respectively, at 1587 and 1415 cm^{-1}.

3.3. *Magnetic properties*

To investigate any effect of hydrogen bonds, C–H$\cdots\pi$ and $\pi\cdots\pi$ interactions of **1** on the magnetism of the system, the VTM studies were initiated. The $\chi_M T$ *versus* T

plot ($\chi_M T$ being the magnetic susceptibility per Cu atom) is given in figure 6. At room temperature the $\chi_M T$ value is $0.39\,cm^3\,mol^{-1}\,K$, which agrees well with that expected for isolated copper(II) ions with $g = 2.04$, clearly demonstrating the weak interactions forming the 2-D or 3-D assembly of 1 do not affect its magnetic properties. The $\chi_M T$ remains almost constant until 20 K and then sharply decreases to a value $0.36\,cm^3\,mol^{-1}\,K$ at 2 K. This decrease is due to very weak intermolecular antiferromagnetic interactions, which are mediated by hydrogen bond, C–H $\cdots \pi$ and $\pi \cdots \pi$ interactions. The magnetic data were analyzed by using the molecular field approximation [23]. The best fit of the susceptibility data to the theoretical equation led to the following parameters: $g = 2.05$ and $zJ = -0.30\,cm^{-1}$. The M *versus* H plot at 2 K (figure 7) is slightly below that calculated from the Brillouin function with $S = 1/2$ and $g = 2.04$, as expected for the existence of weak antiferromagnetic interactions between copper(II) ions. At 5T, the maximum applied magnetic field, the value of the magnetization is $0.92\,N\beta$, thus indicating that at this magnetic field the magnetization is not yet saturated ($Ms = 1\,N\beta$).

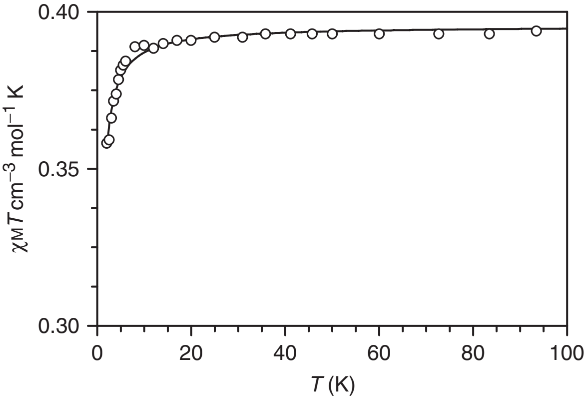

Figure 6. Temperature dependence of $\chi_M T$ for **1**.

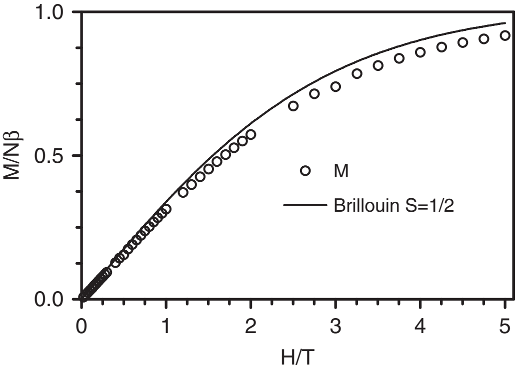

Figure 7. Field dependence of the magnetization at 2K for **1** (circles). Brillouin function for $S = 1/2$ is shown by solid curve.

In summary, anion-π interaction resulted in 1-D propagation of coordination polymers [15], but we have demonstrated that feeble supramolecular $ClO_4^- \cdots \pi$, $NO_3^- \cdots \pi$ or $BF_4^- \cdots \pi$ interactions stitch together 2-D layers formed by the monomeric $[Cu(OAc)(2,2'\text{-dypam})_2]^+$ species leading to a 3-D network. The comprehensive work of Dunbar *et al*. [15a] and Zhou *et al*. [15b] leave the opportunity to exploit feeble anion-π interactions in crystal engineering. The unprecedented role of simple, apparently innocent anions to increase the dimensionality in **1** rather than being trapped by the receptors, offers a challenge to synthetic chemists to explore their potential applications in crystal engineering and supramolecular chemistry and then to judge their roles in crucial biological systems for biochemical structural arrangements that could involve interactions of the π-aromatic rings like in DNA, porphyrins, some amino acids, etc. with anions [2b] and in enzyme-substrate recognition as more than two-thirds of enzyme substrates and cofactors are anionic [24].

Supplementary data

Crystallographic data in CIF format for **1** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC No. 658104. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44(0)-1223-336033 or Email: deposit@ccdc.cam.ac.uk).

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