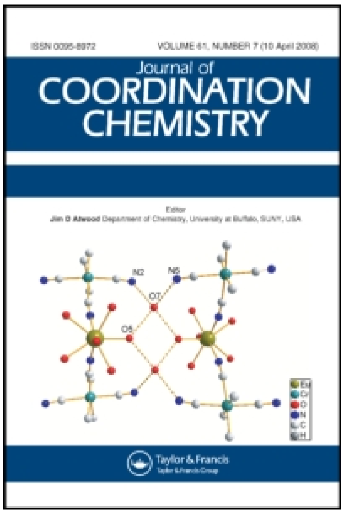

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Interconversion of copper(II) to copper(I): synthesis, characterization of copper(II) and copper(I) 2,2'-biquinoline complexes and their microbiological activity

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Interconversion of copper(II) to copper(I): synthesis, characterization of copper(II) and copper(I) 2,2′-biquinoline complexes and their microbiological activity

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The complexes $[Cu(biq)_2]Cl_2$ and $[Cu(biq)_2]BF_4 \cdot biq$ (biq = 2,2′-biquinoline) have been prepared and characterized. The interconversion to copper(I) complex $[Cu(biq)_2]BF_4 \cdot biq$, from $[Cu(biq)_2]Cl_2$ has been established. The new complexes have been characterized by elemental analysis, conductivity and magnetic measurements, IR, UV-vis and ^1H- and ^{13}C-NMR spectroscopy. The X-ray analysis of the complex $[Cu(biq)_2]BF_4 \cdot biq$ supports the assumption of the interconversion of copper(II) to copper(I) in this case. The crystal structure shows that geometry around the metal is severely distorted from T_d, and displays many supramolecular motifs incorporating both hydrophobic (aryl···aryl) and hydrophilic (C–H···F) intermolecular interactions. The microbiological activity of the complexes against bacteria and fungi was found to be high against *Candida albicans*, and slight to moderate against bacteria. The antimicrobial activity of $[Cu(biq)_2]BF_4 \cdot biq$ was slightly better than that observed for $[Cu(biq)_2]Cl_2$ against both bacteria and fungi.

Keywords: Copper complexes; Interconversion; (aryl···aryl) and (C–H···F) intermolecular interactions; Biological activity

1. Introduction

Copper–diimine complexes have received special interest because of their possible biological activity [1]. Moreover, these complexes are of particular interest due to the interdependence of their coordination geometry and their redox and photochemical

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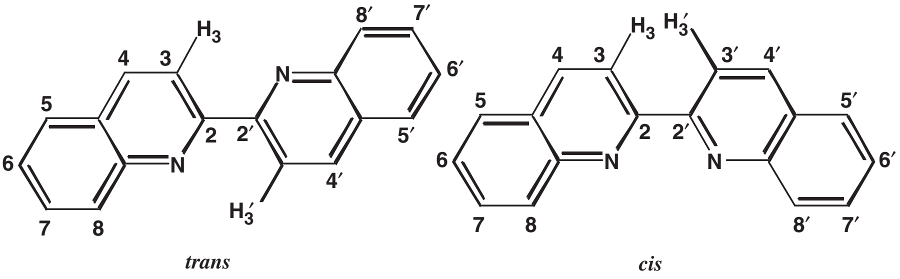

Figure 1. Structure of 2,2′-biquinoline (biq).

behaviour [2]. They have been used as catalysts for the electroreduction of dioxygen and in photocatalytic solar energy harvesting systems [3].

The chemistry of copper(I) and copper(II) complexes with 2,2′-biquinoline (hereafter denoted biq) (figure 1) is well established and the syntheses and full characterization of complexes differing only in the anion have been reported previously [3]. Other metal complexes containing biq have been reported recently, *cis*-$[Rh(biq)_2Cl_2]Cl$, *mer*-$[Rh(biq)Cl_3(H_2O)]$, *mer*-$[Ru(biq)_2Cl_3]\cdot 2H_2O$ and *cis*-$[Pt(biq)Cl_2]$ that exhibit remarkable biological activities [4, 5]. Furthermore, supramolecular motifs were recognized in the crystal structures of metal complexes containing aryl groups such as 2,2′-bipyridine [6], terpyridine ligands [7], and 1,10-phenanthroline [8, 9]. Unusual oxidation states could also be trapped and isolated using this strategy of forming stable lattices [10].

In the present work, we present the synthesis of a copper(II)–biquinoline complex and the interconversion of copper(II) to copper(I) leading to an air stable copper(I) biquinoline complex. The crystal supramolecularity, and the preliminary assay of biological activity as antibacterial and antifungal agents were studied.

2. Experimental

2.1. *Materials*

All solvents were analytical grade, used as purchased. The metal salt and the biq ligand were Aldrich products.

2.2. *Physical measurements*

Melting points were determined on an electrothermal melting point apparatus (Electrothermal 9001). IR spectra were recorded on a Nicolet FT-IR spectrophotometer using KBr discs while far IR spectra were analyzed on a Perkin–Elmer spectrophotometer model 2000 using CsI discs. Conductivity measurements were recorded on a Conductivity Meter LF 538 at 25°C for 10^{-3} M solution in DMF. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX 300 MHz spectrometer, in DMF as solvent using Me_4Si as an internal standard. UV-vis spectra were recorded on a Unicam UV-vis spectrometer. Elemental analyses for C, H and N were carried out using a Perkin–Elmer %C, H, N, analyzer 2400 series (II), in the Central

Laboratories Unit at Al al-Bayt University, Jordan. Metal analysis was recorded on a Unicam 929 AA spectrometer.

2.3. *Synthesis*

Complexes were all dried under vacuum at 25°C. Experimental procedures are given below.

2.3.1. Preparation of [Cu(biq)$_2$]Cl$_2$. To $CuCl_2 \cdot 2H_2O$ (0.050 mmol; 0.085 g) in 50 mL Me_2CO, was added (1.0 mmol; 0.26 g) of the ligand (biq) in 20 mL Me_2CO. The reaction mixture was stirred for few minutes, and an orange solid precipitated. The solid was filtered off, washed several times with Me_2CO and then with Et_2O and dried under vacuum giving a light orange solid, m.p. 198°C. Yield = 85%. Anal. Calcd: C, 66.64; H, 2.80; N, 8.65; Cu, 9.94. Found: C, 67.10; H, 2.91; N, 7.61; Cu, 9.82. $\mu_{eff} =$ 1.89 B.M. $\Lambda_M = 88.6\,\Omega\,cm^2\,mol^{-1}$.

2.3.2. Preparation of [Cu(biq)$_2$](BF$_4$)·biq. To a (0.25 mmol; 0.16 g) stirred solution of $[Cu(biq)_2]Cl_2$ dissolved in EtOH/H_2O mixture (50 : 30 mL), small portions of $NaBF_4$ solution (0.25 mmol; 0.027 g) dissolved in 1 mL Me_2CO were added. The resulting clear, dark red mixture was then stirred for few minutes and allowed to stand at room temperature, whereupon red, block crystals suitable for single crystal crystallography grew during three days. They were filtered off, washed several times with H_2O, EtOH and Et_2O and dried under vacuum. The composition was determined by single crystal diffraction analysis. Dark red solid, m.p. 350°C. Yield = 72%.^{1}H NMR: δ 8.88 (H3, d), 8.70 (H4, d), 7.82 (H5, d), 7.69 (H6, t), 742 (H7, t), 8.28 (H8, d).^{13}C NMR: δ 152.33, 144.87, 139.15, 130.07, 129.49, 128.77, 128.09, 127.36, 120.57. Diamagnetic $\Lambda_M = 62.3\,\Omega\,cm^2\,mol^{-1}$.

2.4. *X-Ray crystallography*

Crystallographic data for $[Cu(biq)_2]BF_4 \cdot$ biq are listed in table 1 while the final atomic parameters are listed in table 2. The unit cell parameters were determined and the data collected with a Bruker SMART difractometer in $\theta/2\theta$ scan mode using graphite monochromatized molybdenum radiation (λ 0.7107 Å). The data were corrected for absorption. The structures were solved by direct methods using the SHELXS-97 program; and refined (full-matrix least squares on F^2) by using the SHELXS-97 program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and were assigned thermal parameters equal to those of the atom to which they were bonded.

3. Results and discussion

The reaction of hydrated copper(II) chloride, $CuCl_2 \cdot 2H_2O$, with biq yielded $[Cu(biq)_2]Cl_2$. The quantitative yield and various physical measurements are commensurate with the formulation. The reaction of $[Cu(biq)_2]Cl_2$ with $NaBF_4$ gave the four-coordinate copper(I) complex $[Cu(biq)_2]BF_4 \cdot$ biq. The interconversion is a redox reaction that converts copper(II) to copper(I) with the other half reaction involving

Table 1. Crystal data and structure refinement for $[Cu(biq)_2]BF_4 \cdot biq$.

Empirical formula	$C_{54}H_{36}BCuF_4N_6$
Formula weight	919.24
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2/n$
Unit cell dimensions (Å, °)	$a = 13.9387(8)$, $\alpha = 90$
	$b = 10.8609(6)$, $\beta = 97.2630(10)$
	$c = 14.2027(9)$, $\gamma = 90$
Volume (Å^3)	2132.8(2)
Z	2
Density (calculated) (Mg m^{-3})	1.431
Absorption coefficient (mm^{-1})	0.577
$F(000)$	944
Crystal size (mm^3)	$0.24 \times 0.16 \times 0.12$
Theta range for data collection	1.88 to 27.50°
Index ranges	$-18 \leq h \leq 17$, $-13 \leq k \leq 14$, $-11 \leq l \leq 18$
Reflections collected	14944
Independent reflections	4890 [$R(\text{int}) = 0.0247$]
Completeness to $\theta = 27.50°$	99.9%
Absorption correction	Sadabs (Sheldrick 2001)
Max. and min. transmission	0.9340 and 0.8739
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4890/0/299
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0533$, $wR_2 = 0.1434$
R indices (all data)	$R_1 = 0.0670$, $wR_2 = 0.1540$
Largest diff. peak and hole (e Å^{-3})	0.854 and −0.372

formation of acetic acid from ethanol used as a solvent (equation (1)). The reduction of copper(II) N-heterocycle and copper(II) halide complexes to copper(I) species in stable lattices have been reported previously [10, 11].

$$4[Cu(biq)_2]Cl_2 + 8NaBF_4 + C_2H_5OH + H_2O \rightarrow 4[Cu(biq)_2]BF_4 + 8NaCl + 4HBF_4 + HC_2H_3O_2. \qquad (1)$$

The complexes are coloured solids, stable in air and soluble in organic solvents. They were isolated in good yields. The analytical and physical data are summarized in the experimental section.

3.1. *Conductivity*

Molar conductances for the complexes (see section 2) are consistent with those reported for similar complexes [12]. The complex $[Cu(biq)_2]BF_4 \cdot biq$ behaves as a 1 : 1 electrolyte, while $[Cu(biq)_2]Cl_2$ acts as a 1 : 2 electrolyte. The smaller conductance values obtained for the complexes compared to reported values may be attributed to the large size of the formed complexes as well as the expected aryl···aryl and C–H···F intermolecular interactions (see crystal supramolecularity section) between the molecules.

3.2. *Magnetic measurements*

The room temperature magnetic moment of $[Cu(biq)_2]Cl_2$ indicates its paramagnetism and is in good agreement with literature values for similar systems [13, 14].

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[Cu(biq)_2]BF_4 \cdot biq$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U*(eq)
Cu(1)	7500	1420(1)	2500	50(1)
N(1)	6202(1)	671(2)	2111(1)	45(1)
N(2)	6731(1)	2408(2)	3347(1)	45(1)
N(3)	−547(2)	8925(2)	715(2)	61(1)
C(1)	5982(2)	−235(2)	1444(2)	47(1)
C(2)	6727(2)	−707(2)	959(2)	55(1)
C(3)	6519(2)	−1598(2)	280(2)	66(1)
C(4)	5577(2)	−2056(2)	65(2)	68(1)
C(5)	4851(2)	−1619(2)	522(2)	63(1)
C(6)	5027(2)	−690(2)	1222(2)	53(1)
C(7)	4306(2)	−162(2)	1700(2)	57(1)
C(8)	4527(2)	735(2)	2354(2)	53(1)
C(9)	5496(1)	1139(2)	2550(2)	44(1)
C(10)	5800(1)	2121(2)	3259(2)	46(1)
C(11)	5153(2)	2702(2)	3813(2)	57(1)
C(12)	5496(2)	3563(2)	4465(2)	60(1)
C(13)	6480(2)	3911(2)	4563(2)	54(1)
C(14)	6897(2)	4795(2)	5230(2)	65(1)
C(15)	7854(2)	5093(2)	5270(2)	69(1)
C(16)	8427(2)	4523(3)	4671(2)	71(1)
C(17)	8064(2)	3642(2)	4033(2)	61(1)
C(18)	7078(2)	3315(2)	3976(2)	47(1)
C(19)	151(2)	9509(2)	358(2)	61(1)
C(20)	1146(2)	9247(3)	620(2)	71(1)
C(21)	1398(2)	8313(3)	1244(2)	73(1)
C(22)	684(2)	7638(2)	1624(2)	66(1)
C(23)	875(2)	6625(3)	2245(2)	74(1)
C(24)	147(2)	6009(3)	2572(2)	83(1)
C(25)	−819(3)	6372(3)	2324(3)	83(1)
C(26)	−1034(2)	7339(3)	1717(2)	73(1)
C(27)	−297(2)	7989(2)	1349(2)	61(1)
B(1)	2500	2987(5)	2500	81(1)
F(1)	2285(1)	2297(2)	1717(1)	98(1)
F(2)	1718(3)	3659(3)	2594(2)	225(2)

The measured value of 1.89 B.M. for the copper(II) complex is consistent with a d^9 configuration, indicating little or no interactions between the copper(II) centres in the monomeric complexes [13, 14]. On the other hand, the magnetic moment for copper(I) in $[Cu(biq)_2]BF_4 \cdot biq$ is as expected for diamagnetic d^{10} configuration.

3.3. *IR spectra*

The IR bands of coordinated biq were assigned on the basis of earlier studies [15–18]. A detailed comparison between the biq ligand (figure 1) in complexes and the free ligand cannot be made since the nitrogen donor atoms are *trans* in the free ligand and *cis* upon coordination, attributable to H(3,3′) repulsion [17, 18]. The characteristic IR bands for the complexes are shown in table 3A. The main points are given below:

(i) The strong bands appearing in the range 1420–1599 and 735–840 cm^{-1} in the IR spectra of the complexes, assigned to [ν(C=C), (C=N)] and ν(C–H), respectively,

Table 3. Important IR frequencies (KBr pellets, cm^{-1}) for the complexes and electronic absorption spectra in DMF (10^{-3} M solutions) for the complexes.

	Physical property	$[Cu(biq)_2]Cl_2$				$[Cu(biq)_2]BF_4 \cdot biq$					
A	Important IR frequencies										
	ν(C=C), ν(C=N)	1588 vs, 1502 vs, 1427 m				1599 s, 1510 s, 1501 s, 1430 w					
	ν(C–H)	836 s, 789 m, 755 m, 735 w				829 vs, 782 s, 749 s					
	Others					ν(B—F): 1080 m, 752 s, 520 m					
B	Electronic absorption spectra										
	λ_{max} (nm)	300	475	525	545	252	272	328	340	524	552
	Band assignment	MLCT	d–d	d–d	d–d	MLCT	MLCT	MLCT	MLCT	MLCT	MLCT
	$\varepsilon \times 10^{-3}$ ($L\,mol^{-1}\,cm^{-1}$)	103	0.22	0.85	2.12	58	77.86	37.76	38.24	0.78	0.30

vs, very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder.

indicate the presence of coordinated biq (table 3A). Such results are in good agreement with other complexes [17, 18].

(ii) The strong absorption at 752 cm^{-1} as well as the medium bands at 1080 and 520 cm^{-1}, for $[Cu(biq)_2]BF_4 \cdot biq$, which are assigned to the ν(B–F) vibrations, indicate the presence of BF_4^- [19].

(iii) The far IR spectra of $[Cu(biq)_2]Cl_2$ and $[Cu(biq)_2]BF_4 \cdot biq$ exhibit no absorption peaks where ν(Cu–X) appears, confirming no Cu–X bonding [19].

3.4. *Electronic absorption spectra*

Upon addition of H$^+$, biq adopts a similar electronic spectrum to the coordinated biq ligand with metal complexes and its UV-vis spectrum exhibits two ligand-centred (LC) bands at ~268, and 372 nm arising from $\pi \rightarrow \pi^*$ [20] (table 3B). The spectra of the prepared complexes exhibit, in addition to LC bands, broad bands which are assigned to metal–ligand charge-transfer (MLCT) transitions and/or d–d transitions responsible for the characteristic colours of these complexes [13, 14] (table 3B). The broadness of the peaks at ca. 250–340 nm may indicate the presence of MLCT bands underlying the LC bands. These results are in good agreement with that which has been reported for complexes containing biq [3, 17, 18].

The complex $[Cu(biq)_2]Cl_2$, exhibits, in addition to the LC bands, d–d bands in the range 475–545 nm, suggesting tetrahedral geometry . This is comparable to analogous complexes containing four-coordinate copper(II) in a tetrahedral environment [3]. In addition, the electronic spectrum of $[Cu(biq)_2]Cl_2$ exhibits an additional MLCT band at 300 nm. $[Cu(biq)_2]BF_4 \cdot biq$ exhibits different electronic spectra as it contains a d^{10} centre. The spectrum shows LC bands within the expected regions. However, other bands in the range 252–340 along with weak shoulders at 524 and 552 nm may be assigned to MLCT transitions [3].

3.5. *^{1}H- and ^{13}C-NMR spectra*

The ^{1}H-NMR spectra for the ligand and $[Cu(biq)_2]BF_4 \cdot biq$ are presented in the experimental section. Coordination of the ligand nitrogens to the metal can be assumed by the general chemical shift differences of the protons in the ^{1}H-NMR spectrum (figure 1). Detailed comparison between the free ligand and complexes cannot be made since the free ligand exists in the *trans* conformation and complexes are *cis*. Therefore, assignments (see section 2) were made with the help of earlier studies [3, 17, 18]. The ^{1}H-NMR spectrum exhibits six different types of protons for the biq hydrogens in the range 7.38–8.85 ppm, as expected for a symmetrical tetrahedral structure [3]. Upon complexation, the chemical shift of H3 was highly deshielded leading to the assumption of a transoid conformation in solution, causing this proton to be proximal to the nitrogen lone pair electrons of the adjacent quinoline. The H4 proton was also shifted downfield which might be explained by the expected decrease of the C4 charge upon complexation. These data are in good agreement with literature values [3].

The protons H5, H6, H7 and H8 all experience an upfield shift attributed to the shielding of the aromatic ring current of the orthogonal ligand [3, 17, 18].

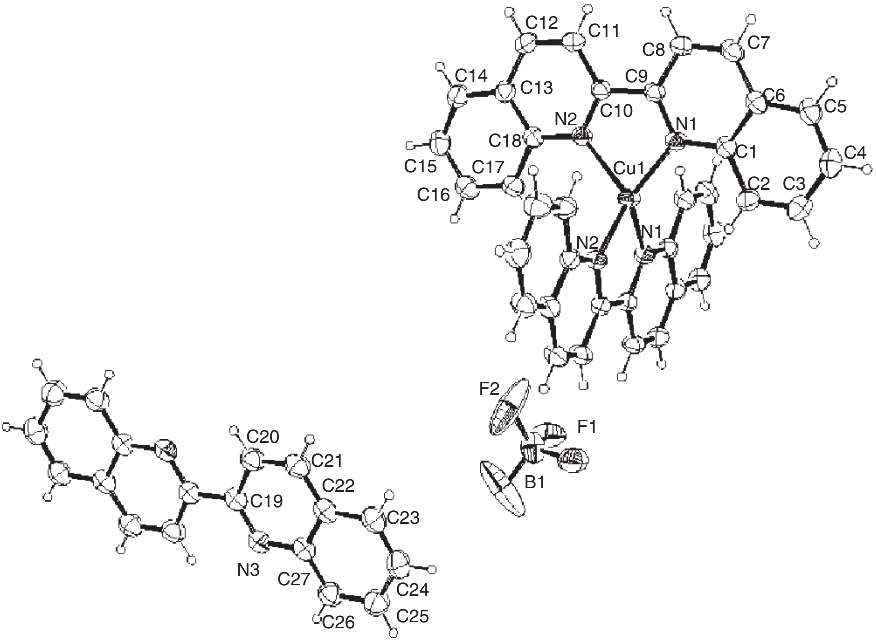

Figure 2. Crystallographic atom labels of $[Cu(biq)_2]BF_4 \cdot biq$.

The ^{13}C-NMR spectrum (see section 2) shows nine different peaks for nine different carbons of the biq rings in the range 120.57–152.33 ppm. The most deshielded chemical shifts are observed for C1 and C9 (and C1′ and C9′), 152.33 and 144.88 ppm, because of their closeness to the nitrogen.

3.6. *Crystal structure of [Cu(biq)₂]BF₄·biq*

The structure consists of discrete molecules of $[Cu(biq)_2]^+$, BF_4^- and biq. A perspective view of the structure together with the atom labeling is shown in figure 2. Selected bond lengths, bond angles and torsional angles for the complex are given in table 4. The copper(I) ion adopts a CuN_4, severely distorted, tetrahedral coordination environment. This distortion is evident in the N–Cu–N angles, the N(1)#1–Cu(1)–N(1), N(1)#1–Cu(1)–N(2), N(1)–Cu(1)–N(2), N(2)–Cu(1)–N(2)#1 being, 131.95(10), 125.66(7), 81.38(7) and 115.74(10)°, respectively (#1 $-x+3/2, y, -z+1/2$). The extent of the distortion, could be a consequence of the sterically hindered biq ligand coordinating to copper(I) in the central core, although crystal packing forces could cause such distortion. The Cu–N bond distances are 1.9973 and 2.0185 Å (table 4) comparable to Cu–N bond distances in similar systems containing N-heterocyclic ligands [3, 9, 21, 22].

3.7. *Crystal supramolecularity*

The structure (figure 2) is made up of one cation, one BF_4^- anion and one free ligand molecule. The cation and anion each lie on a two-fold axis, while the two halves of the free ligand are related by a centre of inversion.

Table 4. Selected bond lengths (Å) and bond angles (°) for $[Cu(biq)_2]BF_4 \cdot$ biq.

Cu(1)–N(1)	1.9973(16)	Cu(1)–N(2)	2.0185(17)
N(1)–C(9)	1.330(3)	N(1)–C(1)	1.374(3)
N(2)–C(10)	1.325(2)	N(2)–C(18)	1.377(3)
B(1)–F(2)	1.332(4)	B(1)–F(1)	1.344(3)
N(1)#1–Cu(1)–N(1)	131.95(10)	N(1)#1–Cu(1)–N(2)	125.66(7)
N(1)–Cu(1)–N(2)	81.38(7)	N(2)–Cu(1)–N(2)#1	115.74(10)
C(9)–N(1)–C(1)	118.95(17)	C(9)–N(1)–Cu(1)	114.35(14)
C(1)–N(1)–Cu(1)	126.69(13)	C(10)–N(2)–C(18)	119.32(18)
F(2)#3–B(1)–F(2)	113.6(5)	F(2)#3–B(1)–F(1)	108.77(19)
F(2)–B(1)–F(1)	106.80(14)	F(1)–B(1)–F(1)#3	112.2(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2, y, -z+1/2$; #2 $-x, -y+2, -z$; #3 $-x+1/2, y, -z+1/2$

The two ligands on the cation are orthogonal, planar and aromatic, and therefore the cations could form the "terpy embrace" [7], which is composed of layers with each ligand forming four EF and four OFF interactions with the ligands of adjacent molecules. This type of packing is prevalent for $M(terpy)_2$ structures, particularly those with small anions such as BF_4 or PF_6 [7]. However, this packing does not occur in this structure, and instead the lattice (figure 3) incorporates a free ligand sandwiched between a pair of cations to form OFF interactions with one ligand of each. In addition, the cation ligands make additional OFF interactions involving only the terminal phenyl rings of a pair of ligands (figure 3).

Evidence for significant non-conventional interactions [C–H$\cdots$C(π); aryl$\cdots$aryl and C–H$\cdots$F; hydrogen bonding] occurs in the short interatomic distances between the hydrogen atoms of biq and the C(π) of another biq and with the fluoride atoms of BF_4^- molecules in the crystal structure.

The crystal packing (figure 3) of the compound shows supramolecular motifs resulting from both hydrophilic and hydrophobic intermolecular interactions. The hydrophobic interactions are aryl$\cdots$aryl interactions involving biq rings (figure 4A), represented in the so called P4AE [6–8] incorporating extra supramolecularity using the free biq ligand via OFF interactions (figures 4B and 4C). This strand interacts with the strand underneath which is related by translation along the *b* axis through additional weak aryl$\cdots$aryl interactions. These weak interactions along with additional hydrogen bonding interactions as a result of the interaction of BF_4^- groups with coordinated and free biq molecules between the complexes ($F_3BF\cdots H$–C(π)). A descriptive view of the role of BF_4^- groups is given in figure 5 where the groups are hydrogen bonded to the coordinated and free biq ligands connecting them all through hydrogen bonding.

3.8. *Microbiological screening*

Tests for antibiotic and antifungal activity were performed according to the disc-diffusion assay and repeated two times to insure reliability. The prepared complexes were tested against bacteria (*Escherichia coli*, *Staphilococcus aureus* and *P. aeruginosa*), and fungi (*Candida albicans*). The culture media were Muller Hinton Agar (MHA) supplemented with 1 g yeast 1. The antibacterial and antifungal activities of each compound were evaluated by the classical Disk Diffusion Agar Plates technique.

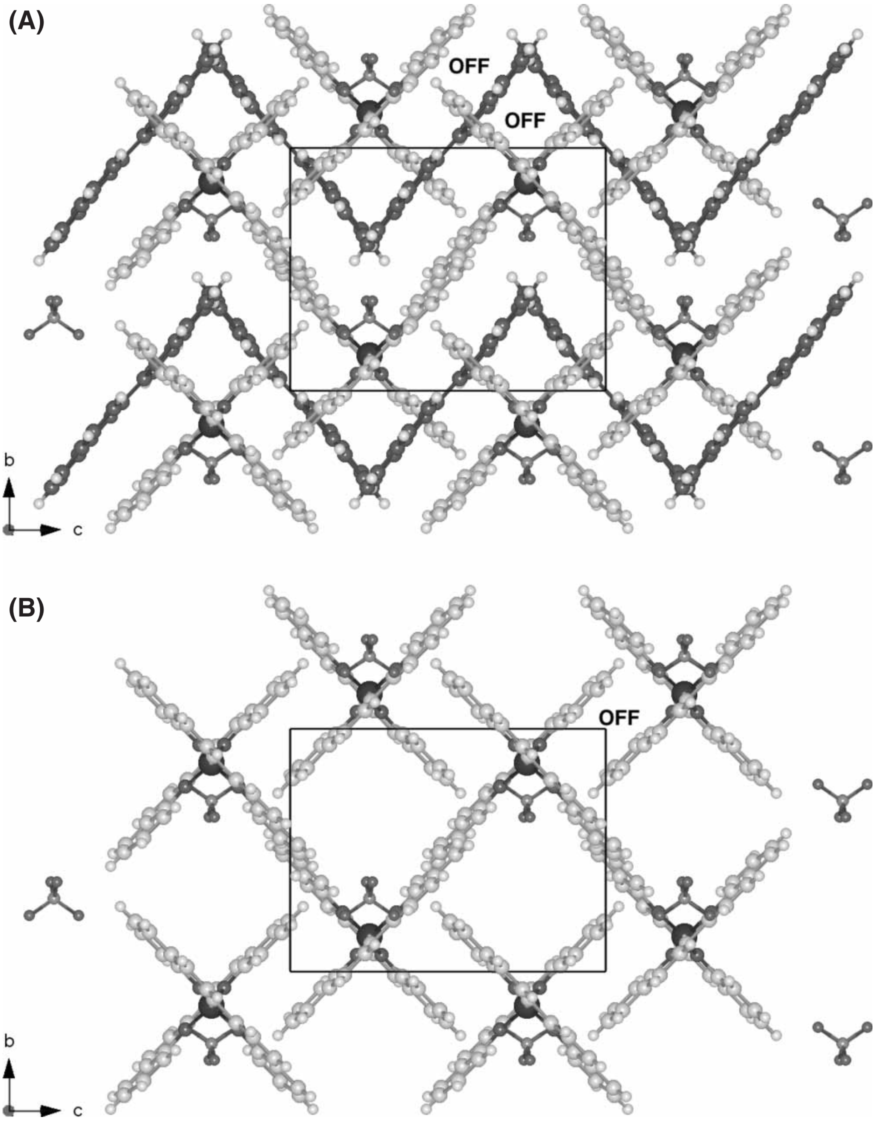

Figure 3. (A) Lattice packing for $[Cu(biq)_2]BF_4 \cdot biq$. The aryl···aryl intermolecular interactions with the free ligand (C is dark gray), which is sandwiched between a pair of cations (C is light gray) forms good OFF interactions. With *b* vertical and *c* horizontal the view is down *a*; (B) Lattice packing with the free ligand removed. There is an OFF interaction between the terminal portions of two cation ligands.

The results of the preliminary tests are listed in table 5 and can be summarized in the following points:

(i) The complex $[Cu(biq)_2]Cl_2$ was found to be slightly to moderately active as an antibacterial agent while $[Cu(biq)_2]BF_4 \cdot biq$ demonstrates moderate activity. A potential explanation for the slight to moderate antibacterial activity exhibited by these compounds could reside in their presumably low lipophilicity. In the penicillin family of antibiotics, potency is directly related to lipophilic

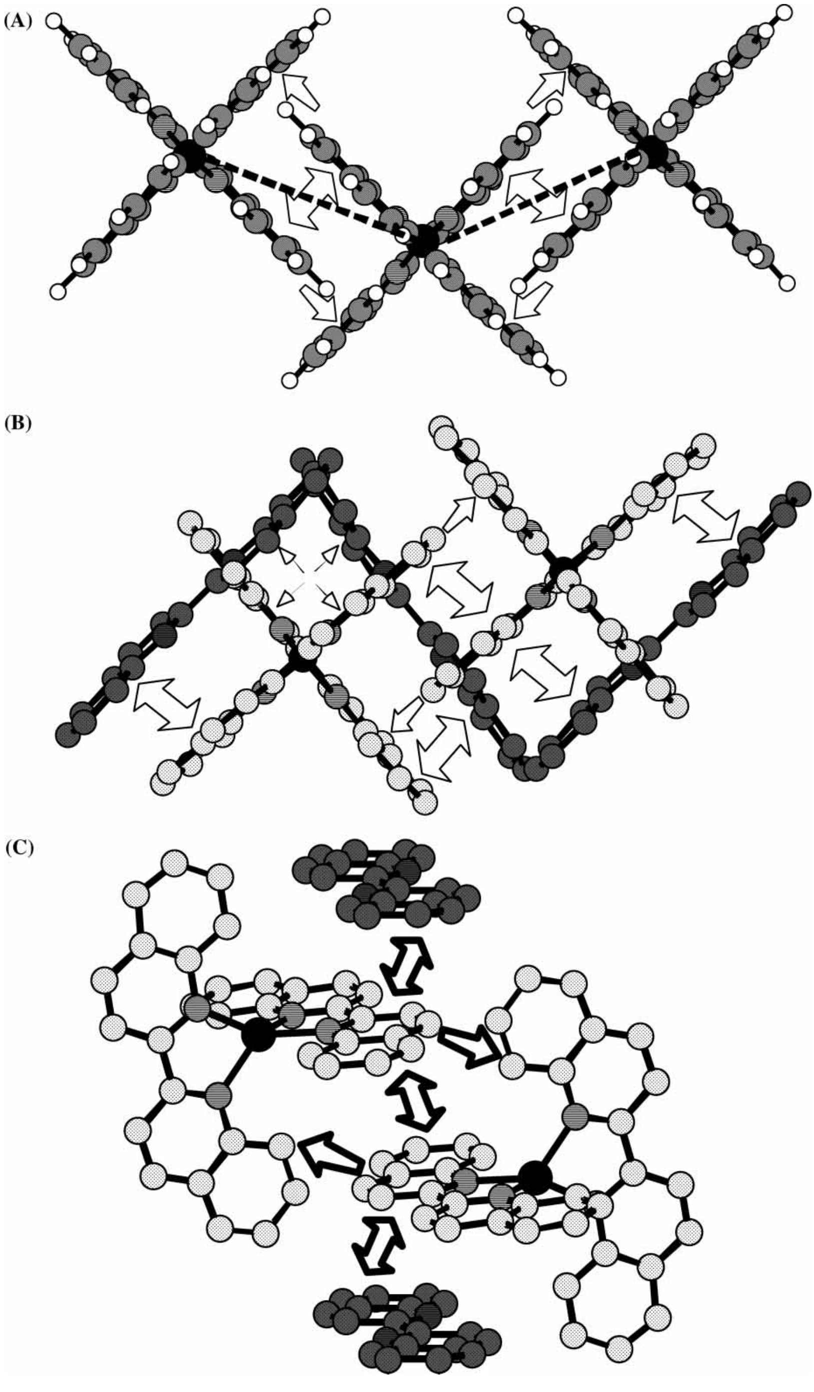

Figure 4. (A) Multiple aryl embraces between the cationic molecules: P4AE with two edge-to-face (ef; single headed arrows) interactions and one offset-face-to-face (off; double headed arrows) interaction (without free biq). (B) Two cationic complexes (light gray) embraced and a free biq (dark gray) ligand (a view along *c* axis). (C) Another view showing details of interactions.

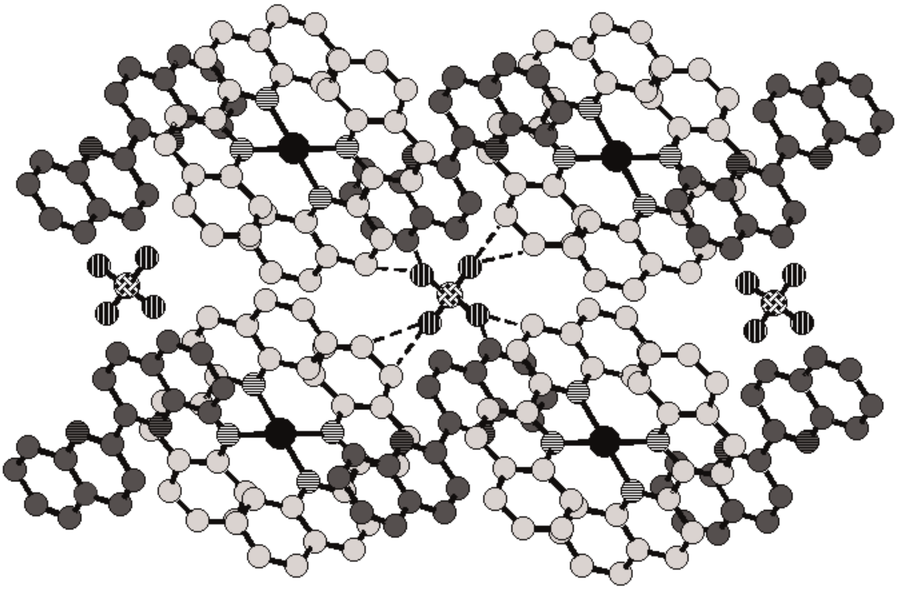

Figure 5. The pseudo-hexagonal net of hydrogen-bonded clusters around one BF_4^- (H-bonds shown as dotted lines; hydrogen atoms omitted for clarity). The view is down *b*.

Table 5. Microbiological screening.[a]

Compound	*Escherichia coli*	*Staphilococcus aureus*	*P. aeruginosa*	*Candida albicans*
$[Cu(biq)_2]Cl_2$	+	++	+	++
$[Cu(biq)_2]BF_4 \cdot biq$	++	++	++	+++

[a] Samples were dissolved in DMSO (30 mg/disk).
Highly active = +++ (inhibition zone > 12 mm); Moderately active = ++ (inhibition zone 9–12 mm); Slightly active = + (inhibition zone 6–9 mm); Inactive = – (inhibition zone < 6 mm);

character, particularly for Gram-positive organisms [23]. It is possible that the aromatic rings found in such compounds do not sufficiently enhance the log *P* of the complexes to allow for effective penetration of the bacterial cell membrane.

(ii) When antifungal activity was assessed, $[Cu(biq)_2]BF_4 \cdot biq$ demonstrated high activity against *Candida albicans* while $[Cu(biq)_2]Cl_2$ was found to be moderately active. The antifungal activity could be related to the importance of lipophilic/hydrophilic interactions in these complexes, or it might be indicative of the need for a hydrophilic interaction (as opposed to charge transfer or van der Waals type interaction) at the receptor surface for effective inhibition of fungal growth [23].

Supplementary materials

CCDC 258207 contains the supplementary crystallographic data for this article, which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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