JOURNAL OF CHEMICAL RESEARCH 2009 SEPTEMBER, 549–551 **RESEARCH PAPER**

Copper(I) complex of 2,2'-biquinoline assembled by non-covalent interactions

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A new 3-D supramolecular Cu(I) complex, [Cu(biq)Cl] (biq = 2,2'-biquinoline), (**1**), has been synthesised and characterised. Single-crystal analysis shows that **1** contains 2-D layers linked by C–H···Cl interactions and the copper centres adopts a distorted trigonal planar geometry. Moreover there are π–π interactions between aromatic rings of the ligands, which connect the layers to form a 3-D supramolecular network.

Keywords: crystal structure, hydrogen bond, π–π interaction, copper(I)

Recently, much effort has been centred upon the use of supramolecular contacts between suitable organic molecules to generate multi-dimensional arrays and networks.[1-5] These noncovalent contacts, in particular π–π and hydrogen bond interactions, play an important role in the metal–organic frameworks. The synthetic strategy used mostly to prepare these frameworks has been hydrothermal synthesis, which has been demonstrated to be an effective and powerful technique for crystal growth of many coordination polymers, hydrogen-bonded systems[6-7] and for reducing various metal ions, including copper.[8] Here, we used the 2,2'-biquinoline ligand, 4,4'-bipyrydine and Cu(II) chloride to obtain a novel complex [Cu(biq)Cl] (**1**) under hydrothermal conditions. During the formation of **1** the reduction of Cu^{2+} has occurred, which may be facilitated by the excess of N-donors during the reaction.

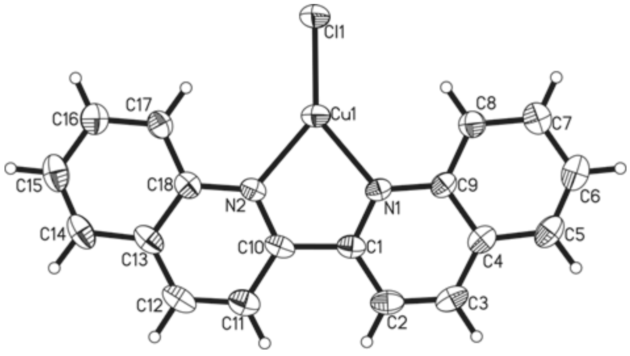

Fig. 1 Displacement ellipsoids are drawn at the 30% probability level. (H atoms have been omitted for clarity).

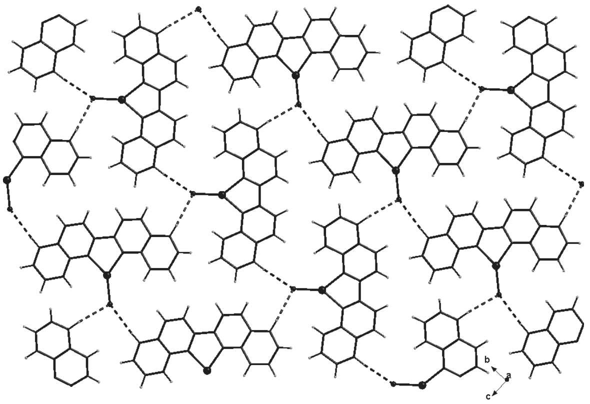

Fig. 2 The 2-D layer of title compound by C–H···Cl interactions (dashed lines) viewed from *a* direction.

Figure 1 gives a perspective view of the molecular structure of **1**. In **1** the copper atom is ligated by one Cl atom and two N atoms of the 2,2'-biquinoline ligand, which commonly acts as a bidentatate nitrogen ligand to form many coordinated complexes in a chelating fashion.[9-13] The angles around Cu atom are in the range of 80.46 (1)–140.46 (1)°, suggesting a distorted trigonal planar arrangement around the Cu atom. The average Cu–N bond length [2.042(4) Å] is in agreement with that of [(Cu(NCS)(C$_{18}$H$_{12}$N$_2$)]$_n$ (2.107(1) Å),[9] while the Cu–Cl bond length [2.1188(2) Å] is slightly shorter than that of the four coordinated Cu complex [CuCl$_2$(C$_{18}$H$_{12}$N$_2$)] [2.2175(1) Å].[10] The bond distances of N1–C1 [1.3284(5) Å] and N2–C10 [1.3227(9) Å] are unusually small, but they are close to those found in [{Cu$_2$(bpy)$_2$(CN)}Cu$_5$(CN)$_6$] [1.3336(2) Å][11] and [Cu$_2$(C$_{10}$H$_7$N$_2$O)$_2$][CuCl$_2$] [1.3389(5) Å].[14] The 2,2'-biquinoline ring, copper atom and chlorine atom lie almost in the same plane. The mean deviation of the whole complex is 0.0333(2) Å and the mean deviations of Cu1 and Cl1 from the mean plane are 0.0062(1) and 0.1195(3) Å, respectively. The dihedral angle between the C1–C9/N1 and C10–C18/N2 mean planes of the coordinated biquinoline is 2.9(3)°, indicating a planar structure for this ligand. The major contacts of hydrogen bonds in the crystal structure are C–H···Cl interactions (Table 1), which connect the isolated molecules to form a 2-D layer from the *bc* plane [Fig. 2]. Figure 3 shows the crystal packing of complex. The crystal structure of **1** is stabilised by π–π interactions along the *a* direction between inversion-related 2,2'-biquinoline ligands.[15] The N1 ring (N1/C1–C9) stacks with neighbouring C13–C18 rings, with offset face-to-face separations of 3.4730(2) and 3.4672(1) Å, and centroid–centroid separations of 3.6107(3) and 3.8588(3) Å [between the centroids of rings

Table 1 Geometrical parameters for hydrogen bonds for **1**

Hydrogen bonds	D–H (Å)	H..A (Å)	D..A (Å)	<DHA (°)
C5-H5A··· Cl1[a]	0.95	2.86	3.679(7)	145
C14-H14A··· O43[b]	0.95	2.90	3.737(7)	148

[a]*x*, *y* + 1, *z*, [b]*x*, –*y* + 0.5, *z*–0.5

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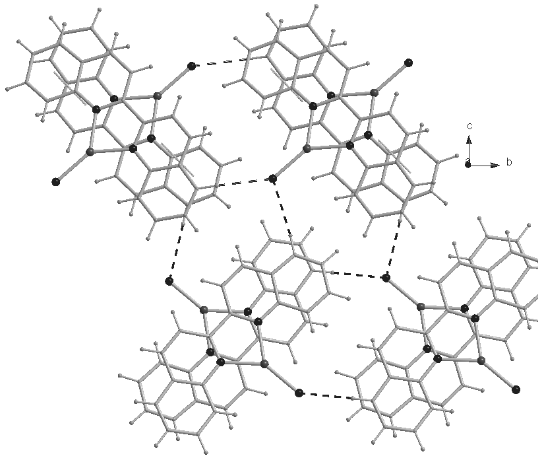

Fig. 3 The packing of title compound viewed from *a* direction, showing the ≠–≠ interactions between inversion related ligand molecules and the C–H···Cl hydrogen bonds (dashed lines).

Table 2 Crystal data and structure refinement for **1**

Empirical formula	C18 H12 Cl Cu N2
Formula weight	355.29
Temperature (K)	173(2) K
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	7.1215(7)
b (Å)	10.0985(10)
c (Å)	20.081(2)
α (°)	90
β (°)	94. 034(2)
γ (°)	90
V (Å^3)	1440.6(3)
Z	2
D_c(g/cm^{-3})	1.638
F (000)	720
Refinement method	Full-matrix least-squares on F^2
Goodness–of–fit on F^2	1.173
Final R indices [$I > 2\sigma(I)$] ^{a}	R^1 = 0.0609, *w*R^2 = 0.1565
R indices (all data)	R^1 = 0.1070, wR^2 = 0.1920
Largest diff. peak and hole (e.Å)$^{-3}$	0.457 and –0.343

^{a} $R^1 = ||F_o|-|F_c||/|F_o|$, $wR^2 = [w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]^{1/2}$

N1/C1–C4/C9 and C13–C18 (–*x*, 1–*y*, 1–*z*), and between the centroids of rings C4–C9 and C13–C18 (–*x*, 1–*y*, 1–*z*), respectively]. The N2 ring (N2/C10–C13/C18) also stacks with the inversión-related N1 ring, with a offset face-to-face separation of 3.4858(8) Å, centroid–centroid separation of 3.8123(3) Å [between the centroids of rings N2/C10–C13/C18 and N1/C1–C4/C9 (–*x*, 1–*y*, 1–*z*)]. As a result, a 3-D supramoleclar network is formed.

In summary, we have synthesised a 3-D supramolecular molecular, in which hydrogen bonds form 2-D layers and π–π interactions determine the framework structure. The role of the noncovalent contacts is clearly important in constructing **1**; this structure was not readily predictable and was only discovered empirically.

Experimental

All chemical reagents were commercially available. Elemental analyses of C, H and N were carried out by an Elemental Vario EL III microanalyser. The IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer, using KBr pellets, in the range 4000–400 cm^{-1}.

A suitable crystal of **1** (0.28 × 0.19 × 0.15 mm) was used for X-ray analysis. Data collections were performed on a Siemens Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073Å). Empirical absorption corrections were applied by using the SADABS program[16] for the Siemens area detector. The structures were solved by direct methods, refined by full-matrix least-squares methods. The Cu atoms were located from the E-map and all non-hydrogen atoms were derived from the successive difference Fourier syntheses. All the hydrogen atoms were calculated on the ideal positions and refined isotropically and all non-hydrogen atoms were refined anisotropically. The programs for structure solution and refinement are SHELXS-97[17] and SHELXL-97,[18] respectively. The crystallographic data, selected bond lengths and angles for **1** are listed in Tables 2 and 3.

General procedure for preparation of [Cu($C_{18}H_{12}N_2$)Cl] (**1**)
Compound **1** was hydrothermally synthesised under autogenous pressure. A mixture of $CuCl_2{\cdot}2H_2O$ (0.17 mg, 0.2 mmol), 2,2'-biquinoline (140 mg, 0.2 mmol), 4,4'-bipyridine (32 mg, 0.2 mmol) and H_2O (8 mL) was sealed in a stainless reactor with a Teflon liner, which was heated to 453K for two days. After slow cooling at a rate of 15 K h^{-1} to room temperature, dark red crystals were obtained as a major phase by filtration, and were washed with distilled water then finally dried in air (45% yield), Anal. Calcd for $C_{18}H_{12}ClCuN_2$: C, 60.85; H, 3.40; N, 7.88. Found: C, 60.72; H, 3.41; N, 7.85%. IR (KBr pellet): 1590(vs), 1524(vs), 1429(m), 836(s), 786(m), 758(m), 732(w).

Table 3 Selected bond lengths (Å) and angles (°) for **1**

Bond distances			
Cu(1)–N(1)	2.039(5)	C(6)–C(5)	1.353(10)
Cu(1)–N(2)	2.044(4)	C(6)–C(7)	1.400(9)
Cu(1)–Cl(1)	2.1188(2)	C(8)–C(9)	1.404(8)
N(1)–C(1)	1.328(7)	C(1)–C(10)	1.501(8)
N(1)–C(9)	1.372(7)	C(10)–C(11)	1.398(8)
N(2)–C(10)	1.322(8)	C(11)–C(12)	1.364(9)
N(2)–C(18)	1.374(8)	C(13)–C(14)	1.422(9)
C(2)–C(1)	1.407(9)	C(16)–C(17)	1.378(9)
C(9)–C(4)	1.407(8)	C(17)–C(18)	1.406(9)
Bond angles			
N(1)–Cu(1)–N(2)	80.46(19)	C(3)–C(4)–C(9)	118.0(6)
N(1)–Cu(1)–Cl(1)	140.46(15)	C(3)–C(4)–C(5)	123.5(6)
N(2)–Cu(1)–Cl(1)	138.98(16)	C(9)–C(4)–C(5)	118.5(6)
C(1)–N(1)–C(9)	119.6(5)	C(3)–C(2)–C(1)	119.5(6)
C(1)–N(1)–Cu(1)	114.3(4)	C(2)–C(1)–C(10)	123.0(6)
C(9)–N(1)–Cu(1)	126.0(4)	C(11)–C(10)–C(1)	122.3(6)
C(10)–N(2)–C(18)	119.3(5)	C(11)–C(12)–C(13)	120.5(6)
C(18)–N(2)–Cu(1)	126.3(4)	C(12)–C(13)–C(18)	117.0(6)
N(1)–C(9)–C(8)	119.1(5)	C(15)–C(14)–C(13)	120.2(6)
N(1)–C(9)–C(4)	121.1(6)	N(1)–C(1)–C(2)	121.7(6)
C(8)–C(9)–C(4)	119.9(6)	N(1)–C(1)–C(10)	115.3(5)
C(7)–C(8)–C(9)	120.1(6)	N(2)–C(10)–C(11)	122.3(6)
N(1)–Cu(1)–N(2)	80.46(19)	N(2)–C(10)–C(1)	115.4(5)

We thank the National Science Foundation of China (30771682), Key Projects in the National Science & Technology Pillar Program in the Eleventh Five-year Plan Period (2008BADA9B0501) and 07B08 Program of Fujian Agriculture and Forestry University.

Received 17 June 2009; accepted 6 August 2009
Paper 09/0644 doi: 10.3184/030823409X12498344384876

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