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Synthesis and coordination chemistry of tetradentate ligands containing two bidentate thioquinoline units: mononuclear complexes with Cu(I) and Cu(II), and a coordination polymer with Cu(I)

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Abstract

Two tetradentate ligands L^3 and L^4 have been prepared by reaction of 2 equiv. of 8-quinolinethiol with 1,2-bis(bromomethyl)benzene and 3,3′-bis(bromomethyl)biphenyl, respectively; in each case displacement of bromide by the thiolate unit affords a thioether linkage, and the two ligands accordingly have bidentate chelating quinoline/thioether units linked to a 1,2-phenyl or 3,3′-biphenyl spacer via methylene linkers. Both ligands have been structurally characterised. In L^3 the two thioquinoline units are close enough to one another for ligand to act as an N_2S_2-donor tetradentate chelate to a single metal ion, as shown by the structural determinations of $[Cu(L^3)][PF_6]$, a pseudo-tetrahedral, four-coordinate Cu(I) complex, and $[Cu(L^3)(MeCN)][BF_4]_2$, a five-coordinate Cu(II) complex with an additional MeCN ligand and a geometric τ parameter of 0.62. In contrast, reaction of L^4 with Cu(I) afforded $\{[Cu(L^4)][PF_6]\}_\infty$, an infinite one-dimensional coordination polymer in which all ligands bridge two four-coordinate Cu(I) centres resulting in an M–L–M–L–... alternation. Evidently, the greater separation of the bidentate termini in L^4 prevents chelation to a single metal ion. Each metal/ligand chain has a pronounced zig-zag structure; Cu···Cu separations between adjacent metal centres sharing a bridging ligand are approximately 12 Å, but the folding of the chain is such that the separations between alternate Cu(I) centres are shorter at approximately 9 Å. The chains have thioquinoline units at their periphery, and two adjacent chains interact by interleaving of these thioquinoline units to give a π-stack parallel to the direction of the chains.
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Keywords: Thioquinoline units; Mononuclear complexes; Coordination polymer

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1. Introduction

The self-assembly of architecturally elaborate complexes from relatively simple bridging ligands and labile metal ions continues to be an intensely popular area of study [1–22]. With regard to the ligands, a minimum condition is that they must act as bridges between two or more metal centres, or simple mononuclear complexes will result. With conformationally flexible ligands, the competition between bridging and chelating coordination modes is an important factor in controlling the self-assembly process. We have recently studied the coordination behaviour of ligands such as L^1 and L^2 (see Scheme 1) [21–23]. Whilst L^1 can act as a simple tetradentate chelate to a single metal ion [21], it can also act as a bridging ligand under the right circumstances to give M_4L_6 tetrahedral cage complexes which incorporate a counterion in the central cavity [22]. L^2 in contrast, because of its greater length, is compelled to act as a bridging ligand spanning two metal centres [23].

In this paper, we describe the synthesis and coordination behaviour of two related ligands, L^3 and L^4 (Scheme 1), in which the bidentate termini are provided by quinoline/thioether units. This is expected to result in coordination of softer metal ions than observed for L^1 and L^2, which will have a preference for lower coordination numbers. Whereas L^3 has (like L^1 and L^2) a single phenylene spacer between the termini, L^4 has a longer biphenyl spacer; it is expected that L^4 will of necessity

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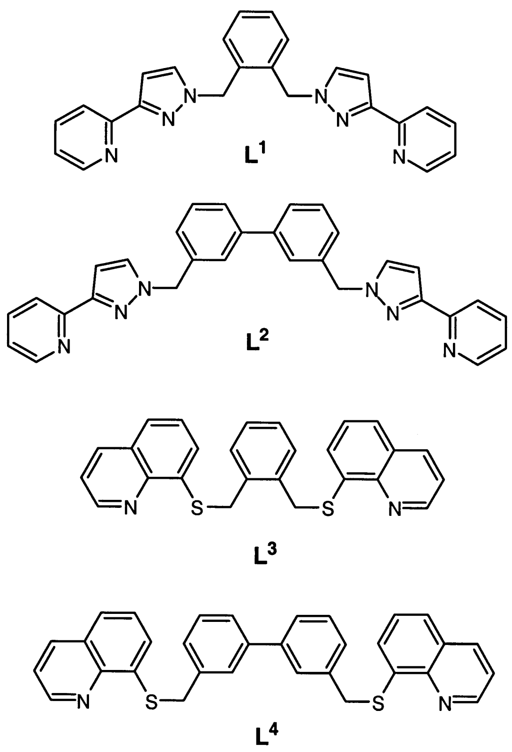

Scheme 1.

act as a bridging ligand, whereas L^3 could coordinate in either a bridging or a chelating manner. Similar ligands, in which two bidentate units derived from 8-quinolinethiol are connected, have been described by other workers recently [24–27] and have been shown to give a variety of unusual polymeric structures with Ag(I) as well as mononuclear complexes with Co(II) and Ni(II). We describe here the coordination behaviour of L^3 and L^4 in complexes with Cu(I) and Cu(II).

2. Results and discussion

2.1. Synthesis and characterisation of ligands

The two new ligands L^3 and L^4 were prepared following the method of Kang and co-workers [24] by reaction of 2.2 equiv. of 8-quinolinethiol hydrochloride with 1 equiv. of 1,2-bis(bromomethyl)benzene or 3,3′-bis(bromomethyl)biphenyl, respectively in EtOH, in the presence of 4 equiv. of NaOH. Because of the air-sensitivity of deprotonated 8-quinolinethiol, the reactions were carried out under N_2. In each case, the product precipitated and was readily isolated in approximately 70% yield; the ligands were characterised by ^1H NMR and mass spectrometry, elemental analysis, and X-ray crystallography.

X-ray quality crystals of L^3 and L^4 were grown by diffusion of di(isopropyl)ether into concentrated CH_2Cl_2 solutions of the ligands; the structures are in Figs. 1 and 2 (see also Table 1). In each case, individual bond distances and angles are unremarkable. The angle between the mean planes of the two thioquinoline units is 86.0 and 11.2° for L^3 and L^4, respectively; for L^4, there is a twist of 40.4° between the two phenyl rings of the biphenyl spacer. It is clear from the structures that in L^4 the bidentate units are too far apart from one another to coordinate to a single metal ion, and L^4 must necessarily act as a bridging ligand; for L^3 this is not the case and a tetradentate chelating mode is also possible.

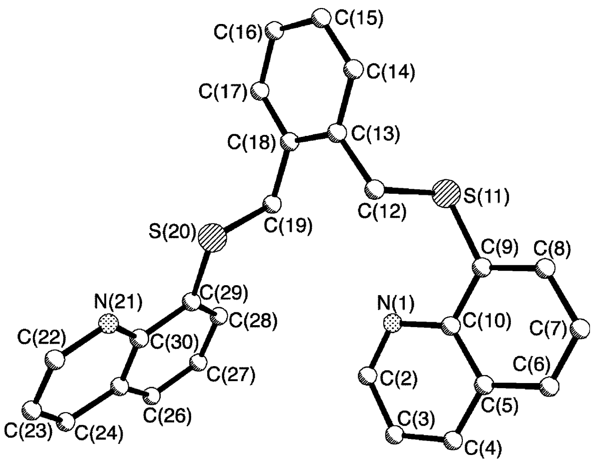

Fig. 1. Molecular structure of L^3.

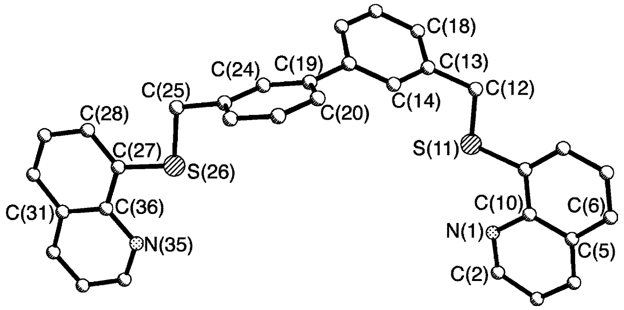

Fig. 2. Molecular structure of L^4.

2.2. Mononuclear complexes of L^3 with Cu(I) and Cu(II)

Reaction of L^3 with $[Cu(MeCN)_4][PF_6]$ (1:1 ratio) in MeCN afforded a clear yellow solution from which a bright yellow solid precipitated on addition of diethyl ether. Mass spectrometric and analytical data were consistent with formation of the mononuclear species $[Cu(L^3)][PF_6]$, with the peak at highest m/z in the FAB mass spectrum occurring at 487, corresponding to $[Cu(L^3)]^+$ with the correct isotope pattern.

X-ray quality crystals of the complex were grown by diffusion of di(isopropyl)ether into a concentrated MeCN solution; the crystal structure is in Fig. 3, and

Table 1
Crystallographic data [a]

Compound	L^3	L^4	$[Cu(L^3)][PF_6]$	$[Cu(L^3)(MeCN)][BF_4]_2$	$[\{Cu(L^4)(PF_6)\}\cdot 2MeCN]_\infty$
Empirical formula	$C_{26}H_{20}N_2S_2$	$C_{32}H_{24}N_2S_2$	$C_{52}H_{40}Cu_2F_{12}N_4P_2S_4$	$C_{28}H_{23}B_2CuF_8N_3S_2$	$C_{144}H_{120}Cu_4F_{24}N_{16}P_4S_8$
Formula weight	424.56	500.65	1266.14	702.77	3165.08
Temperature (K)	173	173	100	90	100
Wavelength (Å)	0.71073	0.71073	0.71073	1.54178	1.54178
Crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a (Å)	9.1127(10)	5.8913(14)	8.0774(6)	7.69070(10)	23.241(6)
b (Å)	10.8405(12)	11.298(3)	15.3386(11)	13.0300(2)	18.081(3)
c (Å)	11.9404(13)	37.653(9)	20.8090(15)	14.9076(2)	34.189(7)
α (°)	112.196(2)	90	75.2320(10)	96.1910(10)	90
β (°)	95.392(2)	92.018(4)	88.8600(10)	98.2380(10)	102.706(9)
γ (°)	105.669(2)	90	89.9710(10)	94.0920(10)	90
V (Å^3)	1025.8(2)	2504.7(10)	2492.5(3)	1464.12(4)	14015(5)
Z	2	4	2	2	4
D_{calc} (Mg m^{-3})	1.375	1.328	1.687	1.594	1.500
μ (mm^{-1})	0.276	0.237	1.174	3.077	2.994
Data/restraints/parameters	4666/0/271	4389/0/325	11182/0/685	3969/0/398	19933/0/1809
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0316$, wR_2 [a] $= 0.0823$	$R_1 = 0.0527$, wR_2 [a] $= 0.1328$	$R_1 = 0.0431$, wR_2 [a] $= 0.1099$	$R_1 = 0.0272$, wR_2 [a] $= 0.0740$	$R_1 = 0.0354$, wR_2 [a] $= 0.0987$

[a] The value of R_1 is based on selected data with $I > 2\sigma(I)$; the value of wR_2 is based on all data.

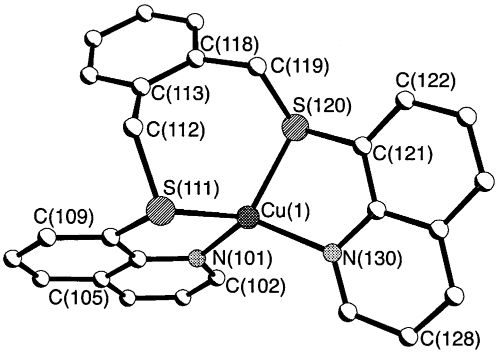

Fig. 3. Structure of the complex cation of $[Cu(L^3)][PF_6]$.

Table 2
Selected bond distances (Å) and angles (°) for the crystal structures of $[Cu(L^3)][PF_6]$ and $[Cu(L^3)(MeCN)][BF_4]_2$

$[Cu(L^3)][PF_6]$			
Bond lengths			
Cu(1)–N(101)	1.999(2)	Cu(1)–S(111)	2.3116(7)
Cu(1)–N(130)	2.027(2)	Cu(1)–S(120)	2.2857(7)
Bond angles			
N(101)–Cu(1)–N(130)	119.70(9)	N(101)–Cu(1)–S(111)	87.82(6)
N(101)–Cu(1)–S(120)	129.39(7)	N(130)–Cu(1)–S(111)	126.57(7)
N(130)–Cu(1)–S(120)	86.21(6)	S(120)–Cu(1)–S(111)	111.73(2)
$[Cu(L^3)(MeCN)][BF_4]_2$			
Bond lengths			
Cu(1)–N(2)	1.9873(17)	Cu(1)–S(1)	2.3493(6)
Cu(1)–N(1)	1.9907(17)	Cu(1)–S(2)	2.4197(6)
Cu(1)–N(30)	2.0641(19)		
Bond angles			
N(2)–Cu(1)–N(1)	177.88(7)	N(30)–Cu(1)–S(1)	140.43(5)
N(2)–Cu(1)–N(30)	90.66(7)	N(2)–Cu(1)–S(2)	84.77(5)
N(1)–Cu(1)–N(30)	89.79(7)	N(1)–Cu(1)–S(2)	97.23(5)
N(2)–Cu(1)–S(1)	93.05(5)	N(30)–Cu(1)–S(2)	97.55(5)
N(1)–Cu(1)–S(1)	85.29(5)	S(1)–Cu(1)–S(2)	122.02(2)

bond distances and angles are in Table 2. There are two similar but independent complex units in the asymmetric unit, of which only one is shown in Fig. 3. The complex is mononuclear and the central Cu(I) ion has the common irregular 'pseudo-tetrahedral' geometry arising from near-perpendicular coordination of the two bidentate N,S-donor units; the angle between the two CuNS planes around each Cu(I) centre is 78.7° for Cu(1) and 78.9° for Cu(2). Individual bond distances and angles are unremarkable, with the Cu···N distances lying in the range 2.00–2.03 Å, and the Cu···S distances in the range 2.28–2.31 Å. The bite angles of the chelating N,S-donor units lie in the range 86.2°–88.2°.

The electronic spectrum of $[Cu(L^3)][PF_6]$ shows two maxima, at 378 ($\varepsilon = 7800$ M^{-1} cm^{-1}) and 291 nm ($\varepsilon = 19000$ M^{-1} cm^{-1}), which we assign as MLCT and ligand-centred π–π^* transitionsm, respectively. The cyclic voltammogram in MeCN showed a symmetric wave at +0.15 V versus the ferrocene/ferrocenium couple with a separation of 70 mV between cathodic and anodic peaks, which we assign as a reversible Cu(I)/Cu(II) couple. Also present were wholly irreversible processes at high negative potential, which resulted in an intense stripping peak on the return scan, indicative of desorption of metallic copper following reduction to Cu(0).

The reversibility of the Cu(I)/Cu(II) process indicates that the Cu(II) species should be isolable. Reaction of L^3 with $Cu(BF_4)_2 \cdot 6H_2O$ in acetonitrile/chloroform afforded a clear emerald green solution; diffusion of diethyl ether vapour into this afforded green needles of a material analysing as $[Cu(L^3)(MeCN)][BF_4]_2$ (the highest *m*/*z* value in the FAB mass spectrum occurred at 487, as for the Cu(I) analogue). The crystal structure is shown in Fig. 4, and shows a mononuclear five-coordinate Cu(II) complex in an N_3S_2 coordination environment arising from one tetradentate ligand L^3 and one MeCN ligand. Bond distances and angles are in Table 2. The geometry about the metal centre is marginally nearer trigonal bipyramidal than square pyramidal, with the τ parameter being 0.62 (where 1 denotes a perfect trigonal bipyramid and 0 denotes a perfect square pyramid) [28]; if the geometry is considered as a distorted trigonal bipyramid, then atoms S(1), S(2) (from L^3) and N(30) (from the MeCN) constitute the equatorial plane, with the two quinoline N atoms N(1) and N(2) being in the axial positions. The angle between the mean planes of the two CuNS planes is 39.8° [cf. the values of approximately 79° for the Cu(I) complex]; it is clear that the flexibility of L^3 arising from the two saturated methylene units allows it to adapt readily to the differing coordination preferences of Cu(I) and Cu(II).

The electronic spectrum of $[Cu(L^3)(MeCN)][BF_4]_2$ in MeCN shows two d–d transitions at 879 and 642 nm ($\varepsilon = 270$ and 200 M^{-1} cm^{-1}, respectively); in principle up to four d–d transitions may occur for Cu(II) in a low-symmetry ligand field, although more commonly only one or two are resolved [29]. A strong ligand-centred π–π^* transition in the UV region at 308 nm ($\varepsilon =$ 65 000 M^{-1} cm^{-1} is also present.

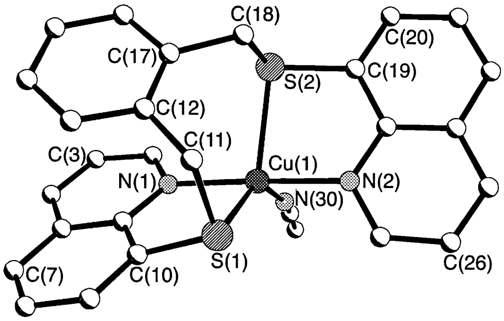

Fig. 4. Structure of the complex cation of $[Cu(L^3)(MeCN)][BF_4]_2$.

2.3. A one-dimensional polymeric complex of L^4 with Cu(I)

Reaction of L^4 with $[Cu(MeCN)_4][PF_6]$ (1:1 ratio) in MeCN afforded a clear yellow/brown solution from which a dark yellow solid precipitated on addition of diethyl ether. Elemental analysis of the solid indicated the empirical formula $[Cu(L^4)][PF_6]$, and the peak at highest *m*/*z* value in the FAB mass spectrum at 563 corresponds to $[Cu(L^4)]^+$ with an isotope pattern correct for one Cu atom. Given the separation between the two bidentate termini of L^4, a mononuclear complex is not possible, and accordingly the crystal structure was determined.

X-ray quality crystals were grown by diffusion of di(isopropyl)ether vapour into a concentrated solution of the complex in MeCN. The structure of the complex in Fig. 5 shows it to be an infinite polymer $\{[Cu(L^4)][PF_6]\}_\infty$; bond distances and angles are collected in Table 2. The chain has a zig-zag arrangement with four independent Cu(I) centres and four independent bridging ligands in the asymmetric unit. The Cu···Cu separations between metals which are linked by the same bridging ligand are all close to 12 Å; however the separations between *alternate* Cu(I) centres such as Cu(1) and Cu(3) are less, in the region of 9 Å, because of the sharp pitch of the zig-zag motif, emphasised in Fig. 6. The four metal ions [Cu(1)–Cu(4)] within each ‘parallelogram-like’ unit are almost coplanar (maximum deviation of a metal ion from the mean plane of all four, 0.03 Å). The angles between the two Cu(NS) planes at each metal centre are 72.9°, 65.5°, 63.6° and 71.6° for Cu(1)–Cu(4), respectively; the bridging ligands have the characteristic twist between the two phenyl rings of the central biphenyl spacer, with twist angles lying in the range 32°–41° for the four independent ligands (Table 3, Fig. 7).

One-dimensional coordination polymers of this nature are becoming well known, with many recent examples reported [30–38]. Sometimes the polymers have a helical structure; the area of self-assembly of helical structures has been reviewed recently by Piguet [20]. The structure of $\{[Cu(L^4)][PF_6]\}_\infty$ does not appear to be of this type—the sequence of bridging ligands between one metal centre and the next does not obviously describe a helical path, but rather a zig-zag path. Given the space group of $P2_1/n$, there are four adjacent chains passing through each unit cell. The adjacent strands which are related by the 2_1 axis are mutually interleaved at the edges via interpenetration of the peripheral thioquinoline units which form an alternating columnar stack. Those strands which are related by inversion however are not interpenetrating in this way; there is a clear gap between them forming channels in the crystal which are occupied by the hexafluorophosphate anions and the MeCN solvent molecules.

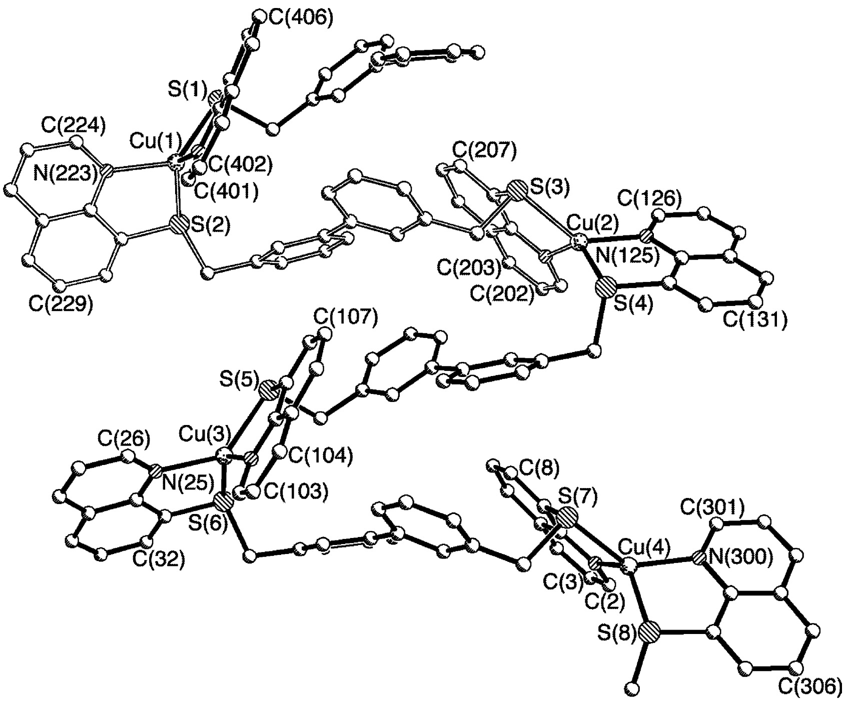

Fig. 5. Structure of the asymmetric unit of the one-dimensional polymer $[\{Cu(L^4)(PF_6)\}\cdot 2MeCN]_\infty$ (omitting anions and solvent molecules).

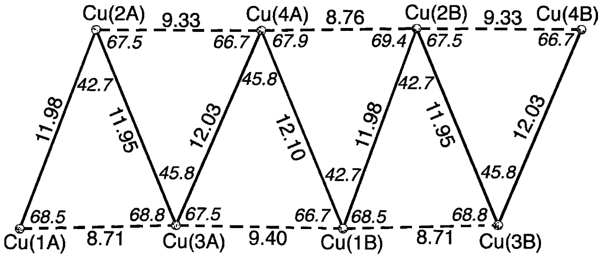

Fig. 6. The zig-zag arrangement of metal centres along the chain of $[\{Cu(L^4)(PF_6)\}\cdot 2MeCN]_\infty$; solid lines denote the path of the bridging ligands. Non-bonded Cu···Cu separations in Å are in upright type; angles (°) are in italic type.

Table 3
Selected bond distances (Å) and angles (°) for the crystal structure of $[\{Cu(L^4)(PF_6)\}\cdot 2MeCN]_\infty$

Bond lengths			
Cu(1)–N(223)	2.028(2)	Cu(3)–N(25)	2.037(2)
Cu(1)–N(400)	2.045(2)	Cu(3)–N(101)	2.044(2)
Cu(1)–S(2)	2.2807(8)	Cu(3)–S(6)	2.2833(8)
Cu(1)–S(1)	2.3148(8)	Cu(3)–S(5)	2.3326(8)
Cu(2)–N(125)	2.034(2)	Cu(4)–N(300)	2.035(2)
Cu(2)–N(200)	2.043(2)	Cu(4)–N(1)	2.052(2)
Cu(2)–S(4)	2.2778(8)	Cu(4)–S(8)	2.2959(8)
Cu(2)–S(3)	2.3229(8)	Cu(4)–S(7)	2.3258(8)
Bond angles			
N(223)–Cu(1)–N(400)	106.65(8)	N(25)–Cu(3)–N(101)	102.62(8)
N(223)–Cu(1)–S(2)	87.57(6)	N(25)–Cu(3)–S(6)	88.20(6)
N(400)–Cu(1)–S(2)	131.42(6)	N(101)–Cu(3)–S(6)	136.42(6)
N(223)–Cu(1)–S(1)	130.46(6)	N(25)–Cu(3)–S(5)	137.07(6)
N(400)–Cu(1)–S(1)	87.69(6)	N(101)–Cu(3)–S(5)	87.00(6)
S(2)–Cu(1)–S(1)	118.14(3)	S(6)–Cu(3)–S(5)	113.38(3)
N(125)–Cu(2)–N(200)	102.03(9)	N(300)–Cu(4)–N(1)	108.72(8)
N(125)–Cu(2)–S(4)	88.37(6)	N(300)–Cu(4)–S(8)	86.98(6)
N(200)–Cu(2)–S(4)	133.82(6)	N(1)–Cu(4)–S(8)	129.90(6)
N(125)–Cu(2)–S(3)	136.68(6)	N(300)–Cu(4)–S(7)	134.87(6)
N(200)–Cu(2)–S(3)	86.98(6)	N(1)–Cu(4)–S(7)	86.94(6)
S(4)–Cu(2)–S(3)	115.64(3)	S(8)–Cu(4)–S(7)	115.48(3)

3. Experimental

3.1. General details

3,3′-Bis(bromomethyl)biphenyl [39] and $[Cu(MeCN)_4][PF_6]$ [40] were prepared according to the literature methods. 1,2-Bis(bromomethyl)benzene, 8-quinolinethiol hydrochloride, and $Cu(BF_4)_2\cdot 6H_2O$ were obtained from Aldrich and used as received. Electron-impact (EI) and Fast atom bombardment (FAB) mass spectra were recorded on a VG-Autospec instrument; proton NMR spectra were recorded on JEOL GX-270 (270 MHz) or ECLIPSE 400 (400 MHz) spectrometers. UV–Vis spectra were recorded on a Perkin–Elmer Lambda 2 spectrometer. Electrochemical measurements were carried out at a Pt-disk working electrode using a PC-controlled EG&G-PAR 273A potentiostat connected to a standard three-electrode cell; ferrocene was added at the end of each measurement as an internal reference, and all potentials are quoted versus the ferrocene/ferrocenium couple which is taken as 0.0 V.

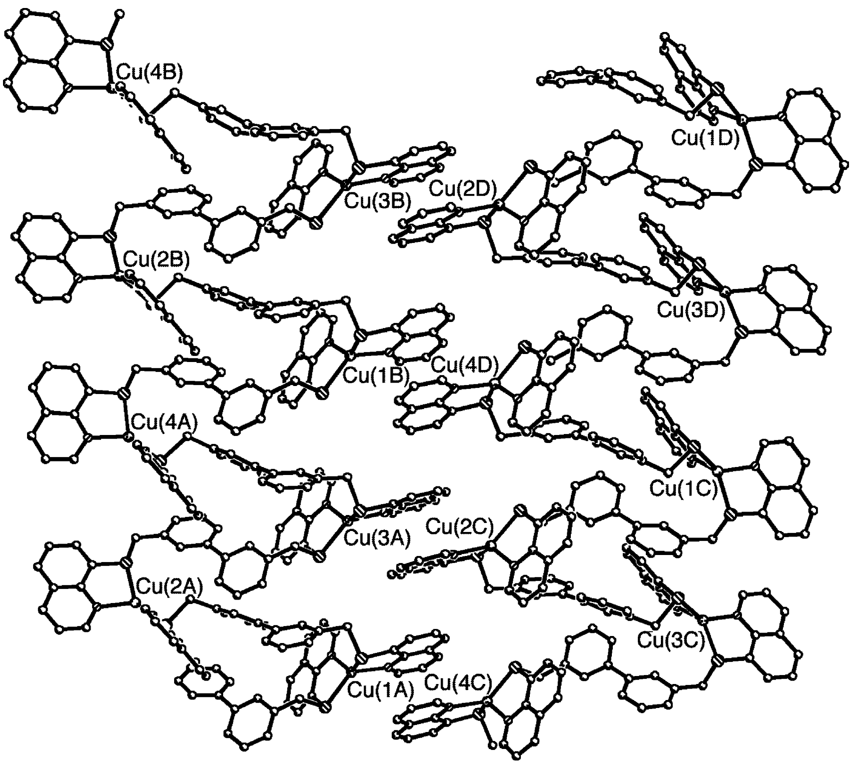

Fig. 7. Interpenetration by π-stacking of two adjacent chains in $[\{Cu(L^4)(PF_6)\} \cdot 2MeCN]_\infty$.

3.2. Synthesis of L^3

8-Quinolinethiol hydrochloride (500 mg, 2.53 mmol) was added to a stirred solution of NaOH (0.2 g, 5 mmol) in EtOH (25 cm^3) under N_2. To this mixture was then added dropwise a solution of 1,2-bis(bromomethyl)benzene (305 mg, 1.15 mmol) in acetone (15 cm^3). The mixture was heated to reflux overnight to give a yellow solution containing a white solid. After cooling to 5 °C, the white solid was filtered off, washed with a little EtOH, and dried. This solid was then partitioned between $CHCl_3$ and water to remove any inorganic salts; the organic phase was separated off, dried over $MgSO_4$, and evaporated to dryness to give L^3 (340 mg, 70%). Found: C, 73.2; H, 4.8; N, 6.9. Required for $C_{26}H_{20}N_2S_2$: C, 73.6; H, 4.8; N, 6.6%. EI MS: *m/z* 424 (30%, $[M]^+$); 263 (100%, $[M-C_9H_7NS]^+$). ^1H NMR (270 MHz, $CDCl_3$, ppm): δ 8.90 (2H, dd, $J=5.4$, 2.7; quinoline H^2), 8.11 (2H, dd, $J=8.1$, 2.7 Hz; quinoline H^4), 7.55 (4H, m; quinoline H^5 and H^7), 7.39 (6H, m; quinoline H^3+H^6; phenyl H), 7.22 (2H, m; phenyl H), 4.50 (4H, s; CH_2).

3.3. Synthesis of L^4

This was prepared in exactly the manner described above for L^3, with the exception that 3,3′-bis(bromomethyl)biphenyl (380 mg, 1.15 mmol) was used in place of 1,2-bis(bromomethyl)benzene. After partition of the crude solid between $CHCl_3$ and water to remove inorganic salts, separation and drying of the organic phase, and removal of the solvent, L^4 was isolated (389 mg, 68%). Found: C, 76.8; H, 4.9; N, 5.3. Required for $C_{32}H_{24}N_2S_2$: C, 76.8; H, 4.8; N, 5.6%. EI MS: *m/z* 500 (55%, $[M]^+$); 339 (100%, $[M-C_9H_7NS]^+$). ^1H NMR (400 MHz, $CDCl_3$): δ 8.98 (2H, dd, $J=4.3$, 1.8; quinoline H^2), 8.16 (2H, dd, $J=8.4$, 1.8 Hz; quinoline H^4), 7.60 (2H, dd, $J=8.0$, 1.2; quinoline H^5 or H^7), 7.55 (4H, m; quinoline H^7 or H^5, and phenyl H^2), 7.44 (8H, m; quinoline H^3 and H^6, phenyl H^4 and H^6), 7.34 (2H, t, $J=7.7$ Hz; phenyl H^5); 4.37 (s, 4H; CH_2).

3.4. Synthesis of $[Cu(L^3)][PF_6]$

To a stirred solution of $[Cu(MeCN)_4][PF_6]$ (88 mg, 0.24 mmol) in MeCN (3 cm^3) under N_2 was added dropwise a solution of L^3 (100 mg, 0.24 mmol) dissolved in the minimum quantity of CH_2Cl_2. The resulting yellow solution was stirred for 1 h, after which time it was concentrated in vacuo until a precipitate started to appear; precipitation of the product was completed by addition of Et_2O. The yellow solid was collected by filtration, washed with MeOH, and dried (yield: 95 mg, 64%). Found: C, 49.7; H, 3.3; N, 4.7. Required for $C_{26}H_{20}CuF_6N_2PS_2$: C, 49.4; H, 3.2; N, 4.4%. FAB MS: *m/z* 487 (75%, $[M-PF_6]^+$).

3.5. Synthesis of [Cu(L^3)(MeCN)][BF_4]$_2$

To a stirred solution of L^3 (50 mg, 0.12 mmol) in the minimum volume of $CHCl_3$ was added a solution of $Cu(BF_4)_2 \cdot 6H_2O$ (42 mg, 0.12 mmol) in MeCN (3 cm^3). The resulting emerald–green solution was stirred for 30 min. Diffusion of $^iPr_2O$ vapour into this solution afforded green crystals of [Cu(L^3)(MeCN)][BF_4]$_2$ (yield: 23 mg, 41%). Found: C, 48.3; H, 3.4; N, 5.8. Required for $C_{26}H_{20}CuF_6N_2PS_2$: C, 47.9; H, 3.3; N, 6.0%. FAB MS: *m*/*z* 487 (100%, $[M-2BF_4]^+$).

3.6. Synthesis of {[Cu(L^3)][PF_6]}$_\infty$

To a stirred solution of [Cu(MeCN)$_4$][PF_6] (38 mg, 0.1 mmol) in MeCN (3 cm^3) under N_2 was added dropwise a solution of L^3 (50 mg, 0.1 mmol) dissolved in the minimum quantity of CH_2Cl_2. The resulting dark yellow solution was stirred for 1 h, and was then concentrated in vacuo until a precipitate started to appear; precipitation of the product was completed by addition of Et_2O. The dark yellow solid was collected by filtration, washed with MeOH, and dried (yield: 30 mg, 42%). Found: C, 53.7; H, 3.4; N, 3.8. Required for $C_{32}H_{24}CuF_6N_2PS_2$: C, 54.2; H, 3.4; N, 4.0%. FAB MS: *m*/*z* 563 (80%, $[M-PF_6]^+$).

3.7. X-ray crystallography

Details of the crystal, data collection and refinement parameters for the new structures are summarised in Table 1. In each case, structure solution and refinement used the SHELX package (version 5.03) comprising SHELXS-97 [41] and SHELXL-97 [42]; absorption corrections were applied to the data using SADABS [43]. H atoms were included in calculated positions (except for on lattice solvent molecules, where they were omitted from the refinement) with isotropic thermal parameters and refined as riding atoms. None of the structural determinations presented any significant problems.

4. Supplementary material

Crystallographic data for the structural analysis (for the compounds, see Table 1) have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 194369–194373. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk).

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