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2,2′:6′,2″-Terpyridine-4′(1′*H*)-thione: a missing link in metallosupramolecular chemistry†

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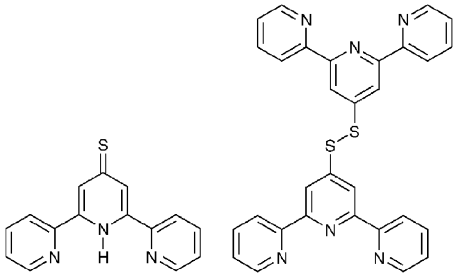
The compound 2,2′:6′,2″-terpyridine-4′(1′*H*)-thione **1** has been prepared and structurally characterised; in both the solid state and in solution, the thione tautomer is dominant. Compound **1** is a key entry into 4′-sulfur-functionalised tpy ligands and a representative alkylation with an electrophilic Fréchet dendrimer is presented and the structural characterisation of the new ligand **4** reported. Oxidation of **1** yields bis(2,2′:6′,2″-terpyridin-4′-yl)disulfide **2** which is a novel homoditopic tpy ligand and which forms a tetranuclear [4 + 4] iron (II) metallomacrocycle. Structural characterisation of **2** and preliminary data for the iron complex are presented.

Introduction

Metallosupramolecular chemistry is concerned with the construction of complex structures using the interaction of specific metal-binding domains with appropriate metal centres.[1] Increasingly, the 2,2′:6′,2″-terpyridine (tpy) metal-binding domain is being used as an assembly motif; in part this is because tpy forms stable complexes with almost every metal centre in the periodic table,[2] and partly because of the stereogenic properties of $\{M(tpy)_2\}$ motifs compared to the more commonly encountered $\{M(bpy)_3\}$ or $\{M(phen)_3\}$ (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) motifs.[3] Complexes of the type $\{M(tpy)_2\}$ are thermodynamically stable, but may be kinetically inert or labile, allowing, respectively, for self-assembly strategies involving the interaction of tpy metal-binding domains with metal centres or the use of building blocks containing $\{M(tpy)_2\}$ units.

A wide-variety of substituents have been introduced onto the basic tpy scaffold in order to imbue additional desired functionality.[4] Sulfur-containing substituents have not been as widely investigated as some others, and examples are primarily limited to thioethers and sulfones. Thioethers are the primary products of the Potts' synthetic method[5] although examples to date are limited to MeS, EtS and ^{n}PrS substituents. The thioethers are readily oxidised to the sulfones, which have interesting photophysical properties.[6] Thioether linkers have proved to be useful in the construction of tpy-bioconjugates with pendant biomolecules.[7] A few derivatives of 2,2′:6′,2″-terpyridine-4′-sulfonic acid have also been reported.[8]



1 **2**

† Electronic supplementary information (ESI) available: Fig. 2 and 6. See DOI: 10.1039/b510792j

General access to thioether derivatives should be analogous to the ether analogues[9] and rely either upon the reaction of an alkanethiol with a 4′-halo-2,2′:6′,2″-terpyridine or of a haloalkane with 2,2′:6′,2″-terpyridine-4′(1′*H*)-thione **1**. The former methodology has been recently reported[10] but the key intermediate 2,2′:6′,2″-terpyridine-4′(1′*H*)-thione **1** is, to date, unknown. In this paper we describe the synthesis and structural characterisation of 2,2′:6′,2″-terpyridine-4′(1′*H*)-thione **1** and its oxidation product bis(2,2′:6′,2″-terpyridin-4′-yl)disulfide **2**; we also illustrate the use of **1** as a sulfur nucleophile for the preparation of functionalised tpy ligands and the formation of a metallomacrocycle from **2**.

Results and discussion

Synthesis and structural characterisation of 2,2′:6′,2″-terpyridine-4′(1′*H*)-thione 1

We prepared the new ligand 2,2′:6′,2″-terpyridine-4′(1′*H*)-thione **1** using the classical reaction of 4′-chloro-2,2′:6′,2″-terpyridine with sodium hydrogen sulfide in DMF (Scheme 1). The ligand **1** was obtained as a yellow solid in 86% yield and fully characterised using conventional methods. Pertinent spectroscopic characterisation includes the observation of a parent ion at m/z 265.1 in the EI mass spectrum. The ^{1}H NMR spectrum of a CD_3SOCD_3 solution of **1** confirms the high symmetry and exhibits a broad singlet at δ 12.4 ppm which should most probably be assigned to an NH proton. The assignment of the correct tautomeric form is not trivial. The prototype compound pyridine-4(1*H*)-thione is known to favour enormously the thione tautomer in the solid state and in polar solvents.[11] In the solid state a number of polymorphs are known, but in all, pyridine-4(1*H*)-thione molecules are present and form N–H···S hydrogen-bonded chains with N···S distances of 2.2–2.5 Å.[12] However, in the solid state the oxygen analogue of **1** exists as a 1 : 1 mixture of 2,2′:6′,2″-terpyridin-4′(1′*H*)-one **2a** and 4′-hydroxy-2,2′:6′,2″-terpyridine **2b**.[13] It is not *a priori* obvious whether the favoured form of **1** will be the thione tautomer **1a** or the thiol tautomer **1b**. The ^{13}C NMR spectrum of a CD_3SOCD_3 solution of **1** exhibits a lowest field peak at δ 195.3 ppm assigned to C4B; and this correlates well with the reported signal at δ 192.8 ppm for pyridine-4(1*H*)-

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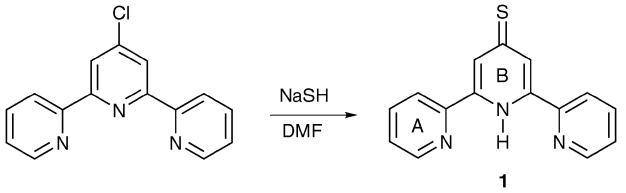


1

Scheme 1 Synthesis of 2,2′:6′,2″-terpyridine-4′(1′*H*)-thione **1** and showing the lettering scheme used for the NMR assignment.

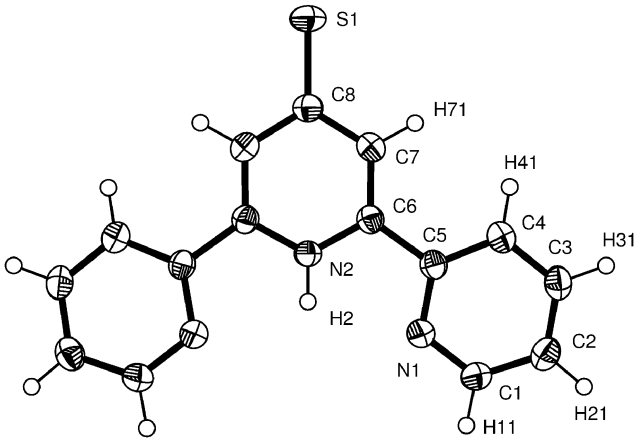
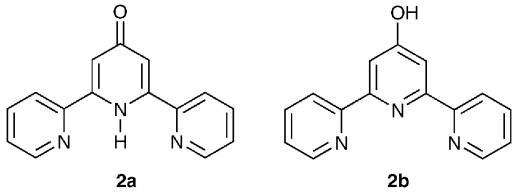


Fig. 1 The molecular structure of 2,2′:6′,2″-terpyridine-4′(1′*H*)-thione **1** showing the labelling scheme adopted.

thione,[14] providing tentative support for the tautomeric thione form **1a**.



2a **2b**

In order to clarify the tautomeric nature of **1**, we have determined the solid state crystal structure. X-Ray quality crystals of $\mathbf{1}\cdot CH_2Cl_2$ were obtained by recrystallisation of **1** from CH_2Cl_2–hexane.‡ The lattice consists of molecules of **1** and CH_2Cl_2 with no close contacts between them. Firstly, compound **1** is unambiguously present in the crystal as the thione tautomer **1a** (Fig. 1) and selected bond lengths and bond angles are presented in Table 1. In contrast to the solid state structure of pyridine-4(1*H*)-thione there are no hydrogen bonds between the molecules of **1**.[12] The tpy adopts a very unusual *cis*,*cis* conformation, as a result of intramolecular hydrogen-bonding between the nitrogen of the terminal rings and the NH of the central ring. The hydrogen atoms were located directly from difference Fourier analyses and the interactions within the *cis*,*cis* tpy are characterised by an ∠NH···N angle of 105.76° and an H···N distance of 2.255 Å. The molecule is non-planar and adopts a sigmoid conformation with a torsion angle ∠N–C–C–N of 10.37°. The structure closely resembles the molecule of **2a** in the crystal structure of the oxygen analogue, which has ∠NH···N angles 108.26 and 107.26° and H···N distances of 2.197 and 2.242 Å although the molecule is closer to planar with ∠N–C–C–N torsion angles of 1.05 and 6.23°.[13] Bond lengths and angles within the central ring of **1** closely resemble those in pyridine-4(1*H*)-thione and the C–S bond length of 1.701(3) Å provides further evidence for the thione tautomer.[12]

‡ CCDC reference numbers 269056 and 283215–283217. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510792j

Table 1 Selected bond lengths (Å) and angles (°) for $\mathbf{1}\cdot CH_2Cl_2$

C1–C2	1.387(3)	C1–N1	1.341(3)
C2–C3	1.382(3)	C3–C4	1.382(3)
C4–C5	1.390(3)	C5–C6	1.480(3)
C5–N1	1.347(3)	C6–C7	1.373(3)
C6–N2	1.357(2)	C7–C8	1.414(3)
C8–S1	1.702(3)	C9–Cl1	1.763(2)
C2–C1–N1	123.5(2)	C1–C2–C3	118.3(2)
C2–C3–C4	119.4(2)	C3–C4–C5	118.6(2)
C4–C5–C6	121.68(18)	C4–C5–N1	122.90(19)
C6–C5–N1	115.41(17)	C5–C6–C7	125.16(18)
C5–C6–N2	115.60(17)	C7–C6–N2	119.24(18)
C6–C7–C8	121.4(2)	C7A–C8–C7	116.3(3)
C7–C8–S1	121.86(13)	Cl1A–C9–Cl1	112.47(19)
C5–N1–C1	117.33(18)	C6–N2–C6A	122.5(2)

Although no conventional hydrogen bonds are present, the molecules of **1** and CH_2Cl_2 form sheets exhibiting a number of interesting C–H···X interactions (Fig. 2). Each molecule of **1** forms a cyclic assembly with a CH_2Cl_2 molecule through two C–H···Cl hydrogen bonds with C1–H11···Cl contacts of 2.946 Å and a ∠C1–H11···Cl angle of 138.75°. Rows of molecules are then formed with a shortest contact between H31 of adjacent molecules of 2.271 Å. This is supported by short H31···S interactions with the thione sulfur of a molecule in the next row of 3.012 Å to give a triangular arrangement with a C3–H31···S angle of 129.62°. This interaction is slightly longer but generally similar to those observed in pyridine-4(1*H*)-thione.[14] The sheets are coplanar with the least squares planes of the sheets being 3.229 Å apart although there is little overlap of aromatic rings in adjacent sheets.

Synthesis and structural characterisation of bis(2,2′:6′,2″-terpyridin-4′-yl)disulfide 2

In the course of characterising **1**, we noted that solutions were air sensitive and over a period of time a new tpy-containing species was observed in the ^{1}H NMR spectrum. Oxidation of **1** with iodine in aqueous alkaline conditions gave the new disulfide bis(2,2′:6′,2″-terpyridin-4′-yl)disulfide **2** as a white solid in 63% yield (Scheme 2). The ^{1}H NMR spectrum of this compound showed it to be highly symmetrical, with the terminal rings of each tpy ring equivalent and the two tpy

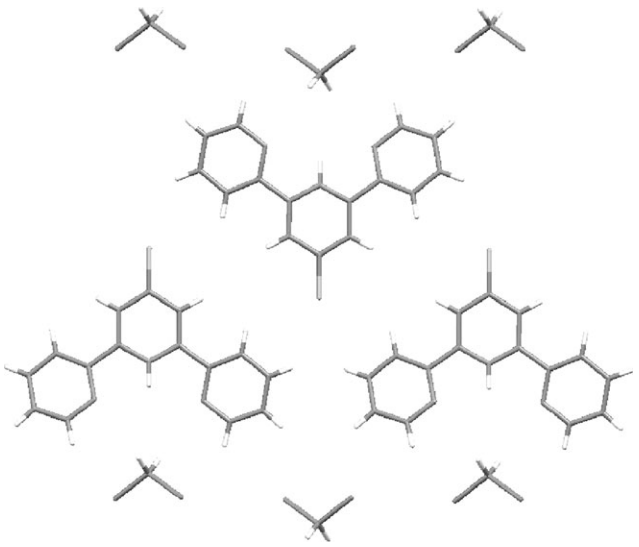
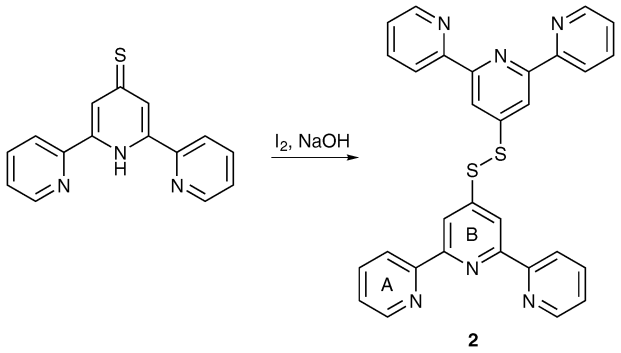


Fig. 2 Sheets are formed containing $\{\mathbf{1}\cdot CH_2Cl_2\}$ units linked by non-classical C–H···X interactions to both the solvent molecule and the sulfur of another molecule of **1**.



2

Scheme 2 Synthesis of bis(2,2′:6′,2″-terpyridin-4′-yl)disulfide **2**

moieties equivalent on the NMR timescale. A parent ion at m/z 529 corresponding to $H\mathbf{2}^+$ was observed in the ES mass spectrum.

The solid-state X-ray determination of compound **2** confirms the proposed structure (Fig. 3) and exhibits a number of interesting features (selected bond lengths and bond angles are presented in Table 2).‡ Firstly, the tpy domains adopt the expected *trans*,*trans* conformation although they are not completely planar, with least squares planes angles between terminal and central rings of 9.07 and 9.97°. Bond lengths and angles within the pyridine rings are typical of tpy ligands. The S–S bond length is 2.0281(12) Å which is strictly comparable to those of 2.037 and 2.032 Å reported for bis(4′-pyridyl)disulfide.[15] In the lattice there is extensive π-stacking, with interplanar distances of 3.360 Å between the least squares planes of adjacent stacked molecules. The C–S–S–C torsion angle is 90.8° and the angle between the least squares planes of the two central pyridine rings is 78.06°. The corresponding angles in bis(4′-pyridyl)disulfide are 83.79° and 88.69°.[15,16] The compound is, accordingly, preorganised to act as a homoditopic ligand which might be used for the preparation of metallomacrocycles in the same way as bis(4′-pyridyl)disulfide.[16]

Synthesis and structural characterisation of 4′-[bis(3,5-benyzloxy)benzylsulfanyl]-2,2′:6′,2″-terpyridine 3

In this section we illustrate the use of the thione **1** for the preparation of a compound for which the reaction of a nucleophilic thiolate with 4′-chloro-2,2′:6′,2″-terpyridine is not appropriate due to the difficult accessibility of the thiol. We are interested in attaching Fréchet-type dendrons[17] to metal-binding domains and subsequently utilising the dendrons as self-organisation motifs for the self-assembly of mono- and multilayers on appropriate substrates.[18,19] In the course of this work we became aware that it would be possible to use STM methods in the conformational analysis of adsorbed molecules in monolayers and as a part of this project we

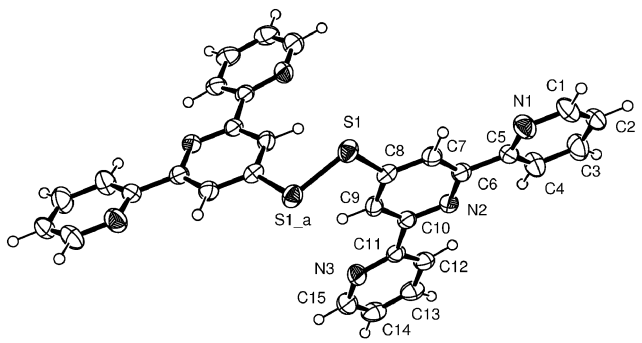
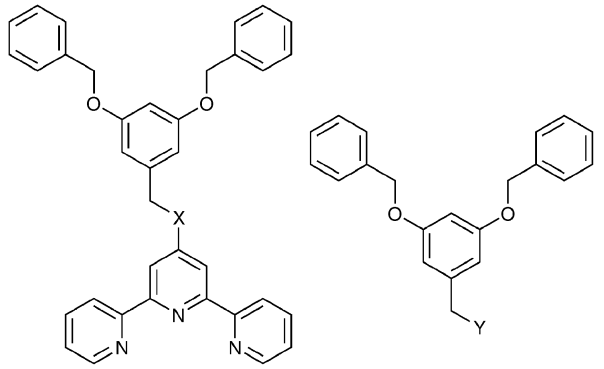


Fig. 3 The crystal and molecular structure of **2** showing the numbering scheme adopted. The two halves of the molecule are symmetry related.

wanted to compare compounds **3** and **4**, containing a first generation Fréchet dendron, which were expected to have C–S–C and C–O–C angles close to 100° (median 103.827° from 10 structures of 4-pyridyl benzyl thioethers in the Cambridge Structural Database[19,20]) and 120° (median 118.055° from 11 structures of 4-pyridyl benzyl ethers in the Cambridge Structural Database[21]) respectively. Although the first generation thiol **5** is known[22] it is particularly air-sensitive and we did not consider that it would survive the reaction conditions for coupling with 4′-chloro-2,2′:6′,2″-terpyridine. In contrast, the first generation electrophilic dendron **6** is well known[19,23] and stable and we considered the best route for the preparation of **3** to be the reaction of **6** with **1**.

The reaction of mesylate **6** with thione **1** proceeded smoothly in acetone in the presence of potassium carbonate to give the desired thioether as a white crystalline solid in 49% yield (Scheme 3).



3 X = S
4 X = O

5 Y = SH
6 Y = OSO_2Me

The new ligand has been fully characterised by conventional methods. The electrospray mass spectrum exhibits a peak at m/z 590 which corresponds to the species $\{\mathbf{3} + Na\}^+$. The ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions are sharp and well-resolved and show that the terminal rings of the tpy are equivalent, as are the two benzyl groups of the substituent. The facile preparation of this compound confirms the preparative utility of the thione **1**.

We have also structurally characterised this ligand which exhibits a number of interesting features. The structure of **3** is presented in Fig. 4 and selected data are presented in Table 3.‡ Firstly, the tpy metal-binding domain exhibits the expected *trans*,*trans* conformation and is much closer to planar than in **2**, with least squares planes angles between the terminal and central rings of 0.63 and 2.09°. The C8–S1–C16 angle is 102.68(6)°, which is remarkably close to the expectation value from the Cambridge Structural Database data. The aromatic S1–C8 bond of 1.7598(13) Å is shorter than the bond to the aliphatic carbon, S1–C16 1.8209(13) Å. The tpy domain and the dendron C-ring are near orthogonal with a least squares plane angle of 88.46° and the torsion angle is 171.11°.

One of the phenyl rings (containing C31–C36) of the benzyl substituents is disordered with two equal occupancy sites related by a rotation of 74.20° about the C31–C34 vector. The occupancy containing C32, C33, C35 and C36 makes a least squares plane of 38.37° with the central benzene ring, whereas the other occupancy is closer to orthogonal, with an angle between the least squares planes of 70.15°. The other benzyl group is ordered and makes a least squares planes angle of 22.37° with the central benzene. Both of the benzyloxy groups adopt an *anti* conformation (defined with respect to H4 of the central ring) with torsion angles C20–C19–O1–C23 and C20–C21–O2–C30 being 177.94 and 169.05° respectively. A search of the Cambridge Structural Database for 1,3-bis (benzyloxy)benzene derivatives gave a total of 18 hits with a grand total of 31 C–C–O–C torsion angles; this revealed an

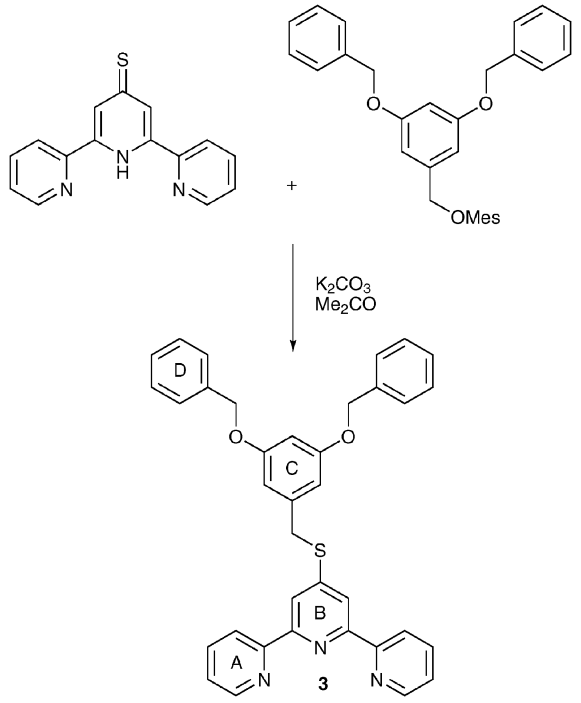
Table 2 Selected bond lengths (Å) and angles (°) for **2**

S1–S1_a	2.0281(12)	S1–C8	1.774(2)
N1–C1	1.344(3)	N1–C5	1.339(3)
N2–C6	1.345(3)	N2–C10	1.342(3)
N3–C11	1.346(3)	N3–C15	1.338(3)
C1–C2	1.363(4)	C2–C3	1.378(4)
C3–C4	1.385(3)	C4–C5	1.382(3)
C5–C6	1.491(3)	C6–C7	1.391(3)
C7–C8	1.391(3)	C8–C9	1.394(3)
C9–C10	1.393(3)	C10–C11	1.493(3)
C11–C12	1.391(3)	C12–C13	1.386(3)
C13–C14	1.380(4)	C14–C15	1.376(4)
S1_a–S1–C8	105.41(8)	C1–N1–C5	117.1(2)
C6–N2–C10	117.81(18)	C11–N3–C15	116.9(2)
N1–C1–C2	124.8(3)	C1–C2–C3	117.4(2)
C2–C3–C4	119.6(3)	C3–C4–C5	118.8(2)
C4–C5–N1	122.4(2)	C4–C5–C6	121.5(2)
N1–C5–C6	116.2(2)	C5–C6–N2	116.46(19)
C5–C6–C7	120.58(19)	N2–C6–C7	123.0(2)
C6–C7–C8	118.4(2)	S1–C8–C7	116.43(17)
S1–C8–C9	124.11(16)	C7–C8–C9	119.4(2)
C8–C9–C10	117.8(2)	C9–C10–N2	123.5(2)
C9–C10–C11	120.40(19)	N2–C10–C11	116.07(19)
C10–C11–N3	116.2(2)	C10–C11–C12	121.0(2)
N3–C11–C12	122.7(2)	C11–C12–C13	118.9(2)
C12–C13–C14	118.7(2)	C13–C14–C15	118.6(2)
C14–C15–N3	124.1(2)		

overwhelming preference for the adoption of the *syn*,*anti* conformation (22 hits) over the *anti*,*anti* conformation (7 hits) with just a single example of a *syn*,*syn* conformation. There appears to be no obvious stereoelectronic or steric reason for the adoption of the *syn*,*anti* conformation. The only significant short contacts in the lattice involve the disordered benzyl rings.

Formation of a metallomacrocycle from preorganised homoditopic disulfide 2

The self-assembly of metallomacrocycles (molecular polygons) from metal centres and di- or polytopic ligands with varying



Scheme 3 Synthesis of the first generation dendritic thioether **3**.

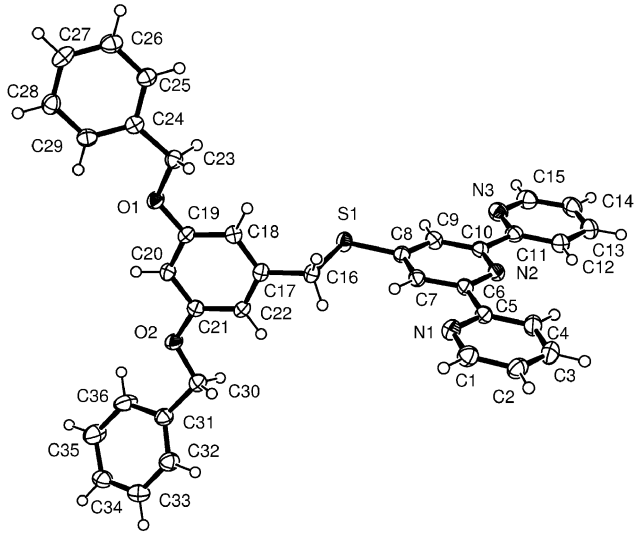


Fig. 4 Crystal and molecular structure of thioether **3** showing the numbering scheme adopted. Only one of the two conformations of the disordered benzyl ring is shown (the one containing C32)—the other orientation of the ring arises from a rotation about C30–C31 of 74.20°.

degrees of preorganisation is currently an area of intense interest.[24] We have demonstrated that tpy metal-binding domains may be utilised for the formation of metallomacrocycles with both highly pre-organised and flexible spacers,[25] and considered that the disulfide **2** might act as a 90° corner unit for the formation of a metallo-square.

The reaction of disulfide **2** with $[Fe(H_2O)_6][BF_4]_2$ in methanol–dichloromethane gave an immediate purple solution, typical of a $\{Fe(tpy)_2\}^{2+}$ chromophore. After removal of solvent, a near-quantitative yield of purple material of stoichiometry $\{Fe(\mathbf{2})(BF_4)_2\}_n$ was obtained. The ^{1}H NMR spectrum of the purple solid showed a single tpy environment and was slightly broadened, although not as broad as typical $\{Fe(tpy)_2\}^{2+}$ metallopolymers. Recrystallisation of the compound from acetonitrile—diethyl ether gave a single very thin deep purple plate, which was characterised by single crystal X-ray analysis.‡ NMR spectra of the recrystallised material and the crude material were similar. The quality of the data did not allow refinement to a satisfactory level and the structure must be regarded as preliminary, although we are confident of the gross structural features. All attempts to subsequently grow better quality crystals have been unsuccessful.

The structure of the cation present is presented in Fig. 5 and confirms that a tetranuclear metallomacrocycle of formula $[Fe_4(\mathbf{2})_4][BF_4]_8$ has been formed. The tetrafluoroborate counterions are ordered and exhibit no close contacts with the octacation. There are considerable amounts of disordered solvent in the lattice, modelled incompletely with 5.5 acetonitrile, 1.5 diethyl ether, one methanol and 4.5 water molecules. The presence of so many solvent molecules is compatible with the elemental analysis data of the bulk microcrystalline material which showed a total of 14 water molecules per tetranuclear formula unit. None of the solvent molecules or the tetrafluoroborate counterions is trapped within the cavity of the metallomacrocycle.

The four iron atoms are approximately planar with none of the atoms being more than 0.24 Å from the least squares plane of the four centres. The Fe···Fe distances are between 9.7 and 11.0 Å and the $\{Fe(tpy)_2\}$ coordination units have typical metrical parameters. The C–S–S–C torsion angles lie between 80 and 99°, indicating a significant degree of flexibility within the ligand and highlighting the danger of predicting the nuclearity of metallocycles formed with relatively conformationally free ligands. Views of the metallomacrocycle from above and from the side are presented in Fig. 6.

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

S1–C8	1.7598(13)	S1–C16	1.8209(13)
N1–C1	1.3373(19)	N1–C5	1.3387(18)
N2–C6	1.3400(18)	N2–C10	1.3423(18)
N3–C11	1.3408(19)	N3–C15	1.3391(19)
O1–C19	1.3631(15)	O1–C23	1.4214(15)
O2–C21	1.3648(16)	O2–C30	1.4280(16)
C1–C2	1.388(2)	C2–C3	1.376(2)
C3–C4	1.388(2)	C4–C5	1.3964(18)
C5–C6	1.4892(18)	C6–C7	1.3995(17)
C7–C8	1.3898(19)	C8–C9	1.3896(19)
C9–C10	1.3910(18)	C10–C11	1.4932(18)
C11–C12	1.3995(19)	C12–C13	1.384(2)
C13–C14	1.380(2)	C14–C15	1.385(2)
C23–C24	1.5006(18)	C30–C31	1.5142(19)
C8–S1–C16	102.68(6)	C1–N1–C5	117.73(12)
C6–N2–C10	117.40(11)	C11–N3–C15	117.31(13)
C19–O1–C23	116.88(10)	C21–O2–C30	117.79(10)
N1–C1–C2	123.74(14)	C1–C2–C3	118.05(13)
C2–C3–C4	119.44(13)	C3–C4–C5	118.53(13)
C4–C5–N1	122.47(13)	C4–C5–C6	120.77(12)
N1–C5–C6	116.75(11)	C5–C6–N2	116.83(11)
C5–C6–C7	120.03(12)	N2–C6–C7	123.14(12)
C6–C7–C8	118.83(12)	S1–C8–C7	124.57(10)
S1–C8–C9	117.15(10)	C7–C8–C9	118.27(12)
C8–C9–C10	119.04(12)	C8–C9–H91	120.38
C9–C10–N2	123.30(12)	O2–C30–C31	107.65(11)
C9–C10–C11	119.96(12)	N2–C10–C11	116.74(11)
C10–C11–N3	116.69(12)	C10–C11–C12	120.73(13)
N3–C11–C12	122.58(13)	C11–C12–C13	118.74(15)
C12–C13–C14	119.16(14)	C13–C14–C15	118.17(14)
C14–C15–N3	124.03(15)	S1–C16–C17	109.47(9)
C16–C17–C18	119.22(11)	C16–C17–C22	119.57(11)
C18–C19–O1	124.26(11)	O1–C19–C20	115.48(11)
C20–C21–O2	114.93(11)	O2–C21–C22	124.20(12)
O1–C23–C24	109.80(10)	C23–C24–C29	123.03(12)

Conclusions

We have described the synthesis of a new starting material for 2,2′:6′,2″-terpyridine chemistry, namely 2,2′:6′,2″-terpyridine-4′(1′*H*)-thione. The compound has been shown to exist in the thione form in the solid state and a few applications in the synthesis of novel tpy derivatives have been demonstrated, including the formation of novel metallomacrocycles.

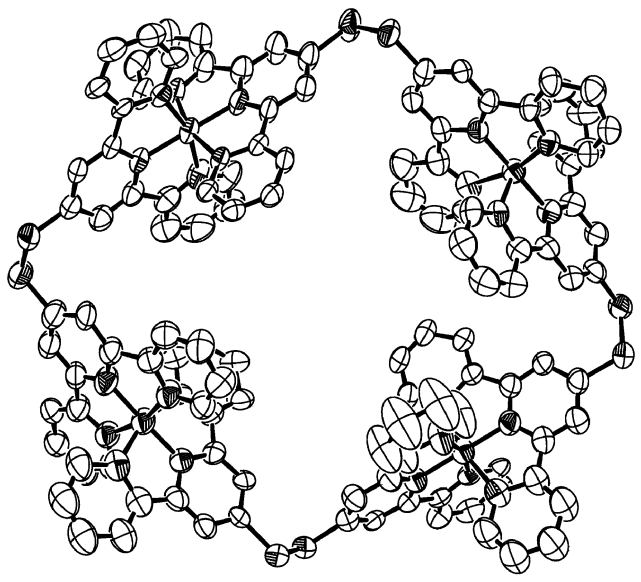


Fig. 5 Partial structure of the $[Fe_4(\mathbf{2})_4]^{8+}$ cation in $[Fe_4(\mathbf{2})_4][BF_4]_8$.

Experimental

2,2′:6′,2″-Terpyridine-4′(1′*H*)-thione 1

A mixture of $NaSH \cdot H_2O$ (1.40 g, 18.9 mmol) and 4′-chloro-2,2′:6′,2″-terpyridine (200 mg, 747 μmol) was refluxed in DMF (50 mL) for 4 h. The resulting green suspension was filtered and the solvent evaporated to give a yellow residue. This was then dissolved in water (30 mL) and the pH of the solution adjusted to 7 with 2 M aqueous HCl solution (*ca.* 2 mL) to give a yellow precipitate, which was collected by filtration and washed with water (50 mL) yielding **1** as a yellow powder (171 mg, 86%); mp 181 °C; (found: C, 68.34; H, 4.71; N, 15.14. $C_{15}H_{11}N_3S$ requires C, 67.90; H, 4.18; N, 15.84%); ν_{max}/cm^{-1} 3248m, 3040w, 1605m, 1566s, 1458m, 1327m, 1119m, 987m and 849m; δ_H/ppm (500 MHz, CD_3SOCD_3, Me_4Si): 12.4 (1H, br s, H^{NH}), 8.86 (2H, d, *J* 4.5 Hz, H^{6A}), 8.44 (2H, d, *J* 8.0 Hz, H^{3A}), 8.14 (2H, s, H^{3B}), 8.06 (2H, d, *J* 8.0, 7.4 Hz, H^{4A}) and 7.64 (2H, dd, *J* 7.4, 4.8 Hz, H^{5A}); δ_C/ppm (100 MHz, CD_3SOCD_3, Me_4Si): 195.3, 150.0, 147.3, 138.7, 138.5, 126.3, 125.4 and 121.7; MS (EI^+, 70 eV): *m*/*z* (EI^+) 265.1 ($[M]^+$).

Bis(2,2′:6′,2″-terpyridin-4′-yl)disulfide 2

1 (70.0 mg, 0.264 mmol), NaOH (12.0 mg (0.300 mmol) and iodine (38.1 mg, 0.150 mmol) were stirred vigorously in water (5 mL) at room temperature for 16 hours. The off-white precipitate was then filtered off and washed with water (10 mL), ethanol (2 mL) and diethyl ether (2 mL) and dried over P_4O_{10} to give **2** (44 mg, 63%); mp 197 °C; (found: C, 67.77; H, 3.78; N, 15.51. $C_{30}H_{20}N_6S_2$ requires C, 68.16; H, 3.81; N, 15.90%); ν_{max}/cm^{-1} 3055w, 2916m, 2854m, 1551s, 1458m, 1381s, 987m, 872m, 787s and 733m; δ_H/ppm (500 MHz, $CDCl_3$, Me_4Si): 8.67 (4H, dd, *J* 4.7, 1.6 Hz, H^{6A}), 8.66 (4H, s, H^{3B}), 8.55 (4H, dd, *J* 7.8, 1.0 Hz, H^{3A}), 7.82 (4H, dd, *J* 7.9, 7.7 Hz, H^{4A}), 7.31 (4H, dd, *J* 7.7, 4.8 Hz, H^{4A}); δ_C/ppm (100 MHz, $CDCl_3$, Me_4Si): 155.7, 155.4, 149.3, 149.2, 136.8, 124.0, 121.4, 117.3; *m*/*z* (ESI^+) 551 ($[M + Na]^+$), 529 ($[M + H]^+$).

4′-[Bis(3,5-benyzloxy)benzylsulfanyl]-2,2′:6′,2″-terpyridine 3

A mixture of 3,5-bis(benzyloxy)benzyl mesylate **6** (50.0 mg, 0.125 mmol), **1** (33.5 mg, 0.125 mmol) and K_2CO_3 (53.0 mg, 0.375 mmol) was refluxed in acetone (5 mL) under a nitrogen atmosphere for 20 min. After cooling to room temperature, the solvent was removed *in vacuo*. Water (20 mL) was added to the residue and the mixture was extracted three times with dichloromethane. The combined organic layers were dried (Na_2SO_4) and the solvent removed *in vacuo* to give a colourless powder, which was recrystallised from EtOH (35 mg, 49%). Mp 126 °C; (found: C, 74.24; H, 5.29; N, 7.11. $C_{36}H_{29}N_3O_2S \cdot H_2O$ requires: C, 73.82; H, 5.33; N, 7.17%); ν_{max}/cm^{-1} 2923w, 2854w, 1605m, 1551s, 1443m, 1381m, 1319m, 1157s and 1057m; δ_H/ppm (500 MHz, $CDCl_3$, Me_4Si): 8.70 (2H, d, *J* 4.1 Hz, H^{6A}), 8.62 (2H, d, *J* 7.8 Hz, H^{3A}), 8.41 (2H, s, H^{3B}), 7.89 (2H, t, *J* 7.1 Hz, H^{4A}), 7.39 (4H, dd, *J* 7.8, 1.6 Hz, H^{2D}), 7.36 (4H, dd, *J* 7.8, 7.0 Hz, H^{3D}), 7.32–7.29 (4H, m, $H^{4D,5A}$), 6.77 (2H, d, *J* 2.2 Hz, H^{2C}), 6.52 (1H, t, *J* 2.2 Hz, H^{4C}), 5.02 (4H, s, PhCH_2O), 4.37 (2H, s, CH_2Stpy); δ_C/ppm (100 MHz, $CDCl_3$, Me_4Si): 160.1, 155.4, 154.5, 148.7, 138.2, 137.4, 136.7, 128.5, 128.2, 127.6, 124.0, 121.6, 118.1, 108.5, 108.2, 101.6, 70.1, 36.1; *m*/*z* (ESI^+) 590 ($[M + Na]^+$).

$[Fe_4(\mathbf{2})_4][BF_4]_8 \cdot 14H_2O$

Disulfide **2** (14.5 mg, 27.4 μmol) and $[Fe(H_2O)_6][BF_4]_2$ (9.25 mg, 27.4 μmol) were heated to reflux in dichloromethane–methanol (1 : 2, 5 mL) for 1 hour to give a deep purple solution. The solvent was removed *in vacuo* and the residue dissolved in MeCN (5 mL) and the solution filtered over cotton wool. The solvent of the filtrate was then removed *in vacuo* to give a

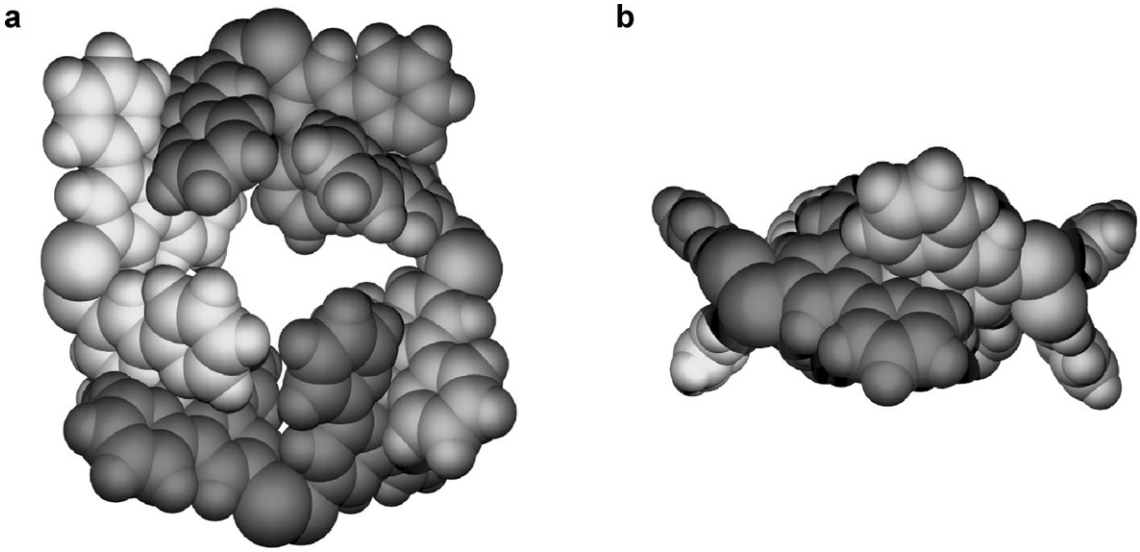


Fig. 6 Space-filling representations of the metallomacrocyclic $[Fe_4(\mathbf{2})_4]^{8+}$ cation in $[Fe_4(\mathbf{2})_4][BF_4]_8$ from (a) above and (b) the side. The individual ligands have been shaded to assist the viewer.

purple residue (21.9 mg, 97.4%); (found: C, 43.71; H, 2.96; N, 10.23. $C_{120}H_{80}N_{24}B_8F_{32}Fe_4S_8 \cdot 14H_2O$ requires: C, 43.88; H, 3.31; N, 10.23%); δ_H/ppm (250 MHz, CD_3CN, Me_4Si): 9.05 (16H, s, H^{3B}), 8.52 (16H, d, *J* 7.7 Hz, H^{6A}), 7.81 (16H, dd, *J* 7.5, 7.0 Hz, H^{5A}), 7.21 (16H, d, *J* 5.0 Hz, H^{3A}), 7.06 (16H, dd, *J* 6.7, 5.0 Hz, H^{4A}); MS (ESI+): *m*/*z* (ESI^+) 848 ($[\mathbf{2} + Fe + 3H + 3BF_4]^+$), 694 ($[\mathbf{2} + Fe + Na + BF_4]^{2+}$), 641 ($[\mathbf{2} + 2Fe + H]^+$), 610 ($[\mathbf{2} + Fe + Na + 3H]^+$), 584 ($[\mathbf{2} + Fe]^+$), 556 ($[\mathbf{2} + Fe]^{2+}$).

X-Ray crystallography

For each complex a suitable crystal was embedded in protective oil and mounted on a Nonius Kappa CCD diffractometer under a stream of cold N_2. Details of the crystal parameters, data collection and refinement for each of the structures are collected in Table 4. After data collection, in each case the usual corrections were applied after integration of the collected images;[26] the structures were then solved by conventional direct methods using SIR92[27] and refined using CRYSTALS.[28] Data collection and refinement was difficult for the structure of $[Fe_4(\mathbf{2})_4][BF_4]_8$ due to the presence of solvent molecules and the low scattering power of the crystal. In the refinement the model was kept as simple as possible, refining some atoms isotropically and using the knowledge of the geometry of structural fragments (for instance the tetrahedral geometry of a BF_4 ion) to keep the number of parameters to be refined as low as possible. It is probable that not all solvent molecules have been localised, but the flat distribution of the residual electron density did not permit any further meaningful interpretation.

Note added in proof. The authors recently became aware that a complex of **1** has been described. [29]

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Table 4 Crystal, data collection and refinement details for the crystal structures

Compound	**1**	**2**	**3**	$[Fe_4(\mathbf{2})_4][BF_4]_8 \cdot 5.5MeCN \cdot 1.5Et_2O \cdot MeOH \cdot 4.5H_2O$
Formula	$C_{16}H_{13}C_{12}N_3S$	$C_{30}H_{20}N_6S_2$	$C_{36}H_{29}N_3O_2S$	$C_{138}H_{114.5}B_8F_{32}Fe_4N_{29.5}O_7S_8$
Formula weight	350.27	528.66	567.71	3472.46
T (K)	173	173	123	153
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2/*c*	*C*2/*c*	$P2_1/n$
a (Å)	7.8119(3)	11.5557(4)	60.749(2)	25.4086(9)
b (Å)	17.8280(6)	5.5221(2)	4.92820(10)	20.1144(8)
c (Å)	11.3151(5)	22.6510(9)	19.1272(7)	34.5052(11)
β (°)	92.703(2)	120.5668(15)	95.9860(11)	91.118(2)
V (Å^3)	1574.11(10)	1244.54(8)	5695.1(3)	17631.5(11)
Z	4	2	8	4
D_{calc} (Mg m^{-3})	1.478	1.411	1.324	1.308
μ (mm^{-1})	0.544	0.247	0.153	0.508
Crystal size (mm)	0.24 × 0.28 × 0.28	0.04 × 0.08 × 0.24	0.05 × 0.08 × 0.38	0.10 × 0.19 × 0.19
Reflections	4572	12042	18807	59868
Collected independent reflections	2305	3333	6411	26995
Final R indices: R_1 ($I > n\sigma I$), *n*, wR_2 (all data)	0.0351, 2, 0.0886	0.0485, 1, 0.0746	0.0472, 1.8, 0.0376	0.1621, 1.4, 0.2587

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