Thiophene S-binding of a conformationally constrained thiophenophane leading to the formation of a copper(I) coordination polymer

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The potentially tetradentate NS$_3$ thiophenophane binds strongly to Cu(I) through a thiophene S, pyridine N and one thioether S, leaving the remaining thioether S donor in an exodentate arrangement forming an infinite polymeric link between Cu(I) atoms.

The thiophenic sulfur is considered to coordinate poorly to transition metals.[1] Only a few S-bound thiophene coordination complexes exist and for several of these the M–S distances exceed the sum of the covalent radii.[2] However, sterically constrained ligand systems incorporating thiophene have been used to successfully achieve S-binding.[2c,3] If incorporated into a macrocycle the rigid thiophene unit may impose limitations on the possible orientations of donor atoms and hence on the size and shape of the macrocyclic cavity and on the coordination properties.[2d,f,3] For example in macrocyclic thioethers, the thiophene may affect the donor properties of the thioethers by influencing the orientation of the sulfur lone pairs and this property may be used to control the structure of transition metal complexes. When the conformation of the ligand causes some of these lone pairs to be arranged in an exodentate fashion the possibility exists for bridging metal centres or coordination-polymer formation. This property of macrocyclic complexes, that the donor groups within the macrocycle are constrained and so provide a degree of control over the final polymeric structure, has not been widely used in coordination-polymer chemistry. Indeed, the use of macrocyclic complexes as structural elements in coordination polymers is surprisingly rare and typically involves specifically arranged exodentate donor groups[4] on the macrocyclic complexes or separate bridging ligands linking the macrocyclic complexes together.[5]

Herein we report the synthesis of 2,10-dithia[3](2,6)pyridino[3](2,5)thiophenophane (L), a small sterically constrained thiophenophane, and its use in the construction of a Cu(I) coordination polymer in which exodentate thioether donors bridge Cu(I) thiophenophane units containing a bound thiophene sulfur. Thiophenophane L was very difficult to prepare and isolate. Initially, it was prepared by high-dilution base coupling of 2,6-bis(chloromethyl)pyridine[6] and 2,5-bis(methylsulfanyl)thiophene[7] in a 1 : 1 molar ratio. Purification by column chromatography gave a stable white crystalline solid in 4% yield. 2,5-Bis(methylsulfanyl)thiophene could only be prepared in low yield and was difficult to purify, therefore the alternate precursors 2,6-bis(methylsulfanyl)pyridine[8] and 2,5-bis(bromomethyl)thiophene[9] were used with a slight improvement in yield (10%). CPK models show L is very strained and inflexible. Sulfur inversion is not possible but ring flipping of the pyridine and 'wobbling' of the thioether bridges can occur. These processes are consistent with the presence in the ^{1}H NMR spectrum of signals from two AB methylene proton systems.†

Given the constrained nature of the thiophenophane, it was of interest to determine the conformation in the solid state and to assess the potential for binding to a metal centre.‡ The thiophenophane exists in an *anti*, boat, boat conformation with the thiophene and pyridine rings tilted at 37.5° with respect to each other (Fig. 1). The pyridine N and thiophene S atoms point in opposite directions. Both thioether S atoms adopt a splayed endodentate conformation with respect to the thiophene S and point in the same direction as the thiophene S atom suggesting coordination to a metal ion may be possible. All bond lengths and angles are within the normal range.[10]

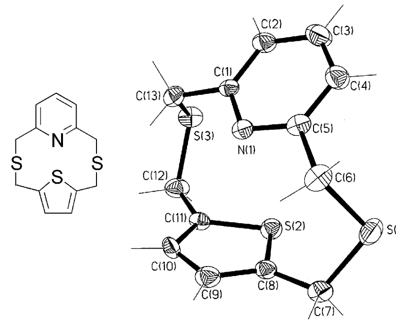

Fig. 1 Thiophenophane L: (left) schematic view; (right) ORTEP view (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): C(6)–S(1) 1.837(3), S(1)–C(7) 1.833(3), C(8)–S(2) 1.735(4), C(8)–C(9) 1.357(5), C(9)–C(10) 1.429(5); C(6)–S(1)–C(7) 103.5(2), C(5)–C(6)–S(1) 113.5(3), C(8)–C(7)–S(1) 115.6(2).

Equimolar reaction of L and [Cu(MeCN)$_4$]PF$_6$ in MeCN gave an air-stable cream solid in 63% yield, which analysed with a 1 : 1 ligand to metal ratio and gave ^{1}H and ^{13}C NMR spectra consistent with a symmetrical but dynamic complex.† In order to establish the disposition of the thiophenophane an X-ray structure analysis was undertaken.‡

The crystal structure is severely disordered. The central Cu(I) and thioether S-donors lie on a mirror plane and the mirror operation causes the unsymmetrical L to be disordered equally over two sites (Fig. 2). The disordered thiophene and pyridine rings are intertwined and tilted by 52.9° with respect to each

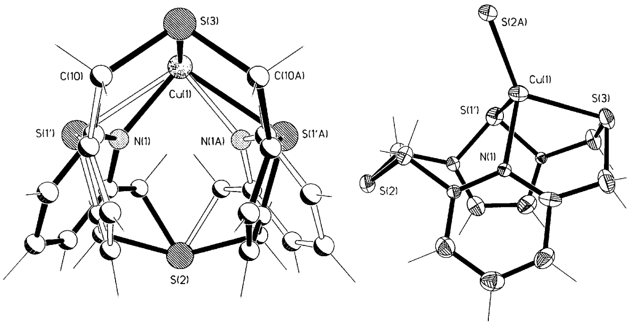

Fig. 2 Cationic [Cu(L)]$^+$ unit with PF$_6^-$ anion omitted: (left) view showing disorder of L about mirror plane; (right) ORTEP view (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.017(10), Cu(1)–S(2A) 2.191(3), Cu(1)–S(3) 2.346(3), Cu(1)–S(1′) 2.550(4); S(2A)–Cu(1)–N(1), 131.1(3), N(1)–Cu(1)–S(3) 87.7(3), N(1)–Cu(1)–S(1′) 92.6(3), S(2A)–Cu(1)–S(3) 126.9(1), S(2A)–Cu(1)–S(1′) 115.12(9), S(3)–Cu(1)–S(1′) 93.05(9).

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other. The two disordered ligands are required by symmetry to occupy the same thioether and Cu(I) positions but, coincidentally, they also occupy the same C(10) position. The central Cu(I) atom adopts a distorted tetrahedral geometry and is bound to a pyridine N, a thiophene S and an endodentate thioether S from one thiophenophane, and to an exodentate thioether S from the arm of a second symmetry related thiophenophane (Fig. 2). Each $[Cu(L)]^+$ unit is bound to another adjacent $[Cu(L)]^+$ unit *via* one of the exodentate thioether sulfur atoms to form a one-dimensional zigzag chain. This is the first reported thiophenophane polymer and the first polymer containing a bound thiophene sulfur. The ligand adopts a skewed *syn*, chair, boat conformation with the pyridine and thiophene rings lying approximately parallel at 16.8° to each other. From the above-mentioned data, the ligand appeared to be rather inflexible. However, the X-ray structure shows that the ligand is flexible enough to allow flipping of the pyridine ring so that the ligand sits in a *syn* conformation to promote thiophene S-binding to the Cu(I) ion. In each $[Cu(L)]^+$ unit the bound endodentate thioether S points in the same direction as the thiophene S while the other arm adopts an exodentate conformation (Fig. 2). This configuration of the thiophenophane prevents positioning of both thioether S-donors for coordination to the Cu(I) ion and promotes an intramolecular π–π-interaction (3.59 Å) between the thiophene and pyridine rings.

The thiophenophane is responsible for a very irregular coordination geometry about the Cu(I) ion. The Cu–S(exodentate) distance of 2.191(3) Å is short when compared to the normal Cu–S(endodentate) distance. The Cu–S(thiophene) bond length of 2.550(4) Å is around the upper quartile of all reported Cu(I)–S distances (2.18–3.01 Å).[10] The shortest M–S(thiophene) bond is a Ni(I)–S distance of 2.143(6) Å in a Ni(I) thiaporphyrin complex.[3b] The only reported Cu(I)–S(thiophene) distances are 2.960(5)[11] and 3.155(5) Å[2f] which are too long to be considered formal bonds but perhaps indicate weak interactions. The coordinated thiophene sulfur in $\{[Cu(L)]PF_6\}_\infty$ is approximately pyramidal, as indicated by the 103.4° angle between the Cu–S bond and the vector from sulfur to the midpoint of the mean plane of the thiophene ring. This angle is at least 10° smaller than any other reported value[2a,c,10] and is a consequence of the very restricted binding by the rigid ligand. The thiophene ring bond lengths show alternation in both the free and bound thiophenophane consistent with a localised bonding scheme. The one-dimensional polymer lies along the two-fold screw axis parallel to the *a*-axis and has a zigzag motif (Fig. 3).

The symmetrical nature of the complex in CD_3CN, as observed by ^1H and ^{13}C NMR spectroscopy, is inconsistent with the asymmetry found in the crystal structure and suggests dissociation of each polymeric chain in solution. Variable temperature ^1H NMR spectra were measured in CD_3CN down to the solvent limit of 238 K. Results showed the methylene protons nearest the thiophene moiety remained as a singlet resonance with no evidence of broadening or coalescence. However, the signals of the methylene protons adjacent to the pyridine ring collapsed and split into an AB system. These results suggest that in solution the pyridine ring remains bound to copper while the thiophene S is not bound. In addition, the complex must undergo an exchange process involving both of the thioether donor atoms and possibly the solvent. Electrospray mass spectrometry under normal operating conditions showed peaks which could be assigned to a number of species including a parent ion $[Cu(L)]^+$ at *m/z* 342 (100%), $[Cu(L)MeCN]^+$ at *m/z* 383 (78%), $[Cu(L)_2]^+$ at *m/z* 621 (15%) and $\{[Cu_2(L)_2]PF_6\}^+$ at *m/z* 813 (37%). This further indicates that $[Cu(L)]^+$ is dynamic and labile in solution and is probably involved in a series of complex equilibria.

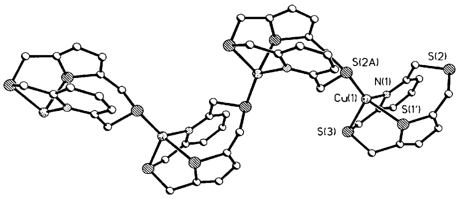

Fig. 3 View of a zigzag polymer chain formed by $[Cu(L)]^+$ units (PF_6^- anions and hydrogen atoms omitted) showing the exodentate thioether coordination linkage.

We have shown that when thiophene was placed in a small sterically constrained macrocycle it not only influenced the conformation of the bound ligand in a metal complex but was also, by its proximity, forced to bind to that metal. In addition, the conformational changes had ramifications for the structure as a whole leading to the formation of a coordination polymer. This work points to the usefulness of macrocyclic complexes as building blocks for coordination polymers.

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Notes and references

† *Selected data* for L: δ_H(300 MHz; $CDCl_3$) 7.44 (t, 1H, ^3J 8 Hz), 7.01 (d, 2H, ^3J 8 Hz), 6.46 (s, 2H), 3.99 (dd, 4H, ^3J 15 Hz), 3.79 (dd, 4H, ^3J 15 Hz). Anal. Calc. for $C_{13}H_{13}NS_3$: C, 55.88; H, 4.70; N, 5.01; S, 34.42. Found: C, 55.84; H, 4.43; N, 4.97; S, 34.20%.

For $\{[Cu(L)]PF_6\}_\infty$: δ_H(300 MHz; CD_3CN) 7.73 (t, 1H, ^3J 8.0 Hz), 7.30 (d, 2H, ^3J 8.0 Hz), 6.23 (s, 2H), 4.14 (d, 4H, ^4J 2.1 Hz), 4.06 (s, 4H). Anal. Calc. for $C_{13}H_{13}NS_3CuPF_6$: C, 32.00; H, 2.69; N, 2.87; S, 19.71. Found: C, 32.27; H, 2.73; N, 3.10; S, 19.04%.

‡ *Crystal data*: L: $C_{13}H_{13}NS_3$, M = 279.42, orthorhombic, space group *Pbca* (no. 61), a = 10.768(5), b = 15.464(5), c = 15.529(5) Å, U = 2586(2) Å^3, T = 163(2) K, Z = 8, μ(Mo-Kα) = 0.549 mm^{-1}, 6628 reflections measured, 1312 independent reflections (R_{int} = 0.041), [959, $I \geqslant 2\sigma(I)$], R_1 = 0.0288, 0.0471 (all data), wR_2 = 0.0649, 0.0680 (all data).

$\{[Cu(L)](PF_6)\}_\infty$: $C_{13}H_{13}CuF_6NPS_3$, M = 487.96, orthorhombic, space group *Pbam* (no. 55), a = 10.727(5), b = 21.194(9), c = 7.553(3) Å, U = 1717(1) Å^3, T = 163(2) K, Z = 4, μ(Mo-Kα) = 1.787 mm^{-1}, 20 131 reflections measured, 1986 independent reflections (R_{int} = 0.027) [1886, $I \geqslant 2\sigma(I)$], R_1 = 0.0876, 0.0900 (all data), wR_2 = 0.1809, 0.1818 (all data). CCDC 182/1842. See http://www.rsc.org/suppdata/cc/b0/b007579p/ for crystallographic files in .cif format.

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