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FULL PAPER

Methyl group influence on the formation of CuI complexes with thio-pyridine ligands

Paula L. Caradoc-Davies,[a] Lyall R. Hanton,*[a] Justin M. Hodgkiss[a] and Mark D. Spicer[b]

[a] *Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. E-mail: lhanton@alkali.otago.ac.nz*
[b] *Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, Scotland G1 1XL*

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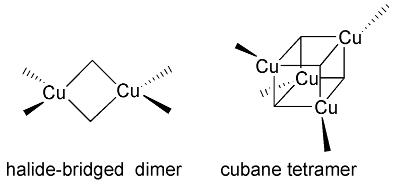
In order to investigate the effect of methyl group substitution adjacent to a pyridyl N donor, three ligands were synthesised and complexed with CuI in a 1 : 2 ratio. The crystal structures of three CuI complexes were determined. The dimethylated ligand bis(6-methyl-2-pyridylmethyl)sulfide (**L**^{1}) gave rise to a tetranuclear complex with two Cu_2I_2 bridges in which the Cu centres were four-coordinate. The asymmetric ligand 2-(6-methylpyridyl)methyl(2-pyridyl)methylsulfide (**L**^{2}) gave a tetranuclear complex which contained two parallel Cu_2I_2 bridges. In each Cu_2I_2 bridge, one Cu centre was three- and the other four-coordinate. In contrast, the ligand bis(2-pyridylmethyl)sulfide (**L**^{3}), with no Me substitution, gave rise to a one-dimensional coordination polymer with CuI chains. It was found that the differences in the complexes were a result of both the electronic and steric effects arising from the Me substitution of the pyridine donors and that no one effect completely dominated.

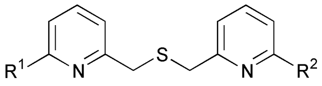
Introduction

A number of copper(I) halide complexes formed from mono- or bi-dentate ligands have previously been investigated.[1] Many of these complexes are derived from two structural motifs namely, the halide-bridged dimer and the cubane tetramer[1,2] (Scheme 1) of which the former is by far the more common. Structurally the two Cu atoms of the halide-bridged dimer can exist with coordination numbers of three and three,[3] three and four[4] or four and four.[5] The three and four combination is the rarest arrangement for such dimers. The formation of these discrete complexes and the exact type of structural motif adopted are influenced by the electronic and steric effects exerted by the ligands.[6] A simple variation such as adding a substituent adjacent to a donor atom can have a noticeable effect on the overall structure of the complex.[7] Previous work examining the effect of ligand substitution on copper(I) halide complexes focused on using simple mono- or rigid bi-dentate ligands.[8]



Scheme 1

In the course of our work we have used small flexible oligopyridine ligands to probe the coordination preferences of more complicated ditopic oligopyridine ligands.[9–11] In preparing these more complicated ditopic ligands we have, as a matter of expediency, incorporated Me groups adjacent to the pyridine nitrogen donor atoms.[10,12] This has been done to amend the properties of the unsubstituted ligand in order to try and increase yields, improve solubility and enhance the chances of crystallising complexes of interest. In order to try and understand the effect of this simple substitution of the ditopic ligands on the complexes formed we have undertaken a systematic study of the simplified oligopyridine ligand system. Herein we report the copper(I) iodide complexes of three ligands with varying degrees of Me substitution adjacent to the pyridine N donors (Scheme 2).



L^1 $R^1 = R^2 = Me$
L^2 $R^1 = H$, $R^2 = Me$
L^3 $R^1 = R^2 = H$

Scheme 2

Results and discussion

Ligand syntheses

The symmetric ligands bis(6-methyl-2-pyridylmethyl)sulfide[13] (**L**^{1}) and bis(2-pyridylmethyl)sulfide[14] (**L**^{3}) were prepared by reaction of 2-(chloromethyl)-6-methylpyridine[15] and of 2-(chloromethyl)pyridine,[15] respectively, with thioacetamide under basic conditions. The asymmetric ligand 2-(6-methylpyridyl)methyl(2-pyridyl)methylsulfide (**L**^{2}) was prepared by the 1 : 1 molar reaction of 2-(chloromethyl)pyridine[15] and 6-methyl-2-(sulfanylmethyl)pyridine[16] in a solution of sodium methoxide. As isolated, ligand **L**^{2} was not analytically pure. Attempts to obtain analytically pure material using column chromatography over silica gel were ineffective. However, high-resolution electrospray mass spectrometry confirmed the successful synthesis of **L**^{2}. Subsequently, the ligand was reacted with CuI to give a microanalytically pure complex.

Synthesis and structure of $[Cu_4(L^1)_2I_4]$ 1

The 1 : 1 molar reaction of **L**^{1} with CuI in MeCN gave a yellow solution from which a tan powder was isolated. The powder gave a microanalysis consistent with a 2 : 1 metal-to-ligand ratio. Subsequently the same tan powder was isolated from the 2 : 1 molar reaction of CuI and **L**^{1} in moderate yield (50.4%). Despite careful workup of the reaction solid and filtrate, the 1 : 1 product could not be isolated.

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The ^{1}H NMR spectrum of **1** in CD_3CN was consistent with a symmetrical species, which was fluxional in solution. Electrospray mass spectrometry under normal operating conditions showed five peaks which had the correct isotopic patterns for $[Cu(\mathbf{L}^1)]^+$ at *m*/*z* 308, $[Cu(\mathbf{L}^1)_2]^+$ at 553, $[Cu_2(\mathbf{L}^1)_2I]^+$ at 743, $[Cu_3(\mathbf{L}^1)_2I_2]^+$ at 934 and $[Cu_4(\mathbf{L}^1)_2I_3]^+$ at 1124. The presence of the latter two peaks suggested that a tetranuclear complex might exist in solution. X-Ray quality crystals were grown by the slow diffusion of diethyl ether into a solution of the complex in MeCN.

The crystal structure of **1** was found to contain one ligand, two Cu(I) ions and two I^- ions in the asymmetric unit. The molecular formula $[Cu_4(\mathbf{L}^1)_2I_4]$ was generated by a centre of inversion (Fig. 1). This was an example of a rare tetranuclear complex with only one other closely related complex $[Cu_4(ddtp)_2Br_4]$ (ddtp = 1,5-bis(3′,5′-dimethylpyrazolyl)-3-thiapentane) previously having been reported.[17] The structure of **1** also had features in common with the recently reported Cl^- bridged Cu(II) tetranuclear molecular rectangle.[18] The tetranuclear complex **1** was constructed from two bridging Cu_2I_2 cores, which linked the two ligands generating the centrosymmetric tetranuclear complex. This form of tetranuclear Cu(I)-halide complex is unusual since such Cu_4X_4 complexes typically exist as cubane or chair forms.[19] The four copper atoms all had similarly distorted tetrahedral geometries, which were provided by NSI_2 donor atoms. The Cu(I) ions within the Cu_2I_2 core were separated by a short distance of 2.551(1) Å.[17,20] The ligand adopted an *endo–anti* conformation in which the pyridine rings were tilted at 12° with respect to each other and the S atom behaved as a bridging donor between two metal centres. The bridging was slightly asymmetric with Cu–S bond distances of 2.570(1) and 2.464(1) Å, which were within the normal range (2.18–3.10 Å).[21] Two pyridine rings of each tetranuclear complex were involved in intermolecular π-stacking (centroid–centroid distance 3.63 Å)[22] to form one-dimensional chains along the diagonal [011] axis (Fig. 2). No other significant interactions were observed between the chains.

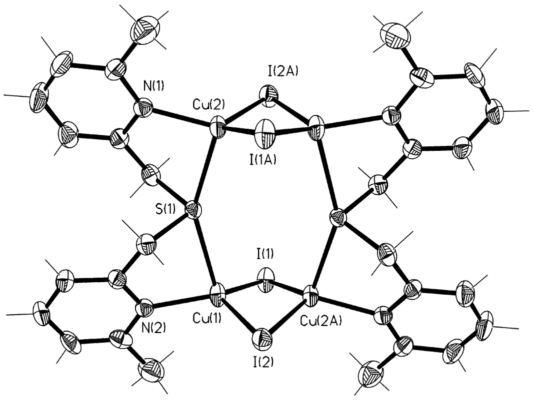

Fig. 1 Perspective view (crystallographic numbering) of **1**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Cu(1)–N(2) 2.031(3), Cu(1)–S(1) 2.570(1), Cu(1)–I(1) 2.582(1), Cu(1)–I(2) 2.652(1), Cu(2)–N(1) 2.046(3), Cu(2)–S(1) 2.464(1), Cu(2)–I(1A) 2.586(1), Cu(2)–I(2A) 2.640(1), Cu(1) ··· Cu(2A) 2.551(1); N(2)–Cu(1)–S(1) 82.47(9), N(2)–Cu(1)–I(1) 129.45(9), S(1)–Cu(1)–I(1) 108.14(5), N(2)–Cu(1)–I(2) 106.26(9), S(1)–Cu(1)–I(2) 100.88(4), I(1)–Cu(1)–I(2) 119.03(2), N(1)–Cu(2)–S(1) 84.79(9), N(1)–Cu(2)–I(1A) 125.11(9), S(1)–Cu(2)–I(1A) 111.83(4), N(1)–Cu(2)–I(2A) 107.85(9), S(1)–Cu(2)–I(2A) 99.29(4), I(1A)–Cu(2)–I(2A) 119.32(3). (Symmetry code: A $-x + 1$, $-y + 1$, $-z + 2$.)

Synthesis and structure of $[Cu_4(\mathbf{L}^2)_2I_4]$ 2

The 1 : 1 molar reaction of CuI and $\mathbf{L}^2$ in MeCN gave a yellow solution from which a yellow powder was isolated in low yield. The complex had a microanalysis consistent with a 2 : 1 metal-to-ligand ratio. Subsequently the same yellow powder was obtained from the 2 : 1 molar reaction of CuI and $\mathbf{L}^2$ in good yield (75%). As in the case of **1**, the 1 : 1 product could not be obtained.

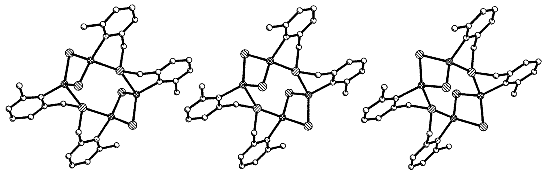

Fig. 2 A view of the polymeric chain of **1**, illustrating the intermolecular π-stacking, hydrogens are omitted for clarity.

The ^{1}H NMR spectrum of **2** in CD_3CN was consistent with a single environment for the ligand in the complex. The presence of only two methylene signals at 4.11 and 3.97 ppm indicated that fluxional processes were occurring in solution at 298 K. Electrospray mass spectrometry gave peaks for $[Cu(\mathbf{L}^2)]^+$ at *m*/*z* 294, $[Cu(\mathbf{L}^2)_2]^+$ at 523 and $[Cu_2(\mathbf{L}^2)_2I]^+$ at 714. The presence of the peak at *m*/*z* 714 suggested that the complex might exist as a dimer. However, this result was inconsistent with the microanalysis and, given the tetranuclear nature of **1**, suggested the peaks might have arisen from fragmentation processes.

The asymmetric unit contained one ligand, two Cu(I) ions and two I^- ions. The X-ray structure showed that a rare tetranuclear Cu(I) complex closely related to **1** had been isolated. The complete complex was generated by a centre of symmetry such that **2** had the molecular formula $[Cu_4(\mathbf{L}^2)_2I_4]$ (Fig. 3). The two ligands were linked together by two Cu_2I_2 cores, which led to the formation of a centrosymmetric-tetranuclear complex. Each Cu_2I_2 core consisted of a three-coordinate and a four-coordinate Cu(I) ion, which is the least common arrangement for Cu_2I_2 bridged species. One three-coordinate and one four-coordinate metal centre was bound to each ligand. Each three-coordinate Cu(I) ion adopted a distorted trigonal-planar arrangement with a coordination sphere provided by an NI_2 donor set. The four-coordinate Cu(I) ions adopted a distorted tetrahedral arrangement with a coordination sphere consisting of two bridging I^- ions, one N and one S donor. The Cu(I) ions within each Cu_2I_2 core were separated by 2.528(1) Å, which was similar to the short distance found for **1**. The ligands in **2** were in an *endo–anti* conformation with the pyridine rings tilted at 14° to each other, similar to that found in **1**. However, in contrast to **1**, the thioether S donors each were bound to only one of the available metal centres. The distance of 3.384(2) Å between the trigonal Cu centre and the adjacent S donor was too long for any bonding interaction to exist between them. The ligands were also oriented in a head-to-tail arrangement such

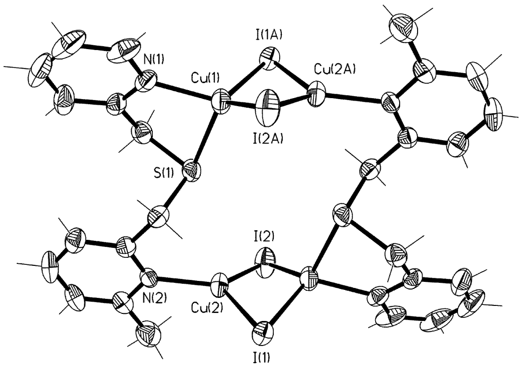

Fig. 3 Perspective view (crystallographic numbering) of **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.050(5), Cu(1)–S(1) 2.418(2), Cu(1)–I(1A) 2.649(1), Cu(1)–I(2A) 2.589(1), Cu(2)–N(2) 1.995(5), Cu(2)–I(1) 2.594(1), Cu(2)–I(2) 2.569(1), Cu(1) ··· Cu(2A) 2.528(1); N(1)–Cu(1)–S(1) 85.6(2), N(1)–Cu(1)–I(2A) 111.6(1), S(1)–Cu(1)–I(2A) 124.61(6), N(1)–Cu(1)–I(1A) 116.0(1), S(1)–Cu(1)–I(1A) 98.40(5), I(1A)–Cu(1)–I(2A) 116.87(3), N(2)–Cu(2)–I(2) 122.5(1), N(2)–Cu(2)–I(1) 117.4(1), I(1)–Cu(2)–I(2) 119.63(3). (Symmetry code: A $-x$, $-y$, $-z + 1$.)

that the methyl arms on the ligands were diametrically opposite to each other. There were no significant interactions between adjacent tetranuclear complexes suggesting that weak nondescript van der Waals interactions controlled the packing.

Synthesis and structure of $[Cu_2(L^3)I_2]_\infty$ 3

The reaction of CuI with **L**^{3} in a 2 : 1 molar ratio in MeCN gave a brown solid. Microanalysis showed the complex was consistent with a 2 : 1 metal-to-ligand ratio. In contrast to **1** and **2**, the 1 : 1 CuI complex with **L**^{3} has been isolated and crystallographically characterised as a discrete Cu_2I_2 bridged dimer.[23]

The ^{1}H NMR spectrum of **3** in $CDCl_3$ was consistent with a symmetrical complex. In addition, the presence of only one methylene signal at 4.05 ppm indicated that fluxional processes were occurring in solution at 298 K. Electrospray mass spectrometry under normal operating conditions in MeCN–H_2O (1 : 1 v/v) showed five major peaks which had the correct isotopic patterns for $[Cu(L^3)]^+$ at *m*/*z* 278, $[Cu(L^3)_2]^+$ at 494, $[Cu_2(L^3)_2I]^+$ at 686, $[Cu_3(L^3)_2I_2]^+$ at 876 and $[Cu_4(L^3)_2I_3]^+$ at 1066. These results and comparison with **1** and **2** suggested that a tetranuclear complex might exist in solution. Surprisingly, X-ray structure analysis showed that **3** existed as a one-dimensional polymer rather than the remaining member of a set of discrete tetranuclear complexes.

In the structure of **3** the asymmetric unit contained one ligand, two Cu(I) ions and two I^- ions. Two zigzag CuI chains were arranged parallel to each other such that alternating Cu(1)–I(1)–Cu(2) and Cu(1)–I(2)–Cu(2) angles were acute and obtuse, respectively (Fig. 4). The chains propagated along the *a* axis and were held together by S donors which bridged Cu centres on adjacent chains. This gave a one-dimensional polymer containing a series of centrosymmetric 12-membered $\overline{\mathrm{CuICuICuSCuICuICuS}}$ *trans*-bridged rings. Both Cu(I) ions adopted distorted tetrahedral geometries. Cu(1) was chelated by **L**^{3} and had a NSI_2 donor set and Cu(2) was bound to two ligands with a $NS'I_2$ donor set. The ligand **L**^{3} was folded in a *syn* fashion with the pyridine rings tilted by 20.3° with respect to each other and with an intramolecular π-stacking centroid–centroid distance of 3.78 Å.[22] Each folded ligand was coordinated to two different Cu centres on the same CuI chain and stacked along the outside of that chain. In addition, very weak intermolecular C–H ··· pyridine ring interactions (2.95 and 3.09 Å) existed between the ligands on the outside of the chains.[24] Although the pyridine rings of parallel one-dimensional chains interdigitated there were no significant intermolecular interactions.

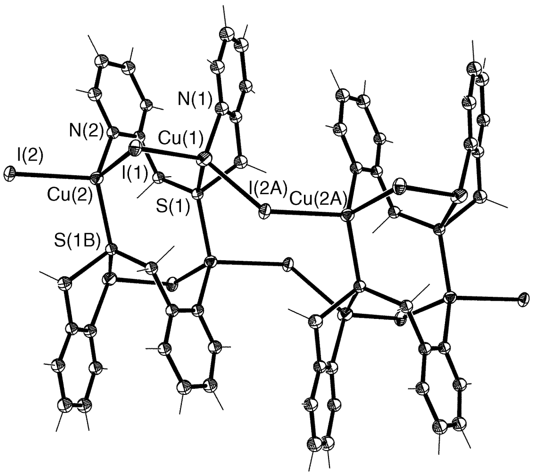

Fig. 4 Perspective view (crystallographic numbering) of **3**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.024(4), Cu(1)–S(1) 2.515(2), Cu(1)–I(1) 2.529(1), Cu(1)–I(2A) 2.588(1), Cu(2)–N(2) 2.055(3), Cu(2)–S(1B) 2.292(2), Cu(2)–I(1) 2.661(1), Cu(2)–I(2) 2.672(2), Cu(1) ··· Cu(2) 3.449(2); N(1)–Cu(1)–S(1) 83.0(1), N(1)–Cu(1)–I(1) 116.6(1), S(1)–Cu(1)–I(1) 120.49(4), N(1)–Cu(1)–I(2A) 119.3(1), S(1)–Cu(1)–I(2A) 96.97(4), I(1)–Cu(1)–I(2A) 114.96(4), Cu(1)–I(1)–Cu(2) 83.25(5), Cu(1)–I(2A)–Cu(2A) 127.63(4), N(2)–Cu(2)–S(1B) 122.9(1), N(2)–Cu(2)–I(1) 101.7(1), S(1B)–Cu(2)–I(1) 111.34(4), N(2)–Cu(2)–I(2) 109.8(1), S(1B)–Cu(2)–I(2) 105.77(4), I(1)–Cu(2)–I(2) 103.89(4). (Symmetry codes: A $x + 1, y, z$; B $1 - x, -y, -z$.)

Comparison

The sequential removal of Me groups from **L**^{1} had a dramatic effect upon the nature of the complexes formed. The most surprising result of all was the structure of **3**, which was polymeric rather than discrete and tetranuclear as in **1** and **2**. One of the major differences between the three structures was the conformation of the ligands. In **1** and **2** the ligands adopted *anti* configurations which appeared to dictate formation of tetranuclear species, while in **3** the ligand adopted a *syn* configuration which allowed intramolecular π-stacking to occur. The presence of Me groups on the pyridyl rings of the ligands in **1** and **2** may have prevented the π-stacking which resulted in polymer formation for **3**. While the different ligand conformations may have led to either tetranuclear or polymeric structure formation, the differences in coordination for **1** and **2** were not explained by such arguments. These differences may have been due to other more subtle electronic and steric effects. The electronic effect of the Me group on the pyridine ring could have increased the electron density in the aromatic ring and made the pyridyl nitrogen a stronger donor. Hence, this could have caused a Cu atom coordinated to a Me-substituted pyridyl nitrogen to be more strongly bound than if it was coordinated to a non-substituted pyridyl nitrogen. This would mean that the more electron deficient Cu centre might be expected to coordinate to another donor atom, S in this case, if it was coordinated to the less strongly donating non-substituted pyridyl nitrogen. This was exemplified by structures **2** and **3**. However, a complication appeared to arise for **1** where despite the presence of the Me groups on the pyridyl rings, the Cu atoms were coordinated to the S donors. This complication might be explained by steric considerations.

It is our belief that in the case of **1**, if electronic effects were predominant, the S atoms should have remained unbound and the ligand would have adopted an exodentate arrangement. However, this would then have meant that the Me substituents clashed unfavourably with the CuI core. Consequently, steric effects caused the ligand to adopt an endodentate conformation through coordination of the S donors and so these unfavourable interactions were avoided.

It can be concluded that the Me groups were non-innocent and were responsible for affecting the gross structure of the complexes through a mix of electronic and steric effects. Therefore, the placement of Me-substituents on ligands should be given some careful consideration in the construction of coordination complexes and arrays.

Experimental

General

The precursors 2-(chloromethyl)pyridine,[15] 2-(chloromethyl)-6-methylpyridine[15] and 6-methyl-2-(sulfanylmethyl)pyridine[16] and the ligands **L**^{1} [13] and **L**^{3} [14] were prepared by literature methods. The ^{1}H and ^{13}C NMR spectra were recorded on either a Varian $^{\mathrm{unity}}$INOVA 300 or 500 MHz spectrometer. Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago. Electrospray mass spectra (ES MS) were collected at the University of Waikato in postive-ion mode with a VG platform II mass spectrometer, using MeCN–H_2O (1 : 1 v/v) as the mobile phase.

Table 1 Crystallographic data for complexes **1**, **2** and **3**

	1	**2**	**3**
Molecular formula	$C_{28}H_{32}Cu_4I_4N_4S_2$	$C_{26}H_{28}Cu_4I_4N_4S_2$	$(C_{24}H_{24}Cu_4I_4N_4S_2)_\infty$
M	1250.46	1222.40	1194.36
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	9.351(5)	10.354(5)	7.854(5)
b/Å	10.314(5)	16.245(5)	9.670(5)
c/Å	10.441(5)	10.528(5)	11.468(5)
α/°	105.338(5)		78.079(5)
β/°	102.112(5)	100.080(5)	70.344(5)
γ/°	102.073(5)		69.319(5)
U/Å^3	1049.9(4)	1744(1)	763.6(7)
Z	1	2	1
T/K	163(2)	168(2)	123(2)
μ/mm^{-1}	5.829	6.091	6.951
Reflections collected	11726	21993	6386
Unique reflections (R_{int})	3680 (0.0196)	3508 (0.0251)	3462 (0.0278)
R_1 indices [$I > 2\sigma(I)$]	0.0273	0.0370	0.0287
$wR2$ (all data)	0.0708	0.1050	0.0634

Ligand preparation

2-(6-Methylpyridyl)methyl(2-pyridyl)methylsulfide (L^2). 6-Methyl-2-(sulfanylmethyl)pyridine (4.0 g, 0.028 mol) was added to degassed MeOH (250 mL) containing 0.60 g (0.028 mol) of Na metal and was stirred for 1 h. 2-(Chloromethyl)pyridine (3.6 g, 0.028 mol) was added to the above solution, refluxed for 4 h and stirred overnight. The resulting solution was reduced in volume to give a brown residue, which was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 × 100 mL), dried ($MgSO_4$) and reduced again to give a crude oil (yield 5.1 g, 80%). Treatment of the crude product (2.7 g) on a silica gel column (5% hydrated v/v) eluted with CH_2Cl_2–$CHCl_3$ (6 : 4 v/v) gave **L**^{2} as a golden oil (0.94 g, 35%). (Found: M$^+$, 231.0963, $^{12}C_{13}{}^1H_{15}{}^{14}N_2{}^{32}S$ requires M, 231.0956); ^{1}H NMR ($CDCl_3$): δ 8.52 [1H, d, ^3J(HH) 4.0], 7.61 [1H, t, ^3J(HH) 7.5], 7.48 [1H, t, ^3J(HH) 7.5], 7.36 [1H, d, ^3J(HH) 7.5], 7.16 [1H, d, ^3J(HH) 7.5], 7.13 [1H, dd, ^3J(HH) 7.5, 4.0], 6.98 [1H, d, ^3J(HH) 7.5 Hz], 3.81 (2H, s), 3.77 (2H, s) and 2.52 (3H, s); ^{13}C NMR ($CDCl_3$): δ 158.4, 157.9, 157.5, 149.2, 136.8, 136.5, 123.2, 121.8, 121.4, 120.1, 37.6, 37.5 and 24.3.

Complexes

[Cu$_4$(L^1)$_2$I$_4$] 1. CuI (156 mg, 0.819 mmol) dissolved in degassed MeCN (20 mL) was added *via* cannula to **L**^{1} (100 mg, 0.409 mmol) dissolved in degassed MeCN (20 mL) and allowed to stir for 1 h. The yellow solution was reduced in volume, diethyl ether was added and a tan powder was isolated (yield 129 mg, 50.4%). Pale yellow–green crystals were grown from the slow diffusion of diethyl ether into a concentrated solution of the complex in MeCN. (Found: C, 27.3; H, 2.7; N, 4.4; S, 5.1. Calc. for $C_{28}H_{32}N_4S_2Cu_4I_4$: C, 26.9; H, 2.6; N, 4.5; S, 5.1%); ^{1}H NMR (CD_3CN): δ 7.67 [2H, t, ^3J(HH) 7.5], 7.24 [2H, d, ^3J(HH) 7.5], 7.21 [2H, d, ^3J(HH) 7.5 Hz], 4.09 (4H, s) and 2.83 (6H, s); ES MS: *m*/*z* 308 [Cu(**L**^{1})]$^+$, 553 [Cu(**L**^{1})$_2$]$^+$, 743 [Cu$_2$(**L**^{1})$_2$I]$^+$, 934 [Cu$_3$(**L**^{1})$_2$I$_2$]$^+$ and 1124 [Cu$_4$(**L**^{1})$_2$I$_3$]$^+$.

[Cu$_4$(L^2)$_2$I$_4$] 2. CuI (83 mg, 0.44 mmol) dissolved in degassed MeCN (20 mL) was added *via* cannula to **L**^{2} (50 mg, 0.22 mmol) dissolved in degassed MeCN (20 mL) and allowed to stir for 1 h. The yellow solution was reduced in volume, diethyl ether was added and a yellow powder was isolated (yield 100 mg, 75%). Pale yellow crystals were grown from the slow diffusion of diethyl ether into a concentrated solution of the complex in MeCN. (Found: C, 25.7; H, 2.1; N, 4.6; S, 5.2. Calc. for $C_{26}H_{28}N_4S_2Cu_4I_4$: C, 25.5; H, 2.3; N, 4.6; S, 5.3%); ^{1}H NMR (CD_3CN): δ 8.95 [1H, d, ^3J(HH) 4.2], 7.70 [1H, t, ^3J(HH) 7.5], 7.60 [1H, t, ^3J(HH) 7.5], 7.37 [1H, d, ^3J(HH) 7.5], 7.35 [1H, d, ^3J(HH) 7.5], 7.18 [1H, dd, ^3J(HH) 7.5, 4.2], 7.03 [1H, d, ^3J(HH) 7.5 Hz], 4.11(2H, s), 3.97 (2H, s) and 3.02 (3H, s); ES MS: *m*/*z* 294 [Cu(**L**^{2})]$^+$, 523 [Cu(**L**^{2})$_2$]$^+$ and 714 [Cu$_2$(**L**^{2})$_2$I]$^+$.

[Cu$_2$(L^3)I$_2$]$_\infty$ 3. CuI (176 mg, 0.924 mmol) dissolved in degassed MeCN (20 mL) was added *via* cannula to **L**^{3} (100 mg, 0.462 mmol) dissolved in degassed MeCN (20 mL) and allowed to stir overnight. The tan precipitate which resulted was filtered and dried *in vacuo* (yield 154 mg, 55.8%). Dark brown crystals were grown from the slow diffusion of diethyl ether into a concentrated solution of the complex in MeCN. (Found: C, 24.8; H, 1.9; N, 5.5; S, 5.4. Calc. for $C_{24}H_{24}N_4S_2Cu_4I_4 \cdot 1/2CH_3CN$: C, 24.7; H, 2.1; N, 5.2; S, 5.3%); ^{1}H NMR ($CDCl_3$): δ 8.94 [2H, d, ^3J(HH) 5.1, py-H], 7.71 [2H, dt, ^3J(HH) 7.5, ^4J(HH) 1.8 Hz, py-H], 7.32 [4H, m, py-H] and 4.05 (4H, s, CH$_2$); ES MS: *m*/*z* 278 [Cu(**L**^{3})]$^+$, 494 [Cu(**L**^{3})$_2$]$^+$, 686 [Cu$_2$(**L**^{3})$_2$I]$^+$, 876 [Cu$_3$(**L**^{3})$_2$I$_2$]$^+$ and 1066 [Cu$_4$(**L**^{3})$_2$I$_3$]$^+$.

X-Ray crystallography

Diffraction data for **1** and **2** were collected on a Bruker SMART CCD diffractometer and data for **3** were collected on a Nonius Kappa-CCD diffractometer, both had graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Intensities were corrected for Lorentz-polarisation effects[25] and for **1** and **2** a multiscan absorption correction[26] was applied. The structures were solved by direct methods (SHELXS)[27] and refined on F^2 using all data by full-matrix least-squares procedures (SHELXL 97).[28] All calculations were performed using the WinGX interface.[29] For **2** a large peak, possibly a Fourier ripple, of 3.2 e Å^{-3} was located at 1.0 Å from an I atom. Crystallographic data for the three structures are listed in Table 1.

CCDC reference numbers 176214–176216.

See http://www.rsc.org/suppdata/dt/b1/b111400j/ for crystallographic data in CIF or other electronic format.

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