Notes

The Synthesis, Crystal and Molecular Structure† of a Copper(I) Complex of 2(1*H*)-Pyridinethione: an Intermediate in Cu_4S_4 Heterocubane Build Up

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The reaction of 2(1*H*)-pyridinethione with copper(II) chloride can give a number of products, one of which is the binuclear complex $[Cu_2(HL)_6]Cl_2$. The crystal structure of this species reveals each metal atom to be in a near-tetrahedral environment, being bonded to two terminal and two bridging thione ligands. The chloride ions are not bonded to the metal. Treatment of this dimer with base results in the formation of a cubane-like $[(CuL)_4]$ cluster.

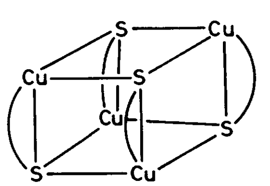
2(1*H*)-Pyridinethione (HL) is a versatile ambidentate ligand which may adopt a number of bonding modes. Examples are known in which the ligand acts as a unidentate *S* donor,[1–3] a chelating bidentate *NS* donor,[4–9] or a bridging *NS* donor ligand.[10] A comparison with the known propensity of benzenethiol to form heterocubane M_4S_4 clusters, in iron and zinc complexes,[11] suggested that 2(1*H*)-pyridinethione might also form such compounds. The proposed role of heterocubanes in biological processes as diverse as photosynthesis and nitrogen fixation prompted us to study the incorporation of pyridyl functionalisation into such species. In this paper, we report the preparation, crystal and molecular structure of $[Cu_2(HL)_6]Cl_2$ which contains both terminal and bridging unidentate ligands, and confirm its conversion into $[(CuL)_4]$.

Results and Discussion

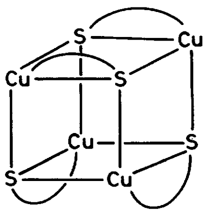
The reaction of ethanolic solutions of copper(II) chloride with 2 or 3 equivalents of 2(1*H*)-pyridinethione led to precipitation of the insoluble yellow diamagnetic copper(I) complex $[Cu_2(HL)_2Cl_2]$, identical with the complex described by Evans and Wilkinson.[12] It is not clear whether this is a chloro-bridged or a 2(1*H*)-pyridinethione-bridged species. The yields of this complex are far from quantitative, and it is clear that one equivalent of 2(1*H*)-pyridinethione is oxidised to bis(2-pyridyl) disulphide for every copper(II) ion which is reduced. The disulphide could be isolated from the mother-liquor as a pale yellow oil, which solidified upon standing (*m*/*z* 220 and 110).

Treatment of this yellow complex with 2 equivalents of HL in ethanol, of ethanolic copper(II) chloride with 6 equivalents of HL, or of an ethanolic suspension of copper(I) chloride with 3 equivalents of HL led to the formation of deep orange solutions from which large orange crystals separated upon standing. Microanalysis suggested a stoicheiometry $Cu(HL)_3Cl$; no mass spectrum could be obtained using electron impact or fast atom bombardment conditions. The ^1H n.m.r. spectrum of a dimethyl sulphoxide (dmso) solution of the complex showed the resonances expected for a complex of HL, in which there is only a single ligand environment. We presume that this is indicative of cleavage of the dimer (see below) by the donor solvent to give $[Cu(HL)_3]^+$ or $[Cu(HL)_3(dmso)]^+$ solution species. The dmso solution was orange. Attempted recrystallisation from methanol or ethanol resulted in decomposition and the deposition of yellow $[Cu_2(HL)_2Cl_2]$; when an excess of 2(1*H*)-pyridinethione was added, the precipitate redissolved to give an orange solution from which orange crystals of the dimer separated on standing.

Treatment of the orange complex with an acetonitrile solution of $[Cu(MeCN)_4][PF_6]$ or an aqueous ethanolic solution of sodium acetate led to the deposition of an extremely insoluble orange compound $[(CuL)_4]$. The mass spectrum of this complex exhibits the highest mass peaks at *m*/*z* 692, 694, 696, 698, and 700, as expected for a tetrameric structure. These results are exactly in accord with those reported previously.[13]



(1)



(2)

We cannot distinguish between the two symmetry-related heterocubane structures (**1**) or (**2**). In order better to understand the cluster build-up to the heterocubane, we have determined the crystal and molecular structure of the orange complex.

The molecular structure of the complex cation $[Cu_2(HL)_6]^{2+}$ is shown in the Figure, together with the atom-numbering scheme adopted. Selected bond lengths and angles are presented in Table 1. The cation exists as a dimer with a crystallographically imposed centre of symmetry. The copper(I) atoms display a slightly distorted tetrahedral geometry. The two chloride ions are not co-ordinated to the metal ions, but are hydrogen bonded to ligand N–H groups [$Cl \cdots H$ 2.133(10) and 2.189(10) Å]. Each copper atom is bonded to the sulphur atoms of two terminal and two bridging 2(1*H*)-pyridinethione ligands. The ligands are all in the thione tautomeric form. The two terminal ligands are similar, but non-equivalent [Cu–S 2.284(2) and 2.315(2) Å]. The bridging sulphur atoms and the two copper atoms form a planar parallelogram, with two short [2.308(2) Å] and two longer Cu–S bonds [2.498(3) Å]. Each bridging sulphur atom exhibits one long and one short Cu–S interaction. The distance between the two copper atoms is

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Selected bond lengths (Å) and interbond angles (°) for $[Cu_2(HL)_6]Cl_2$

S(1)–Cu(1)	2.308(2)	S(2)–Cu(1)	2.284(2)
S(1′)–Cu(1)	2.498(3)	S(3)–Cu(1)	2.315(2)
Cu(1)–Cu(1′)	2.907(2)	S(2)–C(7)	1.719(8)
C(1)–S(1)	1.715(8)	C(7)–N(12)	1.348(11)
C(1)–N(2)	1.357(10)	C(11)–N(12)	1.335(13)
C(3)–N(2)	1.379(12)	C(10)–C(11)	1.384(15)
C(3)–C(4)	1.354(13)	C(9)–C(10)	1.375(15)
C(4)–C(5)	1.349(15)	C(8)–C(9)	1.372(13)
C(5)–C(6)	1.393(13)	C(7)–C(8)	1.401(12)
C(1)–C(6)	1.372(11)	S(3)–C(13)	1.725(9)
C(13)–C(14)	1.393(11)	C(14)–C(15)	1.361(14)
C(15)–C(16)	1.399(16)	C(16)–C(17)	1.362(14)
C(17)–N(18)	1.340(13)	N(18)–C(13)	1.360(10)

S(1′)–Cu(1)–S(1)	105.7(1)	S(1′)–Cu(1)–S(2)	108.8(1)
S(1′)–Cu(1)–S(3)	99.7(1)	S(1)–Cu(1)–S(2)	116.0(1)
S(1)–Cu(1)–S(3)	118.7(1)	Cu(1)–S(1)–Cu(1′)	74.3(1)
Cu(1)–S(1)–C(1)	112.9(3)	Cu(1)–S(1′)–C(1′)	102.0(3)
Cu(1)–S(3)–C(13)	104.5(3)	Cu(1)–S(2)–C(7)	111.5(3)
C(1)–N(2)–C(3)	123.7(7)	N(2)–C(3)–C(4)	118.4(8)
C(3)–C(4)–C(5)	120.0(9)	C(4)–C(5)–C(6)	120.8(9)
C(5)–C(6)–C(1)	120.4(8)	C(6)–C(1)–N(2)	116.7(7)
C(6)–C(1)–S(1)	123.5(6)	S(2)–C(7)–C(8)	125.0(7)
C(7)–C(8)–C(9)	121.3(8)	C(8)–C(9)–C(10)	119.1(9)
C(9)–C(10)–C(11)	119.2(9)	C(10)–C(11)–N(12)	120.0(9)
C(11)–N(12)–C(7)	123.4(8)	N(12)–C(7)–C(8)	116.8(8)
N(12)–C(7)–S(2)	118.2(6)	S(3)–C(13)–C(14)	125.5(7)
C(13)–C(14)–C(15)	119.7(8)	C(14)–C(15)–C(16)	121.8(9)
C(15)–C(16)–C(17)	116.6(10)	C(16)–C(17)–N(18)	121.6(9)
C(17)–N(18)–C(13)	122.7(7)	N(18)–C(13)–C(14)	117.3(8)
N(18)–C(13)–S(3)	117.1(6)	S(2)–Cu(1)–S(3)	106.5(1)
S(1)–C(1)–N(2)	119.8(6)		

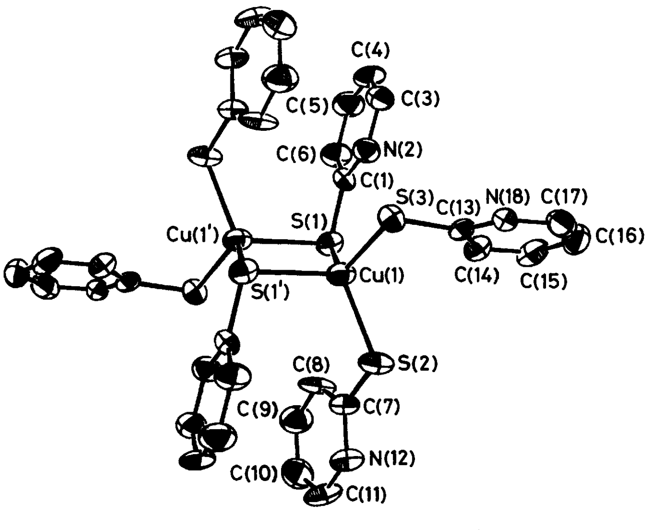

Figure. The molecular structure of the $[Cu_2(HL)_6]^{2+}$ cation showing the numbering scheme adopted. Hydrogen atoms are omitted for clarity

2.907(2) Å, which is considerably greater than the sum of the ionic radii (1.92 Å).[14] The shorter Cu–S bonds are in the range 2.2—2.35 Å regarded as typical for such interactions; the longer bonds between each copper and one of the bridging ligands are only slightly greater than the sum of the tetrahedral covalent radii (2.39 Å).[14]

Table 2. Atomic co-ordinates (× 10⁴)

Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	651(1)	4 569(1)	9 219(1)
S(1)	2 370(3)	5 421(1)	10 246(2)
C(1)	2 359(10)	6 218(4)	9 608(6)
N(2)	1 567(9)	6 271(4)	8 570(5)
C(3)	1 509(14)	6 888(5)	7 993(7)
C(4)	2 259(14)	7 479(5)	8 493(9)
C(5)	3 075(15)	7 452(5)	9 523(9)
C(6)	3 143(12)	6 821(4)	10 089(7)
S(2)	1 786(3)	3 444(1)	9 392(2)
C(7)	2 585(12)	3 228(4)	10 696(7)
C(8)	3 090(13)	3 717(5)	11 519(7)
C(9)	3 768(14)	3 500(5)	12 536(8)
C(10)	3 837(14)	2 788(6)	12 763(8)
C(11)	3 322(13)	2 308(5)	11 948(9)
N(12)	2 761(9)	2 537(4)	10 958(6)
S(3)	−273(3)	4 774(1)	7 422(2)
C(13)	1 626(10)	4 595(4)	6 903(6)
C(14)	3 417(11)	4 614(4)	7 462(7)
C(15)	4 803(13)	4 490(5)	6 948(8)
C(16)	4 486(14)	4 345(5)	5 863(9)
C(17)	2 716(14)	4 297(5)	5 357(7)
N(18)	1 348(9)	4 409(3)	5 865(5)
Cl(1)	7 983(3)	3 754(1)	4 465(2)

The structure of $[Cu_2(HL)_6]Cl_2$ is in marked contrast to that of the previously characterised complex $[Cu(HL)_3][NO_3]$, which forms discrete, mononuclear, trigonal $[Cu(HL)_3]^+$ cations.[2] The Cu–S bonds to the terminal ligands are similar to, but slightly longer than, those in $[Cu(HL)_3]^+$ (*av.* Cu–S 2.222 Å). This serves to support the existence of some multiple-bond character in the Cu–S interaction; the overlap with a trigonal copper(I) centre is expected to be better than with a tetrahedral centre. The S–C bonded distances are all essentially equivalent, with an average of 1.720(9) Å, which is slightly longer than in $[Cu(HL)_3]^+$, but fully in accord with the ligand existing as the thione tautomer.[9]

Experimental

2(1*H*)-Pyridinethione was used as obtained from Aldrich, and was stored under a dinitrogen atmosphere. All preparations and manipulations were conducted under an atmosphere of dinitrogen. Proton n.m.r. spectra were recorded on Varian CFT-20 or Bruker WM 250 spectrometers.

Preparation of $[Cu_2(HL)_2Cl_2]\cdot H_2O$.—2(1*H*)-Pyridinethione (4.4 g, 0.04 mol) was added to a solution of copper(II) chloride (2.7 g, 0.02 mol) in warm 95% ethanol (50 cm³). The solution was heated to reflux for 2 min, and the yellow precipitate collected by filtration (Found: C, 27.4; H, 2.5; N, 6.2. $C_5H_7ClCuNO$ requires C, 27.4; H, 2.7; N, 6.4%).

Preparation of $[Cu_2(HL)_6]Cl_2$.—2(1*H*)-Pyridinethione (4.4 g, 0.04 mol) was added to a solution of copper(II) chloride (0.7 g, 0.005 mol) in warm 95% ethanol (50 cm³) to give a deep orange solution. Upon cooling, orange crystals of the required complex were deposited (Found: C, 41.5; H, 3.6; N, 9.6. $C_{30}H_{30}Cl_2Cu_2N_6S_6$ requires C, 41.7; H, 3.5; N, 9.5%).

Crystal Structure Determination of $[Cu_2(HL)_6]Cl_2$.—Suitable single crystals were obtained as orange blocks by slow cooling of a freshly prepared orange ethanolic solution of the complex.

Crystal data. $C_{30}H_{30}Cl_2Cu_2N_6S_6$, $M = 864.96$, monoclinic, $a = 7.505(11)$, $b = 18.892(17)$, $c = 12.896(15)$ Å, $\beta = 101.49(13)°$, $U = 1\,791.81$ Å³ (by least-squares refinement for 56 automatically centred reflections in the range $18 < 2\theta < 23°$,

$\lambda = 0.710\,69$ Å), space group $P2_1/n$ (alternative $P2_1/c$, no. 14), $Z = 2$, $D_c = 1.603$ g cm^{-3}, $F(000) = 880$, crystal dimensions $0.46 \times 0.21 \times 0.13$ mm, μ(Mo-K_α) = 16.65 cm^{-1}.

Data collection and processing.[15] Stoe-Siemens diffractometer, 30 step ω–2θ scan mode with ω scan width 0.04° per step, ω scan time 0.5—2.0 s per step, graphite-monochromated Mo-K_α radiation. 6 829 Reflections were measured ($5.0 \leqslant 2\theta \leqslant 43.0°$, $-h$, $\pm k$, $\pm l$), 2 062 unique (merging $R = 0.053$, absorption correction not applied), giving 1 649 with $F > 4\sigma(F)$. No significant variation of standard reflections.

Structure analysis and refinement. The Cu atom position was determined from a Patterson synthesis, followed by Fourier difference techniques. Blocked-cascade least squares with all non-hydrogen atoms anisotropic. Hydrogen atoms placed in idealised positions and allowed to ride 1.08 Å from the relevant C atoms and 1.01 Å from the relevant N atoms during refinement; all hydrogen atoms were assigned a common isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F) + 0.003|F|^2]^{-1}$ gave satisfactory agreement analysis. Final R and R' values were 0.060 and 0.065. Complex neutral-atom scattering factors were employed,[16] and all computations were performed on the IBM 3081 computer at the University of Cambridge using SHELX 76.[17] The final atomic fractional co-ordinates are listed in Table 2.

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