Synthesis and Crystal Structure of Hexanuclear Copper(I) Complexes of μ_3-Pyridine-2-thionate†

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1*H*-Pyridine-2-thione (C_5H_4NSH) reacts with $[Cu(MeCN)_4]PF_6$ in acetone to give an orange compound $[Cu_6(C_5H_4NS)_6]$, which crystallized in the monoclinic space group $P2_1/n$, a = 12.257(2), b = 16.029(2), c = 9.581(1) Å, β = 108.859(9)°, and Z = 2. The single-crystal *X*-ray structure of the complex shows a distorted octahedral core of six copper atoms, with metal–metal distances ranging from 2.795(1) to 3.160(1) Å. Each copper has a trigonal geometry constituted by the two thiolate sulphur and one pyridine nitrogen atoms, as distinct from the common copper–thione sulphur co-ordination in other copper(I)–C_5H_4NSH complexes. The copper atom deviates highly from the S_2N co-ordination plane. The reaction solution was examined by ^1H n.m.r. spectroscopy, which reveals the formation of several low-molecular-weight species in the early stages of the reaction.

The great interest in copper(I) complexes stems in part from the unique and sometimes puzzling variation in their structural formats[1] and chemical reactivity with changes in ligands, and also from the desire to understand the mode of action of the proteins having copper centres.[2] The recent findings[3] that copper(I) can form high nuclearity complexes have added an additional and intriguing dimension to this copper(I) chemistry. The size of copper cores ranges from two to twelve.[3] However, copper(I) complexes of high nuclearity are still sparse, and the number of examples sharply decreases with the increasing nuclearity.

1*H*-Pyridine-2-thione (C_5H_4NSH) co-ordinates as such through the sulphur atom in its most common modes of co-ordination (**A**) and (**B**), leading to the formation of mononuclear and binuclear complexes of copper(I).[4] Distinct from other transition-metal complexes,[5] where it can co-ordinate as the conjugate anion, pyridine-2-thionate ($C_5H_4NS^-$), in various ways, the co-ordination of $C_5H_4NS^-$ to copper(I) is rare, indicating that copper(I) seems to prefer C_5H_4NSH. Although the reaction of C_5H_4NSH with copper-(I) or -(II) gives various species,[6] most have not been structurally characterized.

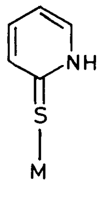
We have found that the reaction of $[Cu(MeCN)_4]PF_6$ with C_5H_4NSH results in the formation of $[Cu_6(C_5H_4NS)_6]$, which has a discrete cluster structure consisting of $C_5H_4NS^-$ groups bonded to the Cu_6 core by Cu–S–Cu and Cu–N bonds, (**C**). This paper concerns the preparation of this complex and its *X*-ray crystallographic structure, and the investigation of the reaction of C_5H_4NSH by ^1H n.m.r. spectroscopy.

Experimental

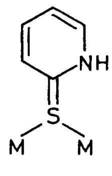
Materials.—The complex $[Cu(MeCN)_4]PF_6$ was prepared according to the literature.[7] 1*H*-Pyridine-2-thione and 2-mercapto-1-methylimidazole [$C_3H_2N(Me)SH$] were purchased from Wako Ltd. 1*H*-4-Methylpyridine-2-thione (4-MeC_5H_3NSH) was synthesized from 2-amino-4-methylpyridine.[8a]

All operations were carried out under dry and purified argon by using the standard Schlenk or vacuum-line technique but products were worked up in the open atmosphere.

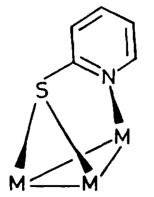
Preparation of $[Cu_6(C_5H_4NS)_6]$ (**1**).—The complex $[Cu(MeCN)_4]PF_6$ (186.4 mg, 0.5 mmol) was added to an acetone solution (100 cm³) of C_5H_4NSH (55.6 mg, 0.5 mmol) and this mixture was stirred for 1 h, giving a clear yellow solution (A). Solution A was transferred to a glass tube and sealed therein. The yellow solution became orange after about 1 d. When the solution was allowed to stand for 1 month brick-shaped crystals were obtained on the walls of the glass tube. One of them was used for *X*-ray diffraction, and the molecular structure successfully determined as $[Cu_6(C_5H_4NS)_6]$. The crystals were collected and the i.r. spectrum measured: 1 578s, 1 549s, 1 450s, 1 414s, 1 268m, 1 126s, 755s, and 721s cm⁻¹.



(**A**)



(**B**)



(**C**)

Solution A was heated under reflux for 24 h. During this time an orange precipitate was obtained. This orange material was filtered off and washed with the solvent. The dried material (4.1 × 10⁻² g) was stable to air. The i.r. spectrum shows that the main bands are in good agreement with those of the single-crystal samples but additional bands are not negligible, indicating that this material contains an impurity. The insolubility of this material made purification difficult.

Crystallography.-Crystal data. $C_{30}H_{24}Cu_6N_6S_6$, monoclinic, space group $P2_1/n$, a = 12.257(2), b = 16.029(2), c = 9.581(1) Å, β = 108.859(9)°, U = 1 781.2 Å³, Z = 2, D_c = 1.943 g cm⁻³, $F(000)$ = 1 032, $\lambda(\text{Mo-}K_\alpha)$ = 0.710 69 Å, μ = 39.0 cm⁻¹, T = 298 K.

X-*Ray data collection.* A single crystal (0.2 × 0.2 × 0.2 mm) of the compound was glued on top of a glass fibre and studied on an Enraf-Nonius CAD4 automatic diffractometer. Preliminary investigation revealed the crystal to be monoclinic. Unit-cell parameters were determined from a least-squares fit of

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Positional parameters for $[Cu_6(C_5H_4NS)_6]$

Atom	*x*	*y*	*z*
Cu(1)	0.097 14(8)	−0.104 56(6)	0.106 19(9)
Cu(2)	0.039 59(8)	−0.046 07(6)	−0.183 4(1)
Cu(3)	−0.140 62(8)	−0.075 89(6)	−0.037 59(9)
S(1)	−0.084 3(2)	−0.149 6(1)	−0.200 2(2)
S(2)	0.256 2(1)	−0.036 1(1)	0.105 9(2)
S(3)	0.031 8(2)	−0.075 6(1)	0.294 5(2)
N(1)	0.064 5(5)	−0.224 1(4)	0.032 3(6)
N(2)	0.204 0(5)	−0.060 6(4)	−0.181 8(6)
N(3)	−0.168 7(5)	−0.141 0(4)	0.130 7(6)
C(11)	0.118 3(6)	−0.290 3(5)	0.111 3(8)
C(12)	0.095 9(7)	−0.370 7(5)	0.062 9(9)
C(13)	0.014 4(7)	−0.383 3(5)	−0.072(1)
C(14)	−0.042 3(7)	−0.317 3(5)	−0.151 6(8)
C(15)	−0.014 6(6)	−0.235 9(5)	−0.097 7(7)
C(21)	0.229 0(7)	−0.073 9(6)	−0.309 2(9)
C(22)	0.339 2(8)	−0.087 2(7)	−0.307 8(9)
C(23)	0.426 3(7)	−0.089 9(7)	−0.176 4(9)
C(24)	0.402 1(7)	−0.077 9(6)	−0.048 8(9)
C(25)	0.289 3(6)	−0.062 2(5)	−0.056 3(7)
C(31)	−0.268 7(7)	−0.183 4(6)	0.106 7(9)
C(32)	−0.294 5(8)	−0.220 1(6)	0.222(1)
C(33)	−0.220 1(8)	−0.213 5(6)	0.361 4(9)
C(34)	−0.120 7(7)	−0.171 5(6)	0.383 7(9)
C(35)	−0.095 9(6)	−0.133 6(5)	0.265 9(7)

Table 2. Bond distances (Å) and angles (°) for $[Cu_6(C_5H_4NS)_6]$

Cu(1)–Cu(2)	2.795(1)	Cu(2)–S(1)	2.220(2)
Cu(1)–Cu(3)	2.829(1)	Cu(2)–S(3′)	2.257(2)
Cu(2)–Cu(3)	3.009(2)	Cu(2)–N(2)	2.024(6)
Cu(1)–Cu(2′)	3.160(1)	Cu(3)–S(1)	2.235(2)
Cu(1)–Cu(3′)	3.051(1)	Cu(3)–S(2′)	2.249(2)
Cu(2)–Cu(3′)	2.853(1)	Cu(3)–N(3)	2.041(7)
Cu(1)–S(2)	2.238(2)	S(1)–C(15)	1.751(7)
Cu(1)–S(3)	2.247(2)	S(2)–C(25)	1.777(8)
Cu(1)–N(1)	2.037(6)	S(3)–C(35)	1.765(8)
Cu(2)–Cu(1)–Cu(2′)	89.62(4)	Cu(1)–Cu(3)–Cu(2′)	67.57(4)
Cu(2)–Cu(1)–Cu(3)	64.69(3)	Cu(1′)–Cu(3)–Cu(2)	62.86(3)
Cu(2)–Cu(1)–Cu(3′)	58.24(3)	Cu(1′)–Cu(3)–Cu(2′)	56.38(4)
Cu(2′)–Cu(1)–Cu(3)	56.58(3)	Cu(2)–Cu(3)–Cu(2′)	91.61(4)
Cu(2′)–Cu(1)–Cu(3′)	57.92(4)	S(2)–Cu(1)–S(3)	115.89(8)
Cu(3)–Cu(1)–Cu(3′)	88.01(4)	S(2)–Cu(1)–S(2)	122.3(2)
Cu(1)–Cu(2)–Cu(1′)	90.38(4)	S(3)–Cu(1)–N(1)	113.1(2)
Cu(1)–Cu(2)–Cu(3)	58.22(3)	S(1)–Cu(2)–S(3′)	117.35(7)
Cu(1)–Cu(2)–Cu(3′)	65.38(3)	S(1)–Cu(2)–N(2)	124.8(2)
Cu(1′)–Cu(2)–Cu(3)	59.22(3)	S(3′)–Cu(2)–N(2)	109.7(2)
Cu(1′)–Cu(2)–Cu(3′)	55.85(3)	S(1)–Cu(3)–S(2′)	121.77(7)
Cu(3)–Cu(2)–Cu(3′)	88.39(4)	S(1)–Cu(3)–N(3)	116.7(2)
Cu(1)–Cu(3)–Cu(1′)	91.99(4)	S(2′)–Cu(3)–N(3)	112.7(2)
Cu(1)–Cu(3)–Cu(2)	57.09(3)		

Numbers in parentheses are estimated standard deviations in the least significant digits. Primed atoms are related to unprimed ones by a centre of symmetry.

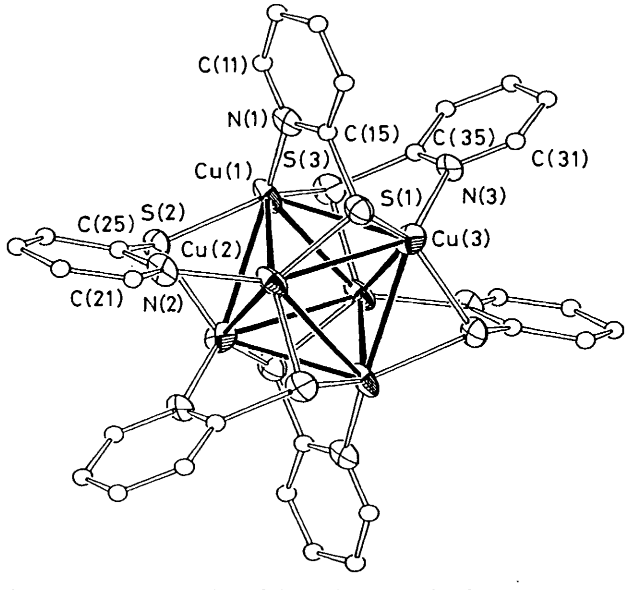

Figure 1. ORTEP drawing of the entire molecule of $[Cu_6(C_5H_4NS)_6]$ with thermal ellipsoids at the 50% probability level for Cu, S, and N atoms. Ellipsoids of the carbon atoms in pyridine rings have been arbitrarily reduced. The numbers of the unlabelled pyridine carbon atoms follow from those given. Only half the atoms are labelled; others are related by a centre of inversion

25 accurately centred reflections. Intensities were gathered in an ω—2θ scan mode. Lorentz, polarization, and absorption corrections were applied. Of the 4 119 unique reflections measured, 2 214 were considered observed [$I > 3\sigma(I)$] and used in the subsequent structure analysis. The Laue class and the axial dimensions were confirmed with oscillation photographs. From the systematic absences, the space group was uniquely determined to be $P2_1/n$.

Solution and refinement of the structure. The positions of the three independent copper atoms were obtained *via* direct methods using the MULTAN[8b] program. Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms of the pyridyl groups were placed in calculated positions and their parameters refined with fixed isotropic thermal parameters. Finally two cycles of refinement led to convergence at $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o| = 0.0489$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.0540$, $w = [\sigma^2(F) + (0.02F)^2]^{-1}$, $S = 1.48$, $\Delta e = 0.96$ e Å^{-3}, and the largest shift/estimated standard deviation (e.s.d.) at final cycle, 0.58. The fractional positional parameters for non-hydrogen atoms are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Physical Measurements.—I.r. spectra were recorded as KBr discs with a Jasco FTIR-800 spectrometer, ^1H n.m.r. spectra on a JEOL GSX-270 spectrometer operating in the Fourier-transform mode (16 K data-points transform of spectral width 3 500 Hz after 700 pulses) at −90 °C ($SiMe_4$ as internal reference). The n.m.r. signal assignments were made with the aid of double-resonance techniques.

Results and Discussion

Structure of $[Cu_6(C_5H_4NS)_6]$ (**1**).—The entire molecule is shown in Figure 1, where the atomic numbering scheme is also given. The C_i symmetry is easily recognized. Table 2 provides a list of important bond distances and angles with their e.s.d.s.

As shown clearly in Figure 1, the molecule (**1**) contains an octahedral core of copper atoms. This Cu_6 core is distorted significantly from precise O_h symmetry, with individual copper–copper bond distances ranging from 2.795(1) to 3.160(1) Å [average 2.950(1) Å]. The overall pattern of metal–metal bond lengths is such that distances within two mutually *trans* faces [*viz.* Cu(1)–Cu(2′)–Cu(3′) and Cu(1′)–Cu(2)–Cu(3)] range from 3.009(2) to 3.160(1) Å [average 3.073(1) Å], while the

Table 3. Structures of hexanuclear copper(I) complexes

	Cu–Cu distance (Å)			
Compounds	shortest, longest	average	Structure[a] of Cu_6 core	Geometry[b] of each copper (donor set)[c]
$[Cu(Pr_2NCOS)]_6$ [d]	2.701(5), 3.057(5)	2.882	o	Trigonal ($2S_b$, O_t)
$[Cu_6(NMe_2Ph)_4(C_2C_6H_4Me\text{-}4)_2]$ [e]	2.466, 2.849	2.602	o-t.a.	Trigonal, equatorial Cu ($2C_b$, N_t) Digonal, apical Cu ($2C_t$)
$[Cu_6H_6(PPh_3)_6]$ [f]	2.494(6), 2.674(5)	2.598	o-t.a.	Distorted tetrahedral [P_t, $2H_b(\mu_3)$]
$[Cu(H)P(NMe_2)_3]_6$ [g]	2.508(2), 2.804(3)		t.a.	Tetrahedral [P_t, $3H_b(\mu_3)$]
$[Cu_6(2\text{-}Me_2NC_6H_4)_4Br_2]$ [h]	2.48,[i] 2.70[j]		o	Trigonal, equatorial Cu (C_b, N_t, Br_b) Digonal, apical Cu ($2C_b$)
$[Cu_6L_4Br_2]$ [k]	2.432(6), 3.033(5)	2.657	o	Trigonal, equatorial Cu (C_b, N_t, Br_b) Digonal, apical Cu ($2C_b$)
$[Cu_6Fe_4(CO)_{16}]^{2-}$ [l]		2.616(3)	o	Digonal [$2Fe_b(\mu_3)$]
$[Cu_6(C_5H_4NSSiMe_3)_6]$ [m]	3.139(1)		s.t.t.	Trigonal ($2S_b$, O_t)
$[Cu_6I_{11}]^{5-}$ [n]	2.961(3) 3.411(3)	3.261	t.p.	Tetrahedral [$2I_b(\mu_4)$, $I_b(\mu_3)$, I_t]
$[Cu_6(C_5H_4NS)_6]$ [o]	2.795(1), 3.160(1)	2.950	o-t.a.	Trigonal ($2S_b$, O_t)

[a] o = Octahedral, t.a. = trigonal antiprismatic, s.t.t. = staggered two trigonal, and t.p. = trigonal prismatic. [b] By assuming no copper–copper bonding. [c] Suffixes b and t denote bridging and terminal co-ordination modes, respectively. [d] Ref. 13. [e] R. W. M. Hoedt, J. G. Noltes, G. V. Koten, and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1978, 1800. [f] dmf solvate (M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, 1972, **11**, 1818); thf solvate (C. F. Albert, P. C. Healy, J. D. Kildea, C. L. Raston, B. W. Skelton, and A. H. White, *Inorg. Chem.*, 1989, **28**, 1300). [g] T. H. Lemmen, K. Folting, J. C. Huffman, and K. G. Caulton, *J. Am. Chem. Soc.*, 1985, **107**, 7774. [h] (*a*) J. M. Guss, R. Mason, K. M. Thomas, G. van Koten, and J. G. Noltes, *J. Organomet. Chem.*, 1972, **40**, C79; (*b*) G. van Koten and J. G. Noltes, *ibid.*, 1975, **102**, 551. [i] Mean separation of the apical and equatorial copper atoms. [j] Mean separation of the bromide-bridged copper atoms. [k] L = 2-(4,4-dimethyl-1,3-oxazolin-2-yl)-5-methylphenyl (E. Wehman, G. van Koten, J. T. B. H. Jastrzebski, M. A. Rotteveel, and C. H. Stam, *Organometallics*, 1988, **7**, 1477). [l] G. Doyle, K. A. Eriksen, and D. V. Engen, *J. Am. Chem. Soc.*, 1985, **107**, 7914. [m] Ref. 14. [n] F. M-H-Abadi, H. Hartl, and J. Fuchs, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 514. [o] This work.

remaining six copper–copper bond lengths vary from 2.795(1) to 2.853(1) Å [mean 2.826(1) Å]. Thus, as shown in Figure 1, the octahedron defining the Cu_6 system has two large transoid 'equilateral' triangular faces and six smaller (approximately) isosceles triangular faces.

Each copper atom is bonded to a pyridine nitrogen and two thiolate sulphur atoms, forming a trigonal geometry. The deviation of the copper atom from a least-squares plane of co-ordinated S (two) and N atoms is nearly 1 Å, indicative of high distortion.

The ligand C_5H_4NSH exists predominantly in the 1*H*-pyridine-2-thione form,[9] that is with hydrogen at nitrogen rather than at sulphur. It has been demonstrated among various copper(I) complexes[4] of C_5H_4NSH that the ligands are co-ordinated to copper in the thione tautomeric form in spite of their terminal or bridged co-ordination. Consequently, no co-ordination of nitrogen atoms to copper occurs due to their hydrogen and thus C_5H_4NSH is a monodentate ligand. On the other hand, the crystal structure of complex (**1**) has no counter ions, indicating that the ligand is in anionic form such as thiolate, which acts as a bridging (μ_3) donor atom.

The thiolate in a complex affords a characteristic bond distance: thus the C–S distance in (**1**) is 1.751(7)—1.777(8) Å, while the C=S distances among copper(I)–C_5H_4NSH complexes fall within 1.706—1.737 Å. The C–S distance is 0.2 Å longer than that of C=S. This trend is supported by the result obtained for $[Rh(C_5H_4NS)_2(C_5H_4NSH)_2]^+$,[9a] where C=S is 1.70(1) and 1.71(1) Å, while C–S 1.74(1) Å.

The Cu–S(bridged thione) distance is 2.403 Å (average) and 2.388 Å (average) for $[Cu_2(C_5H_4NSH)_6]^{2+}$,[4a,b] and $[Cu_2(C_5H_4NSH)_2(PPh_3)_2Br_2]$,[4e] respectively, while that of the bridging thiol in (**1**) is 2.238 Å (average). This shows that Cu–S(thiol) < Cu–S(thione), dissimilar to the trend in C–S distance with the difference being smaller.

The Cu–N distance in complex (**1**) is longer than that of T-shaped copper(I) complexes (1.91—1.93 Å),[10] but similar to that of the corresponding pyridine (py) complexes, $[Cu(2Me\text{-}py)_3]ClO_4$ [1.99 Å (av.)][11] and $[Cu(py)_4]ClO_4$ (2.05 Å).[12]

Table 3 lists hexanuclear copper(I) complexes which have been characterized crystallographically. Most of the Cu_6 cores have near-octahedral skeletons as does that of (**1**). The Cu–Cu distances range from 2.432(6) to 3.411(3) Å, at the upper half of which those of (**1**) are situated. A copper atom on an apex displays digonal-tetrahedral geometry, if no copper–copper bondings are considered. Hence, the copper–copper distance is dependent on the ligand used, the donor atoms being especially important. The molecular structure of (**1**) is similar to that of $[Cu_6(Pr_2NCOS)_6]$[13] and $[Cu_6(C_5H_4NSSiMe_3)_6]$.[14] In the latter case, the ligand has a bulky $SiMe_3$ substituent adjacent to the thione group: the Cu–S and Cu–N distances are close to those of (**1**), indicating no hindered interaction of $SiMe_3$ with the copper atoms. This is because this substituent is attached to C=S. If it were substituted on to the pyridine nitrogen the Cu–N distance would be greatly influenced.

Reaction of C_5H_4NSH *with Copper*(I).—The reaction of C_5H_4NSH with copper(I) ion was monitored by ^1H n.m.r. spectroscopy. Figure 2 shows that, after the addition of C_5H_4NSH to $[Cu(MeCN)_4]PF_6$ there is an immediate change in the spectrum. After 20 min no starting material remained and two species [(**2**) and (**3**)] formed preferentially. The signals of (**2**) and (**3**) are denoted by a and b in Figure 2. The signals a appear the most downfield, indicative of a strong interaction with the copper(I) ion. In acetone species (**2**) is much more soluble than (**3**). The signals a were selectively observed as in Figure 2(*b*) by cooling the 20 mmol dm^{-3} solution to −90 °C, whereupon a large amount of (**3**) precipitated. In the case of a 7 mmol dm^{-3} solution no precipitate formed and thus Figure 2(*c*)

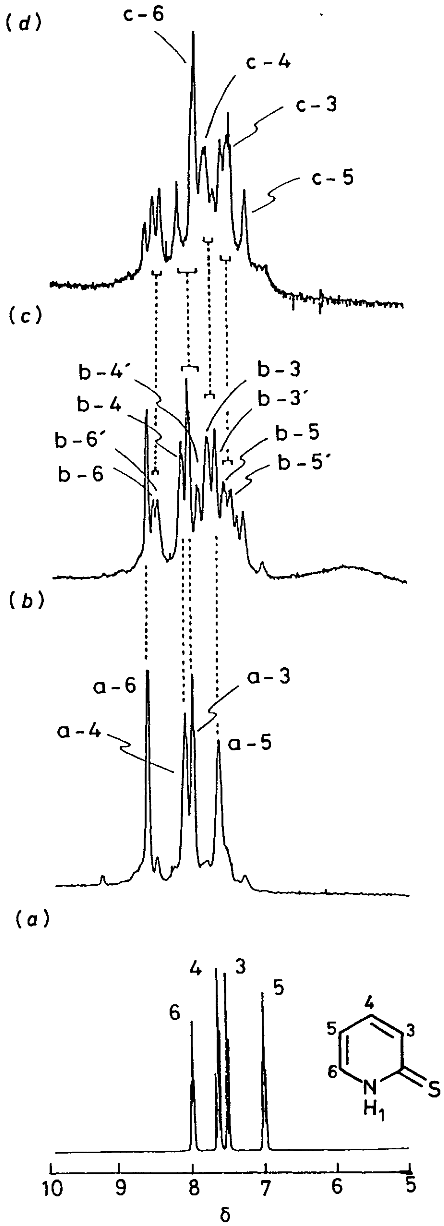

Figure 2. Proton n.m.r. spectra at −90 °C of $(CD_3)_2CO$ solutions of metal-free C_5H_4NSH (*a*), 20 min after the addition of C_5H_4NSH to $[Cu(MeCN)_4]PF_6$ [20 (*b*) and 7 mmol dm^{-3} (*c*)], and after 3 h of heating solution (*c*) at 60 °C (*d*). The metal to ligand molar ratio is 1 : 1 for all the samples. Numbers indicate the signal assignment

Table 4. Observed proton n.m.r. chemical shifts[a] of copper(I) complexes

Complex[b]	3-H	4-H	5-H	6-H	1-H[c]
Metal-free	7.51	7.64	7.01	7.99	13.47
(**2**)	7.96	8.06	7.61	8.58	15.17
(**3**)	7.76	8.10	7.52	8.48	15.73
	7.64	7.88	7.43	8.43	15.24
(**4**)	7.40	7.73	7.18	7.89	—

[a] Chemical shifts (δ) at 270.0 MHz, solvent $(CD_3)_2CO$, −90 °C. [b] Complexes (**2**), (**3**), and (**4**) correspond to signals a, b (and b′), and c in Figure 2, respectively. [c] Hydrogen attached to nitrogen atom.

is the complete ^1H n.m.r. spectrum involving the whole reaction products, (**2**) and (**3**). Species (**3**) affords two sets of signals b and b′ with the same intensity in Figure 2(*c*). This shows that C_5H_4NSH ligands are co-ordinated to the copper(I) ion in different modes. Both (**2**) and (**3**) give NH signals near δ 15, which leads to the conclusion that the ligands are in the thione form. The observed chemical shifts are listed in Table 4. Under the conditions used in Figure 2(*b*) and (*c*), the ^1H signal of MeCN resonates at δ 2.28, more downfield than the metal-free position (2.20).[15] This shift is different from that of the co-ordinated MeCN (2.41),[15] indicating that not all the MeCN in solution is co-ordinated to copper(I) ions and chemical exchange occurs. Evidently, this shift is associated with the co-ordination of MeCN in (**2**) and/or (**3**). On the basis of these facts, species (**2**) and (**3**) are assigned to $[Cu(L)X_n]PF_6$ and $[(L)XCuL_2Cu(L)X][PF_6]_2$ [L = C_5H_4NSH(thione form), X = MeCN, n = 1—3], respectively. Similar mononuclear and binuclear compounds have been characterized crystallographically.[4] Isolation of the present compounds failed because they were precipitated simultaneously.

When the solution was heated at 60 °C for 3 h other signals c appeared as shown in Figure 2(*d*), whose co-ordination shifts are small. The MeCN signal appears at the metal-free position, indicative of its non-co-ordination. Further heating caused the formation of many species, and signals at δ 7—9 occurred as a broad featureless band due to significant overlapping. At this time a yellowish orange material precipitated which gives a complicated i.r. spectrum, indicative of a mixture of (**1**) and other polymeric species. Interestingly, there is an apparent difference between the species in solution and in the solid state concerning the co-ordination mode of C_5H_4NSH; all the solution species give a signal due to the NH group, revealing thione-type co-ordination to copper(I). On the other hand, the solid precipitates show no i.r. band at 844 cm^{-1} characteristic of PF_6^- anion, indicating that they have thiolate $C_5H_4NS^-$ instead of PF_6^-, as in (**1**). The identification of species c and the solid materials is difficult.

As distinct from the conclusion that a Cu_6 core can be prepared with the aid of steric constraints,[14] which avoid the exclusive formation of polymeric complexes, the present observations clearly show that C_5H_4NSH results intrinsically in a Cu_6 core. The reaction is readily controlled by temperature; the higher the temperature of the solution the more readily (**1**) forms.

Complex (**1**) is fairly insoluble in the usual organic solvents. Attempts to enhance its solubility by use of $4\text{-}MeC_5H_3NSH$ were unsuccessful. Instead, 2-mercapto-1-methylimidazole was used, which readily reacts with $[Cu(MeCN)_4]PF_6$ in acetone. The resultant complexes are very soluble, giving no precipitates. Their structure is under investigation.

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