Synthesis and crystal structures of tetra- and hexanuclear copper(I) complexes of pyrimidine derivatives, [Cu₄(C₄H₈N₂S)₄](ClO₄)₄ and [Cu₆(C₅H₅N₂S)₆]

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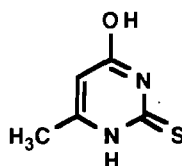
Abstract

4-Hydroxy-6-methylpyrimidine-2-thione (Me(OH)pymtH) and 3,4,5,6-tetrahydropyrimidine-2-thione (H₄pymtH) give hexanuclear and tetranuclear copper(I) complexes, [Cu₆(C₅H₅N₂S)₆] (**1**) and [Cu₄(C₄H₈N₂S)₄](ClO₄)₄ (**2**), respectively. Complex **1** crystallizes in the monoclinic space group $C2/c$, $a = 23.103(6)$, $b = 12.053(8)$, $c = 24.018(3)$ Å, $\beta = 113.56(1)°$ and $Z = 4$. Complex **2** crystallizes in the triclinic space group $P\bar{1}$, $a = 12.005(2)$, $b = 19.597(3)$, $c = 11.609(2)$ Å, $\alpha = 105.61(1)$, $\beta = 101.23(1)$, $\gamma = 100.82(1)°$ and $Z = 2$. The single-crystal X-ray structure of complex **1** reveals an anti-prismatic copper core of six copper atoms, each copper having a trigonal geometry with two thiolate sulfur donors and a nitrogen donor of a μ_3-type Me(OH)pymt⁻ ligand, while **2** affords a distorted tetrahedral core of four copper atoms containing only thione sulfur donors of an H₄pymtH ligand. ¹H NMR spectra of the reaction solution demonstrate that **1** is the final product through the low-molecular weight polynuclear copper species of Me(OH)pymtH or its anionic form whereas **2** is the principal species of H₄pymtH even in solution.

Introduction

Ligands containing a thioamide structure have considerable coordination potential. The flexibility based on the tautomerism, thiol ($-N=C(-SH)-$) ↔ thione ($-NH-C(=S)-$), can afford various coordination modes [1, 2]. Pyridine-2-thione (pytH) and 1,3-imidazoline-2-thione (imtH₂) are representative of heterocyclic thioamide ligands, which have .so far provided various metal complexes. By using these ligands a large number of copper(I) complexes have been isolated and characterized. Among copper(I) complexes, a terminal or bridged thione form [3] is very common, while a thiolate form is shown by only a few. Recently, not only a bridging thiolate sulfur but also a rare μ_3-type coordination of a thioamide ligand has been found in polynuclear copper(I) complexes of pytH and imtH₂ [4–6], adding an additional and intriguing dimension to thioamide copper(I) chemistry. In order to expand this coordination chemistry, pyrimidinethione (pymtH)

complexes of copper(I) should also be examined because pymtH has a unique thioamide structure and is expected to bind copper(I) to give a variety of complexes as well as pytH and imtH₂. For instance, [Cu(H₄pymt)₂Cl] (H₄pymtH = tetrahydropyrimidine-2-thione) [7] and [Cu₄(Mepymt)₆](BF₄)₄ (MepymtH = 1-methylpyrimidine-2-thione [8] are mononuclear and tetranuclear complexes, respectively, both having a coordinated thione form. There are other copper(I) complexes, which have been isolated but not crystallographically characterized [9–11]. In order to better understand the copper(I)–pyrimidine chemistry, it is important to investigate the structures both in solution and in the solid state. This paper presents the synthesis, structure determination and solution behavior of these complexes. The ligands used are as follows.
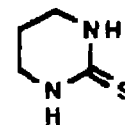
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4-Hydroxy-6-methyl-pyrimidine-2-thione (Me(OH)pymtH)

3,4,5,6,-Tetrahydropyrimidine-2-thione (H₄pymtH)

Experimental

All operations were carried out under an atmosphere of purified argon. Solvents were dried by conventional methods and distilled under argon. $[Cu(CH_3CN)_4]PF_6$ was prepared according to the literature [12]. $[Cu(C_2H_4)ClO_4]$ was obtained from the reduction of $Cu(ClO_4)_2 \cdot 6H_2O$ by copper wire; the preparation has already been reported [13]. 4-Hydroxy-6-methylpyrimidine-2-thione (Me(OH)pymtH) and 3,4,5,6-tetrahydropyrimidine-2-thione (H_4pymtH) were purchased from Aldrich Chemicals.

Preparation of complexes

$[Cu_6(Me(OH)pymt)_6]$ (1)

10 cm^3 of a tetrahydrofuran (thf) solution of Me(OH)pymtH (1.4 mg, 0.01 mmol) were added to $[Cu(CH_3CN)_4]PF_6$ (3.7 mg, 0.01 mmol) and stirred for 10 min. The colorless solution was transferred to a glass tube and kept at room temperature. Yellow microcrystals began to form after 5 days. Yellow plate crystals were obtained by leaving the solution to stand for one month. Yield 23%.

One of these crystals was used for X-ray crystallography. The crystals are insoluble in methanol and acetone. IR: ν(C=S) 1179 cm^{-1}.

$[Cu_4(H_4pymtH)_6](ClO_4)_4$ (2)

The ligand H_4pymtH (116 mg, 0.10 mmol) was added to 10 cm^3 of a methanol solution of $[Cu(C_2H_4)ClO_4]$ (0.10 mmol) and stirred under ethylene atmosphere. After ethylene was purged with argon, the colorless solution was sealed in a glass tube and kept at room temperature for 5 days. Colorless plate crystals were obtained. Yield 11.3%. ^{1}H NMR (methanol-d$_4$, redissolved crystals), 7.93, 7.43, 8.59 and 7.81 ppm for 2, 3, 4, 5, and 11,12-H, respectively.

Physical measurements

UV–Vis spectra were recorded with an Hitachi 150-20 spectrophotometer. IR spectra were obtained with a Jasco FT/IR-8000 spectrophotometer. ^{1}H NMR spectra were measured with a Jeol GSX-270 spectrometer operating in the Fourier transform mode (16K datapoints transform of spectra width 3500 Hz after $100 \sim 200$ pulses) at ambient temperature (SiMe$_4$ as an internal reference).

Crystallography

Crystals were glued on top of glass fibers. For each compound unit cell constants were determined from the geometric parameters of 25 well-centered reflections with 2θ values in the range of $20 < 2\theta < 32°$. Then, a unique data set was measured to a 2θ limit predetermined from the scope of the data, using a Rigaku (AFC5R and AFC6S for 1 and 2, respectively) automated diffractometer fitted with a monochromatic Mo Kα radiation source ($\lambda = 0.71073$ Å) and operating in a conventional ω–2θ scan mode at 25 °C. The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout the data collection, indicating crystal and electronic stability (no decay correction was applied). An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. N Independent reflections were obtained, N_o with $I > 3.00\sigma(I)$ being considered 'observed' and used in the least-squares refinement.

For crystal 1 systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$) characteristic of the space groups $C2/c$ and Cc were observed. The former centrosymmetric group was chosen because this choice was subsequently shown to be correct by successful refinement and reasonable positional and thermal parameters. The structure was solved by direct methods [14]. The non-hydrogen atoms except for thf were refined anisotropically. After anisotropic least-squares refinement for non-hydrogen atoms, all hydrogen atoms except the alcoholic and tetrahydrofuran hydrogens were located in the difference Fourier map, but their parameters were not refined. There are two types of thf molecules in the crystal, one (C(16)–C(17)–C(18)–C(19)–O(4)) having a full occupancy and the other (C(20)–C(21)–C(22)–C(23)–O(5)) being disordered with the site occupancies of 0.5 about a crystallographic inversion center, which coincides with that of the Cu$_6$ core. For the final refinement the multiplicities were fixed at those values. The significance of the disordered thf is verified by its stable refinement. The final cycle of full-matrix least-squares refinement was based on N_o and n variable parameters and converged (large parameter shift was Δs times its e.s.d.) with unweighted and weighted agreement factors of $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $R_w = [(\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2)]^{1/2}$, where $w = 4F_o^2 / \sigma^2(F_o^2)$.

For crystal 2 the structure was solved by direct methods [14]. The non-hydrogen atoms were refined anisotropically. After anisotropic least-squares refinement for non-hydrogen atoms, all hydrogen atoms were located in the difference Fourier map, but their parameters were not refined. The final cycle of full-matrix least-squares refinement was based on N_o.

The positional parameters for complexes 1 and 2 are listed in Tables 1 and 2, respectively.

Crystal data

1: $Cu_6S_6O_9N_{12}C_{42}H_{24}$, $M = 1414.36$, monoclinic, space group $C2/c$, $a = 23.103(6)$, $b = 12.053(8)$, $c = 24.018(3)$

Atom	x	y	z	B_{eq}
Cu(1)	0.27442(6)	0.0865(1)	0.04336(6)	3.91(6)
Cu(2)	0.20389(6)	0.1365(1)	−0.07783(6)	3.95(6)
Cu(3)	0.33959(6)	0.2085(1)	−0.01067(6)	3.82(6)
S(1)	0.3364(1)	0.1975(3)	0.1193(1)	3.3(1)
S(2)	0.1758(1)	0.1104(2)	0.0390(1)	3.5(1)
S(3)	0.2941(1)	0.0781(3)	−0.0800(1)	3.6(1)
O(1)	0.5621(3)	0.2799(9)	0.2259(4)	5.9(4)
O(2)	−0.0341(4)	−0.0543(8)	−0.0726(4)	5.9(4)
O(3)	0.3544(5)	−0.3135(8)	−0.0621(6)	8.9(6)
O(4)	0.7081(7)	0.132(2)	0.1909(7)	12.9(5)
O(5)	0.557(2)	0.197(3)	0.700(2)	15(1)
N(1)	0.4192(4)	0.1973(8)	0.0664(4)	3.4(4)
N(2)	0.1326(4)	0.0392(7)	−0.0764(4)	3.4(4)
N(3)	0.3056(4)	−0.0497(8)	0.0143(5)	4.1(4)
N(4)	0.4594(4)	0.2368(8)	0.1716(4)	3.5(4)
N(5)	0.0654(4)	0.0146(7)	−0.0243(4)	3.6(4)
N(6)	0.3237(4)	−0.1347(8)	−0.0659(5)	4.8(5)
C(1)	0.4112(4)	0.2104(9)	0.1174(5)	3.3(4)
C(2)	0.1212(5)	0.0481(9)	−0.0276(5)	3.4(5)
C(3)	0.3093(5)	−0.046(1)	−0.0376(6)	3.9(5)
C(4)	0.5206(5)	0.256(1)	0.1763(5)	4.4(5)
C(5)	0.5290(5)	0.244(1)	0.1203(6)	4.8(6)
C(6)	0.4800(5)	0.215(1)	0.0700(5)	4.3(5)
C(7)	0.4862(6)	0.199(1)	0.0107(6)	6.2(7)
C(8)	0.0173(6)	−0.029(1)	−0.0748(6)	4.4(5)
C(9)	0.0304(6)	−0.040(1)	−0.1278(5)	4.6(6)
C(10)	0.0878(5)	−0.008(1)	−0.1265(5)	4.0(5)
C(11)	0.1050(6)	−0.018(1)	−0.1807(5)	5.3(6)
C(12)	0.3397(6)	−0.236(1)	−0.0368(8)	6.4(8)
C(13)	0.3374(6)	−0.242(1)	0.0216(8)	5.9(7)
C(14)	0.3205(6)	−0.152(1)	0.0443(7)	5.6(7)
C(15)	0.3141(8)	−0.151(1)	0.1028(8)	8(1)
C(16)	0.743(1)	0.048(3)	0.229(2)	16(1)
C(17)	0.776(2)	0.088(3)	0.294(2)	20(1)
C(18)	0.764(1)	0.202(2)	0.286(1)	14.2(8)
C(19)	0.721(1)	0.239(2)	0.224(1)	13.7(8)
C(20)	0.586(2)	0.095(4)	0.720(2)	11(1)
C(21)	0.559(3)	0.052(5)	0.657(2)	13(2)
C(22)	0.502(2)	0.052(4)	0.644(2)	10(1)
C(23)	0.506(2)	0.153(4)	0.640(2)	11(1)

Å, $\beta = 113.56(1)°$, $U = 6130(7)$ Å^3, $Z = 4$, $D_c = 1.532$ g/cm^3, λ(Mo Kα) = 0.71069 Å, $F(000) = 2808$, $\mu = 23.01$ cm^{-1}, $T = 23$ °C. Transmission factors: 0.90–1.00; specimen size: $0.30 \times 0.40 \times 0.30$ mm. $2\theta_{max} = 55.0°$; N, $N_o = 7343, 3171$; $n = 311$; $R, R' = 0.060, 0.079$; $\Delta s = 0.50$.

2: Cu$_4$Cl$_4$S$_6$O$_{16}$N$_{12}$C$_{24}$H$_{48}$, $M = 1349.07$, triclinic, space group $P\bar{1}$, $a = 12.005(2)$, $b = 19.597(3)$, $c = 11.609(2)$ Å, $\alpha = 105.61(1)$, $\beta = 101.23(1)$, $\gamma = 100.82(1)°$, $U = 2495.4(8)$ Å^3, $Z = 2$, $D_c = 1.795$ g/cm^3, λ(Mo Kα) = 0.71069 Å, $F(000) = 1368$, $\mu = 22.15$ cm^{-1}, $T = 23$ °C. Transmission factors: 0.91–1.00; specimen size: $0.25 \times 0.40 \times 0.30$ mm. $2\theta_{max} = 55.0°$; $N, N_o = 11446, 5246$; $n = 595$; $R, R' = 0.053, 0.058$; $\Delta s = 0.09$.

Atom	x	y	z	B_{eq}
Cu(1)	0.56233(9)	0.21301(5)	0.3603(1)	4.63(4)
Cu(2)	0.71114(8)	0.17329(5)	0.5342(1)	4.54(4)
Cu(3)	0.8027(1)	0.28206(6)	0.4120(1)	4.98(4)
Cu(4)	0.68073(8)	0.32479(5)	0.5932(1)	4.39(4)
Cl(1)	0.6340(2)	0.4802(1)	0.8253(2)	5.9(1)
Cl(2)	0.8150(2)	0.0340(1)	0.6510(2)	6.0(1)
Cl(3)	0.2713(2)	0.1496(2)	0.0643(2)	6.5(1)
Cl(4)	1.0100(3)	0.3431(2)	0.2193(3)	8.6(1)
S(1)	0.5200(2)	0.1175(1)	0.4310(2)	4.27(7)
S(2)	0.6693(2)	0.2221(1)	0.2243(2)	4.73(8)
S(3)	0.8835(2)	0.1986(1)	0.4823(2)	4.38(7)
S(4)	0.5073(2)	0.3144(1)	0.4640(2)	4.42(7)
S(5)	0.7139(2)	0.2562(1)	0.7193(2)	3.98(7)
S(6)	0.8435(2)	0.3908(1)	0.5594(2)	4.45(7)
O(11)	0.6141(8)	0.5199(4)	0.7420(7)	9.7(4)
O(12)	0.6525(7)	0.5229(4)	0.9453(6)	8.3(3)
O(13)	0.541(1)	0.4228(5)	0.7987(7)	15.0(5)
O(14)	0.729(1)	0.4532(7)	0.810(1)	15.6(7)
O(21)	0.7875(7)	−0.0202(5)	0.7060(8)	10.3(4)
O(22)	0.7151(7)	0.0607(4)	0.6133(7)	9.4(4)
O(23)	0.9043(8)	0.0902(4)	0.724(1)	16.2(5)
O(24)	0.847(1)	0.0020(6)	0.545(1)	14.9(7)
O(31)	0.297(1)	0.1771(5)	−0.0259(8)	13.3(5)
O(32)	0.1559(8)	0.1334(6)	0.048(1)	14.6(5)
O(33)	0.3292(7)	0.2014(5)	0.1804(7)	11.8(4)
O(34)	0.311(1)	0.0875(6)	0.0523(8)	14.6(6)
O(41)	1.1218(7)	0.3522(6)	0.2062(8)	11.7(4)
O(42)	0.9289(7)	0.2866(5)	0.1155(8)	10.5(4)
O(43)	0.976(1)	0.4081(6)	0.229(1)	15.8(7)
O(44)	0.997(1)	0.3252(7)	0.3247(9)	15.9(7)
N(12)	0.4527(7)	0.0223(4)	0.2032(7)	6.4(3)
N(16)	0.5597(6)	−0.0139(4)	0.3498(6)	5.2(3)
N(22)	0.6935(7)	0.3138(5)	0.0969(7)	6.7(4)
N(26)	0.5253(7)	0.3005(4)	0.1589(8)	6.7(3)
N(32)	0.8693(6)	0.0630(4)	0.3457(7)	6.4(3)
N(36)	0.9040(6)	0.1531(5)	0.2522(7)	6.2(3)
N(42)	0.2964(6)	0.2313(4)	0.4279(7)	6.0(3)
N(46)	0.4026(6)	0.2808(4)	0.6318(7)	5.6(3)
N(52)	0.9037(6)	0.3644(3)	0.8463(5)	4.4(2)
N(56)	0.9298(6)	0.2477(4)	0.8122(5)	4.7(3)
N(62)	0.8359(7)	0.4652(4)	0.3986(7)	6.6(3)
N(66)	0.7322(7)	0.4935(4)	0.5427(7)	6.1(3)
C(11)	0.5129(7)	0.0358(4)	0.03176(7)	4.2(3)
C(13)	0.436(1)	−0.0466(7)	0.108(1)	10.4(6)
C(14)	0.454(1)	−0.1013(6)	0.153(1)	11.6(7)
C(15)	0.543(1)	−0.0876(5)	0.266(1)	6.9(4)
C(21)	0.6250(8)	0.2845(5)	0.1553(7)	4.7(3)
C(23)	0.659(1)	0.3626(7)	0.027(1)	9.1(6)
C(24)	0.539(2)	0.364(1)	0.021(2)	25(2)
C(25)	0.478(1)	0.3462(6)	0.091(1)	8.2(5)
C(31)	0.8836(6)	0.1307(5)	0.3461(8)	4.6(3)
C(33)	0.873(1)	0.0043(6)	0.238(1)	8.1(5)
C(34)	0.945(1/)	0.0348(7)	0.165(1)	8.6(5)
C(35)	0.905(1)	0.0985(7)	0.1350(9)	8.2(5)
C(41)	0.3933(7)	0.2722(4)	0.5118(7)	4.7(3)
C(43)	0.1923(9)	0.1964(6)	0.458(1)	8.2(5)
C(44)	0.222(1)	0.1863(8)	0.578(1)	10.7(6)
C(45)	0.306(1)	0.2489(6)	0.676(1)	7.1(4)
C(51)	0.8629(7)	0.2920(5)	0.7988(7)	4.1(3)
C(53)	1.0296(8)	0.3989(5)	0.9072(8)	6.2(4)

TABLE 2. (continued)

Atom	x	y	z	B_{eq}
C(54)	1.1011(8)	0.3485(7)	0.864(1)	7.2(4)
C(55)	1.0544(8)	0.2743(6)	0.8736(8)	6.2(4)
C(61)	0.7984(7)	0.4554(4)	0.4948(8)	4.5(3)
C(63)	0.814(1)	0.5241(7)	0.350(1)	9.2(6)
C(64)	0.750(2)	0.565(1)	0.409(2)	20(1)
C(65)	0.694(1)	0.5500(6)	0.495(1)	8.3(5)

Results and discussion

Crystal structures of complexes 1 and 2

The entire molecule of **1** having C_i symmetry is shown in Fig. 1. Table 3 provides a list of important bond distances and angles with their e.s.d.s. The molecule displays an octahedral core of copper atoms. Each copper atom is coordinated to a nitrogen and two thiolate sulfur atoms, forming trigonal geometries which are classified into two types: the apical Cu(1) has a regular Y-shaped form with 105.4(1) and 124.8(3)° for S–Cu–S and S–Cu–N_{av}, respectively. The other type is a distorted Y-shaped form found for the basal Cu(2) and Cu(3) atoms, whose geometrical angles are 127.4(3), 108.6(3), and 119.4(1)° for S–Cu–S_{av}, S–Cu–N_{av}, and S–Cu–N_{av}, respectively. In the Cu_6 framework, there are two types of triangular faces, which are considered approximately equilateral: two faces of the A type (Cu(1')–Cu(2)–Cu(3) and one related to the inversion center) and six residual faces of the B type as shown in Fig. 2. The copper atoms of the A type are all bridged by sulfur atoms, while the copper atoms of the B type are constructed by nitrogen and μ_2-sulfur atoms of the μ_3 type pymt anion. The Cu_6 core, thus, lacks octahedral symmetry, individual copper–copper distances ranging from 2.770(2) to 3.465(2) Å (av. 3.123(2) Å). The structure is best described as a trigonal antiprism constructed of two parallel equilateral triangles (A type faces having long Cu–Cu distances) on opposite faces. The apices of these triangles are interconnected by six shorter Cu–Cu distances. A similar trigonal-antiprismatic Cu_6 form is also seen in $[Cu_6(pyt)_6]$ (**3**) [4]. The averaged distances of Cu–N (2.03(1) (**1**) and 2.034(7) (**3**) Å) and Cu–S (2.248(3) (**1**) and 2.241(2) (**3**) Å) are similar to each other. The difference between **1** and **3** is found only in the Cu_6 framework, in particular the distances of the long sides (Cu(1')–Cu(2) and Cu(1')–Cu(3) of the type A triangles: 3.447$_{av}$ Å in **1** compared to 3.106$_{av}$ Å in **3**. This is not ascribed to the Cu–S distances, but to the bite (Cu–S–Cu) angles, which average 99.3° for **1** compared to an average of 87.4° for **3**. The substituents of Me(OH)pymtH increase the steric bulk of the ligand, and require the Cu coordination sphere to expand and therefore the Cu_6 core spreads out. The bite angles of a bridging thiolate vary from 84 to 124° [4, 6, 15, 16]; the angles of **1** are in the normal range. The coordination geometry of the bridging thiolate sulfur is sufficiently flexible so that
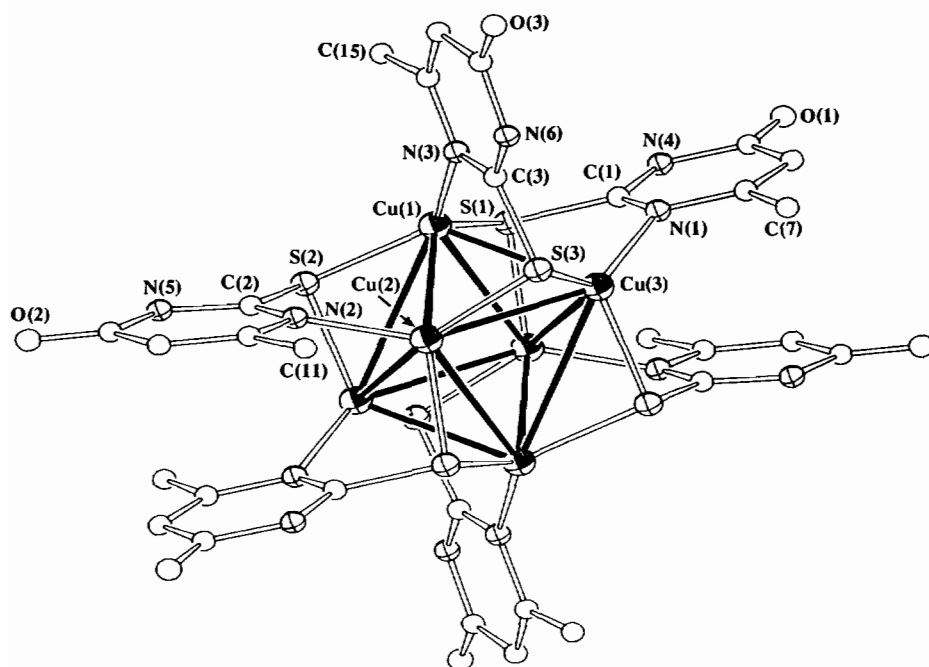

Fig. 1. ORTEP drawing of the molecule of $[Cu_6(Me(OH)pymt)_6]$ with thermal ellipsoids at the 50% probability level for Cu, S and N atoms. Ellipsoids of the carbon atoms in pyrimidine rings have been arbitrarily reduced. The numbers of the unlabelled pyrimidine carbon atoms follow from those given. Only half the atoms are labelled: other are related by a center of inversion.

TABLE 3. Selected bond distances (Å) and bond angles (°) for 1

Bond distances

Cu(1)–Cu(2)	2.774(2)	Cu(2)–S(1′)	2.263(4)
Cu(1)–Cu(3)	2.770(2)	Cu(2)–S(3)	2.219(3)
Cu(1)–Cu(2′)	3.429(3)	Cu(2)–N(2)	2.033(9)
Cu(1)–Cu(3′)	3.465(2)	Cu(3)–S(2′)	2.272(4)
Cu(2)–Cu(3)	3.023(2)	Cu(3)–S(3)	2.224(3)
Cu(2)–Cu(3′)	3.275(2)	Cu(3)–N(1)	2.025(8)
Cu(1)–S(1)	2.254(3)	S(1)–C(1)	1.75(1)
Cu(1)–S(2)	2.258(3)	S(2)–C(2)	1.76(1)
Cu(1)–N(3)	2.03(1)	S(3)–C(3)	1.77(1)

Bond angles

Cu(2)–Cu(1)–Cu(3)	66.09(5)	Cu(2)–N(2)–C(10)	124.1(8)
Cu(2)–Cu(1)–Cu(2′)	90.57(6)	Cu(1)–N(3)–C(3)	118.7(8)
Cu(2)–Cu(1)–Cu(3′)	62.17(5)	Cu(1)–N(3)–C(14)	126(1)
Cu(3)–Cu(1)–Cu(2′)	62.73(5)	S(1)–Cu(1)–S(2)	105.4(1)
Cu(3)–Cu(1)–Cu(3′)	91.24(6)	S(1)–Cu(1)–N(3)	124.2(3)
Cu(2′)–Cu(1)–Cu(3′)	52.02(5)	S(2)–Cu(1)–N(3)	125.4(3)
Cu(1)–Cu(2)–Cu(3)	56.88(5)	Cu(1)–Cu(2)–S(1′)	128.3(1)
Cu(1)–Cu(2)–Cu(1′)	89.43(6)	Cu(1)–Cu(2)–S(3)	78.01(9)
Cu(1)–Cu(2)–Cu(3′)	69.32(5)	Cu(1)–Cu(2)–N(2)	89.8(3)
Cu(3)–Cu(2)–Cu(1′)	64.61(5)	S(1)–Cu(2)–S(3)	119.7(1)
Cu(3)–Cu(2)–Cu(3′)	90.66(6)	S(1)–Cu(2)–N(2)	108.9(3)
Cu(1′)–Cu(2)–Cu(3′)	48.75(4)	S(3)–Cu(2)–N(2)	126.3(3)
Cu(1)–Cu(3)–Cu(2)	57.02(5)	Cu(1)–Cu(3)–S(2′)	127.0(1)
Cu(1)–Cu(3)–Cu(2′)	68.52(6)	Cu(1)–Cu(3)–S(3)	78.0(1)
Cu(1)–Cu(3)–Cu(1′)	88.76(6)	Cu(1)–Cu(3)–N(1)	90.1(3)
Cu(2)–Cu(3)–Cu(1′)	63.37(5)	S(2)–Cu(3)–S(3)	119.0(1)
Cu(2)–Cu(3)–Cu(2′)	89.34(6)	S(2)–Cu(3)–N(1)	108.3(3)
Cu(2′)–Cu(3)–Cu(1′)	48.51(4)	S(3)–Cu(3)–N(1)	128.4(3)
Cu(2)–Cu(1)–S(1)	129.6(1)	Cu(1)–S(1)–Cu(2′)	98.7(1)
Cu(2)–Cu(1)–S(2)	76.39(9)	Cu(1)–S(1)–C(1)	110.2(4)
Cu(2)–Cu(1)–N(3)	87.4(3)	Cu(2)–S(1)–C(1)	98.4(4)
Cu(3)–Cu(1)–S(1)	77.04(9)	Cu(1)–S(2)–Cu(3′)	99.8(1)
Cu(3)–Cu(1)–S(2)	129.7(1)	Cu(1)–S(2)–C(2)	109.3(4)
Cu(3)–Cu(1)–N(3)	86.2(3)	Cu(3)–S(2)–C(2)	99.7(4)
Cu(3)–N(1)–C(1)	115.4(7)	Cu(2)–S(3)–Cu(3)	85.8(1)
Cu(3)–N(1)–C(6)	125.0(7)	Cu(2)–S(3)–C(3)	103.2(4)
Cu(2)–N(2)–C(2)	115.1(7)	Cu(3)–S(3)–C(3)	104.1(4)

Fig. 2. Distances (Å) and angles (°) of Cu₃ faces. (A) type A with bridged sulfur atoms and (B) one of type B faces with a μ_3-ligand.

Fig. 3. ORTEP drawing of a cation moiety of [Cu₄(H₄pymtH)₆](ClO₄)₄ with thermal ellipsoids at the 50% probability level for Cu, S and N atoms. Ellipsoids of the carbon atoms in tetrahydropyrimidine rings have been arbitrarily reduced. The numbers of the unlabelled tetrahydropyrimidine carbon atoms follow from those given.

the Cu₆ core of 1 is stabilized. This Cu₆ core is concluded to be characteristic of μ_3-type pyt⁻ and pymt⁻ ligands.

Mepymt in [Cu₄(μ_3-Mepymt)₂(μ_2-Mepymt)₄]⁴⁺ [8], gives a tetranuclear Cu core, whose geometry is not a tetrahedron but a parallelogram of two nearly equilateral triangles. This irregular form is ascribed to the mixed coordination modes (μ_2 and μ_3) of the neutral MepymtH. It is worth noting that thioamide ligands with a five-membered ring provide a tetrahedral copper core. [Cu₄(Meimt)₄] is a typical example, with an average Cu–Cu distance of 2.825(2) Å [5], and Meimt in the thiolate form, giving μ_3-type coordination. Based on these results, it can be seen that the geometry of the copper cores is associated with the form of the sulfur atom, thiolate or thione, and the ring size of the thioamide ligands, which is related to the bite angles of S,N-bridging coordination. Consequently, the thio-
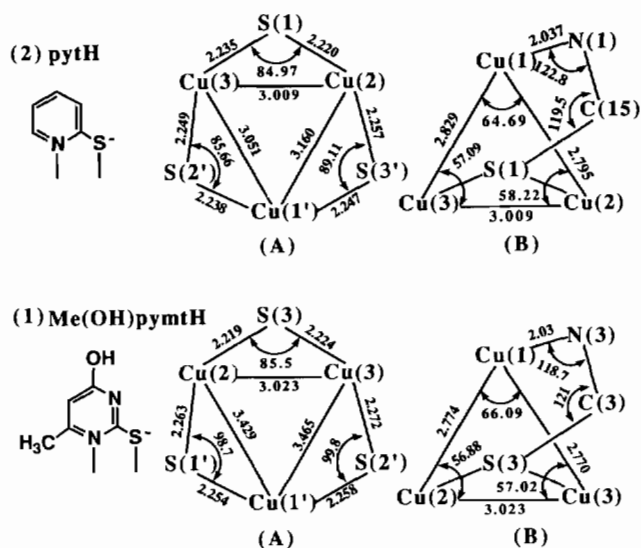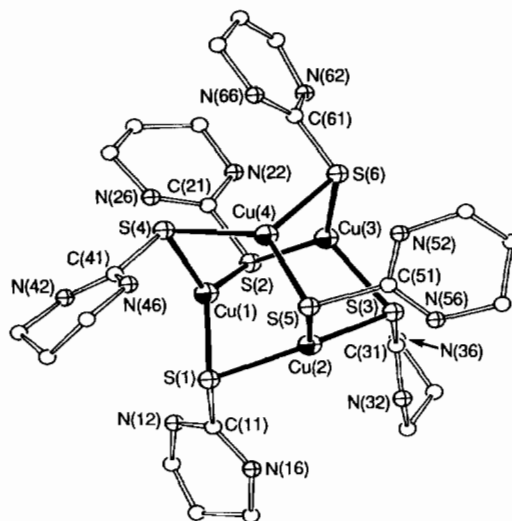
amide ligand is relevant when polynuclear copper cores are built as it controls the structure of the ligands.

Distinct from pytH and Me(OH)pymtH, H₄pymtH gives the tetranuclear complex 2, where the coordinated sulfur atoms are all of the thione form and bridged to two copper atoms. The cationic copper core is depicted in Fig. 3. Table 4 provides a list of important bond distances and angles with their e.s.d.s. This core displays a distorted tetrahedron, whose Cu–Cu distances range from 2.799(2) to 3.019(2) Å (av. 2.855(2) Å). Each copper atom shows a three-coordinate Y-shaped

TABLE 4. Selected bond distances (Å) and bond angles (°) for 2

Bond distances

Cu(1)–Cu(2)	2.799(2)	Cu(3)–S(2)	2.291(2)
Cu(1)–Cu(3)	2.818(2)	Cu(3)–S(3)	2.300(2)
Cu(1)–Cu(4)	2.877(2)	Cu(3)–S(6)	2.243(2)
Cu(2)–Cu(3)	3.019(2)	Cu(4)–S(4)	2.256(2)
Cu(2)–Cu(4)	2.971(2)	Cu(4)–S(5)	2.267(2)
Cu(3)–Cu(4)	2.826(2)	Cu(4)–S(6)	2.295(2)
Cu(1)–S(1)	2.251(2)	S(1)–C(11)	1.753(8)
Cu(1)–S(2)	2.243(2)	S(2)–C(21)	1.740(9)
Cu(1)–S(4)	2.314(2)	S(3)–C(31)	1.771(8)
Cu(2)–S(1)	2.276(2)	S(4)–C(41)	1.727(9)
Cu(2)–S(3)	2.270(2)	S(5)–C(51)	1.755(8)
Cu(2)–S(5)	2.310(2)	S(6)–C(61)	1.752(8)

Bond angles

Cu(2)–Cu(1)–Cu(3)	65.04(4)	Cu(2)–Cu(1)–Cu(4)	63.11(4)
Cu(3)–Cu(1)–Cu(4)	59.49(4)	Cu(1)–Cu(2)–Cu(3)	57.78(4)
Cu(1)–Cu(2)–Cu(4)	59.72(4)	Cu(3)–Cu(2)–Cu(4)	56.28(3)
Cu(1)–Cu(3)–Cu(2)	57.18(4)	Cu(1)–Cu(3)–Cu(4)	61.30(4)
Cu(2)–Cu(3)–Cu(4)	61.00(4)	Cu(1)–Cu(4)–Cu(2)	57.16(3)
Cu(1)–Cu(4)–Cu(3)	59.22(4)	Cu(2)–Cu(4)–Cu(3)	62.73(4)
S(1)–Cu(1)–S(2)	126.58(9)	S(1)–Cu(1)–S(4)	113.15(9)
S(2)–Cu(1)–S(4)	119.71(9)	S(1)–Cu(2)–S(3)	136.29(9)
S(1)–Cu(2)–S(5)	107.67(8)	S(3)–Cu(2)–S(5)	111.74(8)
S(2)–Cu(3)–S(3)	109.06(8)	S(2)–Cu(3)–S(6)	136.66(9)
S(3)–Cu(3)–S(6)	112.44(9)	S(4)–Cu(4)–S(5)	126.12(9)
S(4)–Cu(4)–S(6)	115.76(9)	S(5)–Cu(4)–S(6)	116.44(8)
Cu(1)–S(1)–Cu(2)	76.39(7)	Cu(1)–S(2)–Cu(3)	76.84(8)
Cu(2)–S(3)–Cu(3)	82.72(7)	Cu(1)–S(4)–Cu(4)	78.02(7)
Cu(2)–S(5)–Cu(4)	80.96(7)	Cu(3)–S(6)–Cu(4)	77.01(8)

form. For each copper atom one of three S–Cu–S angles opens more (126.12(9)–136.66(9)°) than the other two (107.67(8)–119.71(9) Å). Interestingly, the bond distance opposite the larger angle (126.12(9)–136.66(9)°) is lengthened more than the other distances: the average distance for the longer Cu–S bond is 2.305(2) Å; it is 2.262(2) Å for the shorter one. Among tetrahedral copper cores constructed by bridged sulfur donors, few complexes having neutral thiones are known whereas there are several complexes with anionic thiolates [17–20]. Complex 2 is a representative of tetrahedral copper cores constructed by thione donors.

¹H NMR spectra of the solutions

In order to elucidate the difference in the structure from Me(OH)pymtH and H₄pymtH, the ¹H NMR spectra of the solutions were measured. Since crystals of 1 are insoluble in any solvent, time-dependent ¹H NMR spectra of the reaction solution were examined. These indicate the progress of the reaction: in the early stage of the reaction low-molecular weight complexes such as dimers appear and then complex 1 forms as a final product. This behavior is very similar to that of copper(I) complexes with pytH [4]. On the other hand, H₄pymtH gives a simple spectrum dissimilar to that of pytH.
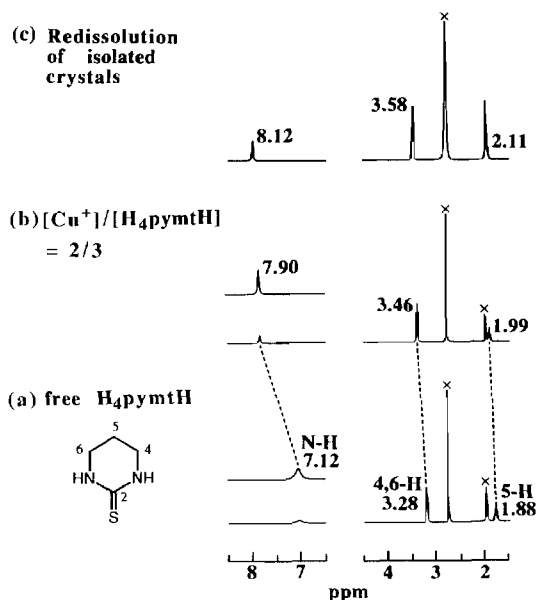

Fig. 4. ¹H NMR spectra at 23 °C of a metal-free H₄thptH and its copper(I) complexes in acetone-d₆. x denotes acetone and water signals.

Figure 4 shows ¹H NMR spectra of the reaction solution. This well illustrates the presence of simple species in solution, and this spectrum remains unchanged for a long time. Crystals of 2 were redissolved in acetone and the ¹H NMR spectrum was also measured, which is essentially the same one as that of the reaction solution (Fig. 4(c)). On this basis, H₄pymtH provides the tetranuclear copper complex 3 as a final product. This is associated with the stability of the tautomers [11]. The thione form of H₄pymtH should be very stable in acetone and thus the thione complex forms with a very high yield. If any base is added to H₄pymtH and the thiolate species is generated, the hexanuclear core will eventually form.

The nuclearity of the Cu clusters depends on the coordination mode of the N(H)–C(=S) moiety, which affords a tetranuclear and/or hexanuclear copper core, and the key to controlling the structure is related to the stability of the thiolate form.

Acknowledgement

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