

# SYNTHESES AND STRUCTURES OF TETRANUCLEAR AND HEXANUCLEAR COPPER(I) COMPLEXES WITH IMINOMETHANETHIOLATO BRIDGES DERIVED FROM ISOTHIOCYANATE

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**Abstract**—Methylisothiocyanate,  $\text{MeN}=\text{C}=\text{S}$ , in ethanol reacted with copper(I) giving a tetranuclear complex  $[\text{Cu}\{\mu_3\text{-SC}(=\text{NMe})(\text{OEt})\}]_4$  (**1**). Similar reaction of allyl-isothiocyanate,  $\text{CH}_2=\text{CHCH}_2\text{N}=\text{C}=\text{S}$ , and copper(I) in methanol gave a hexanuclear copper(I) complex,  $[\text{Cu}\{\mu_3\text{-SC}(=\text{NC}_3\text{H}_5)(\text{OMe})\}]_6$  (**2**). They show tetrahedral  $\text{Cu}_4$  and octahedral  $\text{Cu}_6$  cores, respectively. There are two structural similarities in both complexes: (i) a thiolato moiety  $[-\text{N}=\text{C}(\text{S}^-)-]$  which bridges three copper atoms with a monodentate nitrogen atom and a bridging sulphur atom and (ii) a trigonal planar geometry for copper(I) coordinated by one nitrogen atom and two sulphur atoms. Each iminomethanethiolato ligand is formed *in situ* in solvent.  $^1\text{H}$  NMR shows the reaction is initiated by a coordination of an isothiocyanate to copper(I).

Recent progress on copper(I) coordination chemistry has involved characterizations of polynuclear complexes with bridging ligands.<sup>1</sup> Heterocyclic thiones such as pyridine-2-thione<sup>1a</sup> or 3-trimethylsilylpyridine-2-thione<sup>1b</sup> can form hexanuclear copper(I) complexes which have an interesting paddlewheel-like structure with an octahedral  $\text{Cu}_6$  core. Also constructed was a tetrahedral  $\text{Cu}_4$  core by using 1-methylimidazoline-2-thione.<sup>2</sup> In these complexes each ligand with the thione form  $[-\text{NHC}(=\text{S})-]$  is converted to the thiolato form  $[-\text{N}=\text{C}(\text{S}^-)-]$  and acts as an effectively tridentate ligand with a monodentate nitrogen atom and a bridging sulphur atom, although a terminal or bridged thione form is common among copper(I)

complexes.<sup>3</sup> A similar coordination mode and a resulting paddlewheel-like structure were also found in the hexanuclear complex,  $[\text{Cu}\{\mu_3\text{-SC}(=\text{NPh})(\text{OPh}')\}]_6$  ( $\text{Ph}' = 4\text{-MeC}_6\text{H}_4$ ),<sup>4</sup> derived from an insertion reaction of a phenylisothiocyanate into a  $\text{Cu}^1\text{-OPh}'$  bond.

During the course of our studies on the characterization of copper(I) coordination chemistry with unsaturated compounds,<sup>5</sup> we found that copper(I) and isothiocyanate in alcoholic solvent give tetranuclear<sup>6</sup> and hexanuclear complexes with tetrahedral and octahedral copper(I) cores, respectively. They are surrounded by tridentate iminomethanethiolato ligands formed *in situ*. Here we report the syntheses and structures of two copper complexes with isothiocyanate-derived ligands and an NMR study of the reaction solution of allylisothiocyanate and copper(I).

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Table 1. Crystallographic data for  $[\text{Cu}\{\mu_3\text{-SC(=NMe)(OEt)}\}]_4$  (**1**) and  $[\text{Cu}\{\mu_3\text{-SC(=NC}_3\text{H}_3\text{)(OMe)}\}]_6$  (**2**)

Empirical formula	$[\text{C}_{16}\text{H}_{32}\text{N}_4\text{O}_4\text{S}_4\text{Cu}_4]$ ( <b>1</b> )	$[\text{C}_{30}\text{H}_{48}\text{N}_6\text{O}_6\text{S}_6\text{Cu}_6]$ ( <b>2</b> )
Colour; habit	yellow plate	yellow cubic
Crystal size (mm)	$0.25 \times 0.25 \times 0.15$	$0.20 \times 0.20 \times 0.20$
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell dimensions		
$a$ (Å)	17.699(1)	12.269(2)
$b$ (Å)	10.201(2)	17.890(3)
$c$ (Å)	15.4469(9)	12.035(2)
$\alpha$ (°)	90.000	97.17(1)
$\beta$ (°)	106.618(4)	119.328(8)
$\gamma$ (°)	90.000	79.62(1)
$V$ (Å <sup>3</sup> )	2672.4(8)	2263(1)
$Z$	4	2
Formula weight	363.44	1162.38
Density (calc.) (g cm <sup>-3</sup> )	1.81	1.71
Absorption coefficient (mm <sup>-1</sup> )	3.48	3.09
$F(000)$	1472	1176

## EXPERIMENTAL

### General

All operations were carried out under argon using the standard Schlenk technique.  $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$ <sup>7</sup> and  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ <sup>8</sup> were synthesized and purified by literature methods. Reagent grade methylisothiocyanate and allyl-isothiocyanate were purchased from Wako Pure Chemical, Inc. MeOH and EtOH were dehydrated on magnesium cake and distilled before use.

### Synthesis of $[\text{Cu}\{\mu_3\text{-SC(=NMe)(OEt)}\}]_4$ (**1**)

A solution of methylisothiocyanate (3.9 mg, 0.053 mmol) in ethanol (7 cm<sup>3</sup>) was added to  $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$  (14.3 mg, 0.044 mmol) and stirred for 1 h. The colourless clear solution was transferred to a glass tube and kept at  $-15^\circ\text{C}$ . After 7 months yellow plate crystals were obtained.

### Synthesis of $[\text{Cu}\{\mu_3\text{-SC(=NC}_3\text{H}_3\text{)(OMe)}\}]_6$ (**2**)

A solution of allyl-isothiocyanate (5.3  $\mu\text{l}$ , 0.054 mmol) in methanol (7 cm<sup>3</sup>) was added to  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  (6.4 mg, 0.017 mmol) and stirred for 30 min. The solution was then filtered and the colourless filtrate was transferred to a glass tube and kept at  $-15^\circ\text{C}$ . After 3 months yellow cubic crystals were obtained.

### X-ray data collections, structure solution and refinement

Diffraction data were collected at ambient temperature on a Rigaku AFC5R four-circle diffractometer equipped with graphite monochromated Mo- $K_\alpha$  radiation. Crystal data and details of measurements for both complexes are summarized in Table 1. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection for two complexes, indicating crystal and X-ray stability. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

Both structures were solved by direct methods and expanded using Fourier techniques.<sup>9</sup> All non-hydrogen atoms of **1** were refined anisotropically, while for **2** some non-hydrogen atoms were refined anisotropically and the rest were refined isotropically. Hydrogen atoms were included for **1** and refined isotropically, but not included for **2**. Any correlations effects were not considered in refinements. Reliability factors are defined as  $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$  and  $R_w = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2\}^{1/2}$ . Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.<sup>10</sup> The calculations were performed on the IRIS computer by using the program system TEXSAN.<sup>11</sup> Refinements of the parameters were accomplished by full-matrix least-squares and converged with  $R = 0.027$  and  $R_w = 0.020$  for the 2255

observed reflections and  $R = 0.080$  and  $R_w = 0.072$  for the 2817 observed reflections for **1** and **2**, respectively. The slightly high  $R$  values for **2** may be caused by the poor quality of its crystal and/or the exclusion of hydrogen atoms in the final refinement. Selected bond lengths and angles for **1** and **2** are given in Tables 2 and 3, respectively.

### NMR spectroscopy

$^1\text{H}$  NMR spectra were recorded on a Jeol GSX-270 spectrometer at  $23^\circ\text{C}$  using  $(\text{CD}_3)_2\text{CO}$  or  $\text{CD}_3\text{OD}$  as a solvent. All reported peak positions are relative to tetramethylsilane.

## RESULTS AND DISCUSSION

### Molecular structure of **1**

Figure 1 shows the molecular structure of **1** together with the numbering of atoms. Four copper atoms define a distorted tetrahedron, the faces of which are capped by four tridentate  $\text{MeN}=\text{C}(\text{OEt})\text{S}^-$  ligands formed *in situ* (see below). The nitrogen atom and the sulphur atom of each ligand coordinate to one and two copper atoms, respectively. The coordination geometry around the copper atom can be regarded as a regular triangle, though the  $\text{S}-\text{Cu}-\text{S}'$  angle (mean value  $123.9^\circ$ ) is

slightly greater than the  $\text{N}-\text{Cu}-\text{S}$  and  $\text{N}-\text{Cu}-\text{S}'$  angle (mean value  $118.0^\circ$ ). Other structural features have been mentioned in detail elsewhere.<sup>6</sup>

### Molecular structure of **2**

The unit cell of this complex contains two centrosymmetric molecules, as shown in Fig. 2. A skeleton of one of them is shown in Fig. 3, from which we can see a paddlewheel-like structure with six planes made by the ligands. Although the structural parameters of these two molecules are very similar to each other, as listed in Table 3, they are crystallographically independent as indicated by the angle of  $18.6^\circ$  between the two axes of these paddlewheels. Each molecule has a centre of inversion. Six copper atoms form a distorted octahedron and six surfaces of the eight are capped by six  $\text{C}_3\text{H}_5\text{N}=\text{C}(\text{OMe})\text{S}^-$  ligands (formed *in situ*) in the same fashion as in the case of **1**. Each copper atom shows a trigonal, almost planar, geometry coordinated by one nitrogen atom and two sulphur atoms. The  $\text{S}-\text{Cu}-\text{S}'$  ( $113^\circ$ ) is slightly smaller than the average  $\text{N}-\text{Cu}-\text{S}$  or  $\text{N}-\text{Cu}-\text{S}'$  angles ( $121^\circ$ ), in contrast to the case of **1**, indicating that these angles are dependent on the size of the polyhedron. The average  $\text{Cu}-\text{N}$  and  $\text{Cu}-\text{S}$  distances of 2.01 and 2.250 Å, respectively, are comparable with those reported for three-coordinated copper(I)

Table 2. Selected bond lengths (Å) and bond angles ( $^\circ$ ) for **1**

$\text{Cu}(1)-\text{Cu}(1)^*$	2.8270(7)	$\text{S}(2)-\text{C}(6)$	1.761(3)
$\text{Cu}(1)-\text{Cu}(2)$	2.5974(5)	$\text{N}(1)-\text{C}(1)$	1.468(4)
$\text{Cu}(1)-\text{Cu}(2)^*$	2.6344(5)	$\text{N}(1)-\text{C}(2)$	1.282(3)
$\text{Cu}(1)-\text{S}(1)^*$	2.2953(8)	$\text{N}(2)-\text{C}(5)$	1.467(4)
$\text{Cu}(1)-\text{S}(2)^*$	2.2706(9)	$\text{N}(2)-\text{C}(6)$	1.285(3)
$\text{Cu}(1)-\text{N}(1)$	1.982(2)	$\text{O}(1)-\text{C}(2)$	1.344(3)
$\text{Cu}(2)-\text{Cu}(2)^*$	2.8628(7)	$\text{O}(1)-\text{C}(3)$	1.444(4)
$\text{Cu}(2)-\text{S}(1)^*$	2.2680(9)	$\text{O}(2)-\text{C}(6)$	1.345(3)
$\text{Cu}(2)-\text{S}(2)^*$	2.2974(9)	$\text{O}(2)-\text{C}(7)$	1.450(4)
$\text{Cu}(2)-\text{N}(2)$	1.983(2)	$\text{C}(3)-\text{C}(4)$	1.479(5)
$\text{S}(1)-\text{C}(2)$	1.766(3)	$\text{C}(7)-\text{C}(8)$	1.467(6)
$\text{N}(1)-\text{Cu}(1)-\text{S}(2)$	116.44(7)	$\text{O}(1)-\text{C}(2)-\text{S}(1)$	119.0(2)
$\text{N}(1)-\text{Cu}(1)-\text{S}(1)^*$	119.33(7)	$\text{C}(2)-\text{O}(1)-\text{C}(3)$	121.8(2)
$\text{S}(2)-\text{Cu}(1)-\text{S}(1)^*$	124.22(3)	$\text{Cu}(2)-\text{Cu}(1)-\text{Cu}(2)^*$	66.34(2)
$\text{N}(2)-\text{Cu}(2)-\text{S}(1)^*$	119.19(7)	$\text{Cu}(2)-\text{Cu}(1)-\text{Cu}(1)^*$	57.93(1)
$\text{N}(2)-\text{Cu}(2)-\text{S}(2)^*$	117.23(7)	$\text{Cu}(2)^*-\text{Cu}(1)-\text{Cu}(1)^*$	56.66(1)
$\text{S}(1)^*-\text{Cu}(2)-\text{S}(2)^*$	123.57(3)	$\text{Cu}(1)-\text{Cu}(2)-\text{Cu}(1)^*$	65.41(2)
$\text{C}(2)-\text{N}(1)-\text{C}(1)$	117.8(3)	$\text{Cu}(1)-\text{Cu}(2)-\text{Cu}(2)^*$	57.45(1)
$\text{C}(1)-\text{N}(1)-\text{Cu}(1)$	121.6(2)	$\text{Cu}(1)^*-\text{Cu}(2)-\text{Cu}(2)^*$	56.21(1)
$\text{C}(2)-\text{N}(1)-\text{Cu}(1)$	120.6(2)	$\text{Cu}(1)^*-\text{S}(1)-\text{Cu}(2)^*$	69.39(3)
$\text{N}(1)-\text{C}(2)-\text{O}(1)$	118.5(3)	$\text{Cu}(1)-\text{S}(2)-\text{Cu}(2)^*$	70.44(3)
$\text{N}(1)-\text{C}(2)-\text{S}(1)$	122.5(2)		

\* Atoms with expanded symmetry.

Table 3. Selected bond lengths (Å) and bond angles (°) for **2**

Molecule I			
Cu(1)—Cu(2)	2.911(4)	Cu(1)—N(1)	1.97(2)
Cu(1)—Cu(3)	2.852(4)	Cu(2)—N(2)	2.02(2)
Cu(2)—Cu(3)*	3.011(4)	Cu(3)—N(3)	2.04(2)
Cu(1)—Cu(2)*	3.311(5)	S(1)—C(2)	1.69(2)
Cu(1)—Cu(3)*	3.364(4)	S(2)—C(7)	1.76(3)
Cu(2)—Cu(3)	3.254(4)	S(3)—C(12)	1.77(2)
Cu(1)—S(2)	2.246(6)	N(1)—C(2)	1.28(3)
Cu(1)—S(3)	2.256(7)	N(2)—C(7)	1.25(3)
Cu(2)—S(1)	2.246(7)	N(3)—C(12)	1.24(2)
Cu(2)—S(3)*	2.247(7)	N(1)—C(3)	1.52(3)
Cu(3)—S(1)	2.253(7)	N(2)—C(8)	1.50(3)
Cu(3)—S(2)*	2.251(7)	N(3)—C(13)	1.52(3)
N(1)—Cu(1)—S(2)	123.4(6)	Cu(2)—Cu(1)—Cu(2)*	90.6(1)
N(1)—Cu(1)—S(3)	120.7(6)	Cu(3)—Cu(1)—Cu(3)*	90.6(1)
S(2)—Cu(1)—S(3)	111.2(3)	Cu(2)—Cu(1)—Cu(3)	68.71(1)
N(2)—Cu(2)—S(1)	122.1(5)	Cu(2)—Cu(1)—Cu(3)*	56.79(9)
N(2)—Cu(2)—S(3)*	118.45(5)	Cu(3)—Cu(1)—Cu(2)*	57.9(1)
S(1)—Cu(2)—S(3)*	114.3(3)	Cu(2)*—Cu(1)—Cu(3)*	58.33(9)
N(3)—Cu(3)—S(1)	123.6(6)	Cu(3)—Cu(2)—Cu(3)*	90.1(1)
N(3)—Cu(3)—S(2)*	118.8(6)	Cu(1)—Cu(2)—Cu(1)*	89.4(1)
S(2)*—Cu(3)—S(1)	114.1(3)	Cu(1)—Cu(2)—Cu(3)	54.78(9)
C(2)—S(1)—Cu(2)	105.0(9)	Cu(3)—Cu(2)—Cu(1)*	61.6(1)
C(2)—S(1)—Cu(3)	99.6(9)	Cu(1)—Cu(2)—Cu(3)*	69.2(1)
Cu(2)—S(1)—Cu(3)	92.6(3)	Cu(3)*—Cu(2)—Cu(1)*	53.38(9)
C(7)—S(2)—Cu(1)	107.7(8)	Cu(1)—Cu(3)—Cu(1)*	89.4(1)
C(7)—S(2)—Cu(3)*	101.7(8)	Cu(2)—Cu(3)—(2)*	89.9(1)
Cu(1)—S(2)—Cu(3)*	96.8(3)	Cu(1)—Cu(3)—Cu(2)	56.48(9)
C(12)—S(3)—Cu(1)	103.9(8)	Cu(1)—Cu(3)—Cu(2)*	68.7(1)
C(12)—S(3)—Cu(2)*	103.3(8)	Cu(2)—Cu(3)—Cu(1)*	60.0(1)
Cu(1)—S(3)—Cu(2)*	94.7(2)	Cu(1)*—Cu(3)—Cu(2)*	53.99(9)
Molecule II			
Cu(4)—Cu(5)	2.829(4)	Cu(4)—N(4)	2.02(2)
Cu(4)—Cu(6)	2.995(4)	Cu(5)—N(5)	1.99(2)
Cu(5)—Cu(6)*	2.948(4)	Cu(6)—N(6)	2.02(2)
Cu(4)—Cu(5)*	3.359(5)	S(4)—C(17)	1.81(3)
Cu(4)—Cu(6)*	3.232(4)	S(5)—C(22)	1.77(2)
Cu(5)—Cu(6)	3.270(5)	S(6)—C(27)	1.80(3)
Cu(4)—S(5)	2.246(7)	N(4)—C(17)	1.31(3)
Cu(4)—S(6)	2.253(8)	N(5)—C(22)	1.24(2)
Cu(5)—S(4)	2.248(7)	N(6)—C(27)	1.21(3)
Cu(5)—S(6)*	2.259(7)	N(4)—C(18)	1.47(3)
Cu(6)—S(4)	2.248(8)	N(5)—C(23)	1.51(3)
Cu(6)—S(5)*	2.247(7)	N(6)—C(28)	1.59(3)
N(4)—Cu(4)—S(5)	124.9(6)	Cu(5)—Cu(4)—Cu(5)*	89.9(1)
N(4)—Cu(4)—S(6)	117.1(6)	Cu(6)—Cu(4)—Cu(6)*	90.3(1)
S(5)—Cu(4)—S(6)	112.7(3)	Cu(5)—Cu(4)—Cu(6)	68.3(1)
N(5)—Cu(5)—S(4)	124.5(6)	Cu(5)—Cu(4)—Cu(6)*	57.8(1)
N(5)—Cu(5)—S(6)*	120.0(6)	Cu(6)—Cu(4)—Cu(5)*	54.9(1)
S(4)—Cu(5)—S(6)*	110.4(3)	Cu(5)*—Cu(4)—Cu(6)*	59.5(1)
N(6)—Cu(6)—S(4)	117.9(7)	Cu(6)—Cu(5)—Cu(6)*	90.4(1)
N(6)—Cu(6)—S(5)*	122.5(7)	Cu(4)—Cu(5)—Cu(4)*	90.1(1)
S(5)*—Cu(6)—(4)	115.7(3)	Cu(4)—Cu(5)—Cu(6)	58.3(1)
C(17)—S(4)—Cu(5)	103.5(9)	Cu(6)—Cu(5)—Cu(4)*	58.3(1)
C(17)—S(4)—Cu(6)	104.1(9)	Cu(4)—Cu(5)—Cu(6)*	68.0(1)
Cu(5)—S(4)—Cu(6)	93.3(3)	Cu(6)*—Cu(5)—Cu(4)*	56.2(1)
C(22)—S(5)—Cu(4)	105.5(8)	Cu(4)—Cu(6)—Cu(4)*	89.7(1)
C(22)—S(5)—Cu(6)*	100.8(8)	Cu(5)—Cu(6)—Cu(5)*	89.6(1)
Cu(4)—S(5)—Cu(6)*	92.0(3)	Cu(4)—Cu(6)—Cu(5)	53.46(9)
C(27)—S(6)—Cu(4)	102(1)	Cu(4)*—Cu(6)—Cu(5)	62.2(1)
C(27)—S(6)—Cu(5)*	105(1)	Cu(5)*—Cu(6)—Cu(4)	68.8(1)
Cu(4)—S(6)—Cu(5)*	96.2(3)	Cu(5)*—Cu(6)—Cu(4)*	54.24(9)

\* Atoms with expanded symmetry.

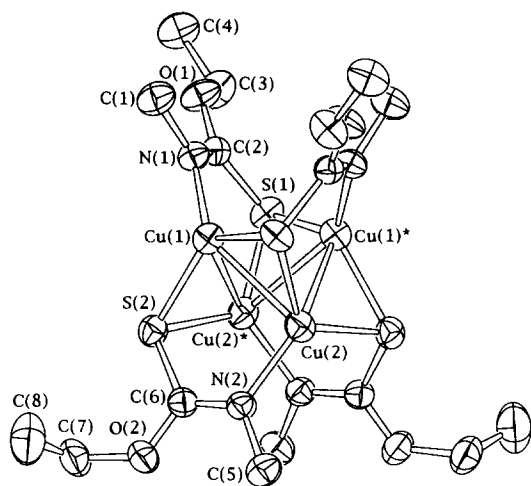


Fig. 1. Molecular structure of  $[\text{Cu}\{\mu_3\text{-SC(=NMe)}\}]_4$  (**1**) viewed from near the *a*-axis, showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. Copper atoms and only half of the constituent atoms except for the copper atoms are labelled; others are related by a rotation around the  $C_2$ -axis.

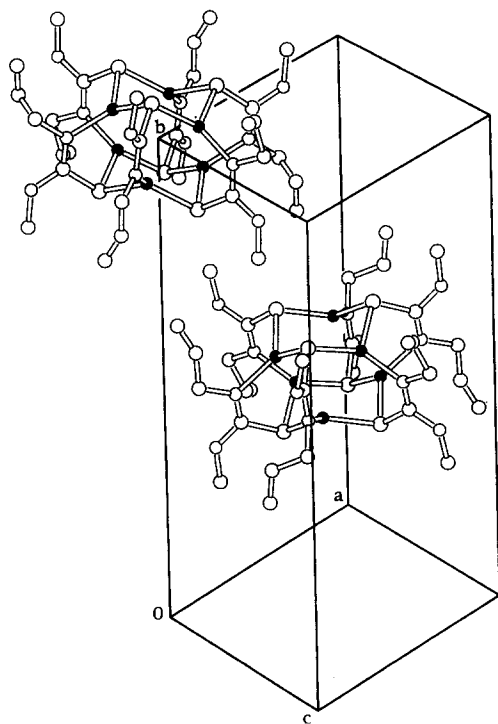


Fig. 2. Crystal packing of  $[\text{Cu}\{\mu_3\text{-SC(=NC}_3\text{H}_5\text{)(OMe)}\}]_6$  (**2**), showing two independent molecules. Only copper atoms are indicated by filled circles. Hydrogen atoms are omitted for clarity.

complexes.<sup>12</sup> The short N(1)—C(2) distance of 1.28(3) Å shows a C=N double bond character, which is also reflected on a ligand structure which is planar except for the vinyl and methyl groups.

Table 4 lists the Cu—Cu distances of **1** and **2**,

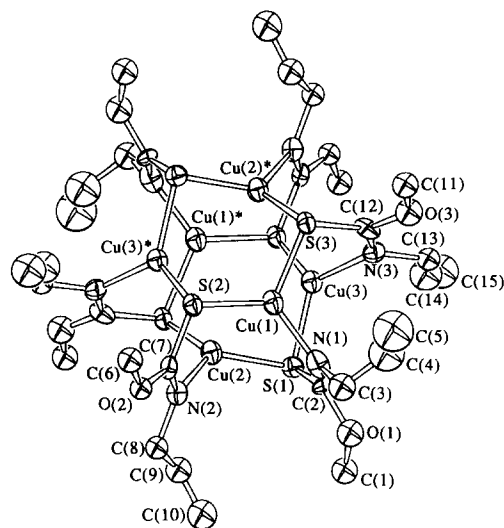


Fig. 3. Molecular structure **1** in  $[\text{Cu}\{\mu_3\text{-SC(=NC}_3\text{H}_5\text{)(OMe)}\}]_6$  (**2**) viewed from near the *b*-axis, showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. Copper atoms and only half of the constituent atoms except for the copper atoms are labelled; others are related by a centre of inversion.

together with tetranuclear and hexanuclear copper(I) complexes with S—C=N bridging moieties so far reported.<sup>1,2,4,13</sup> In hexanuclear complexes, those bridged by sulphur atoms are longer than those bridged by S—C=N moieties, with the exception of 3-trimethylsilylpyridine-2-thiolato. However, this is not true for tetranuclear complexes. The Cu—Cu distances bridged by sulphur atoms in this class of complexes range widely from 2.616 to 3.306 Å, suggesting that they are strongly influenced by characteristics of ligands and the nuclearity of each complex.

#### <sup>1</sup>H NMR spectra of the reaction solution

In both complexes iminomethanethiolato ions were found as bridging ligands; however, the ligand initially provided into the reaction vessel was isothiocyanate. It seems likely that nucleophilic attack of alkoxyl oxygen on an isothiocyanate carbon results in the formation of an iminomethanethiole. However, our <sup>1</sup>H NMR measurements of a solution of allylthiocyanate in deuterated methanol showed no signal change for 1 week, indicating that the nucleophilic attack does not proceed in the absence of copper(I) ions. On the other hand, when copper(I) ions were added as  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  to the above solution, a gradual change of proton signals were observed (Fig. 4a,b). Signals with an asterisk in Fig. 4b (1 h after addition) can be tentatively assigned to an allylthiocyanate—copper(I) monomer complex. The doublet at 3.94 ppm

Table 4. Cu—Cu distances (Å) in polynuclear copper(I) complexes with  $\text{XN}=\text{C}(\text{Y})\text{S}^-$  bridging moieties

$n^a$	X	Y	Cu—Cu <sup>b</sup>	Cu—Cu <sup>c</sup>	Average	Ref.
4	Me	OEt	2.616	2.845	2.692	This work
4		MeNC <sub>2</sub> H <sub>2</sub> <sup>d</sup>	2.671	3.132	2.825	2
6	Ph	SBU	2.878	2.839	2.859	13b
6		C <sub>4</sub> H <sub>4</sub> <sup>e</sup>	3.073	2.826	2.950	1a
6		C <sub>8</sub> H <sub>6</sub> <sup>f</sup>	3.140	2.797	2.969	1d
6	Ph	OPh	3.184	2.836	3.010	4
6	Ph	N(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> O	3.232	2.844	3.038	13a
6		Me <sub>3</sub> SiC <sub>4</sub> H <sub>3</sub> <sup>g</sup>	2.952	3.139	3.046	1b
6	C <sub>3</sub> H <sub>5</sub>	OMe	3.298	2.924	3.111	This work
6		C <sub>5</sub> H <sub>5</sub> N <sub>2</sub> OS <sup>h</sup>	3.306	2.940	3.123	1c

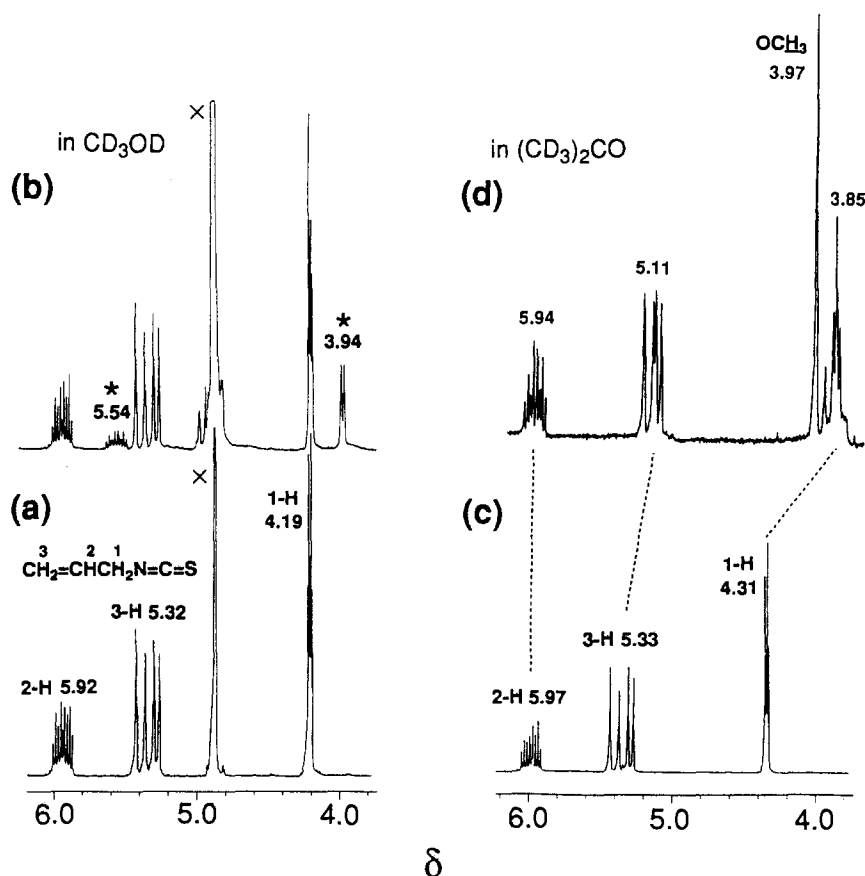
<sup>a</sup> Nuclearity.<sup>b</sup> Bridged by sulphur atoms.<sup>c</sup> Bridged only by SC=N moieties of ligands.<sup>d</sup> 1-Methylimidazoline-2-thiolato.<sup>e</sup> Pyridine-2-thiolato.<sup>f</sup> Quinoline-2-thiolato.<sup>g</sup> 3-Trimethylsilylpyridine-2-thiolato.<sup>h</sup> 4-Hydroxy-6-methylpyrimidine-2-thiolato.

Fig. 4. <sup>1</sup>H NMR spectra of: (a) a CD<sub>3</sub>OD solution of allyl isothiocyanate (14 mM); (b) 1 h after addition of Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (4.6 mM) to (a); (c) a (CD<sub>3</sub>)<sub>2</sub>CO solution of allyl isothiocyanate; (d) a (CD<sub>3</sub>)<sub>2</sub>CO solution of **2**. Signals with an asterisk (\*) appearing in (b) are tentatively assigned to a copper(I)–isothiocyanate monomer complex. Signals with a cross (×) are due to undeuterated solvent (CH<sub>3</sub>OD).

and the multiplet at around 5.54 ppm may be assigned to H(1) and H(2) of allylisothiocyanate in the monomer complex, respectively. The upfield shift of about 0.4 ppm of the latter signal from the metal-free position is reasonable for olefinic protons complexed to copper(I).<sup>5</sup> Twenty hours after addition of [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub>, the former signal grew in intensity to almost the same as that of the signal at 4.19 ppm and the latter shifted upfield about 0.15 ppm, giving more complicated signals. Also shown in Fig. 4 is the <sup>1</sup>H MNR spectrum of a deuterated acetone solution of **2** (Fig. 4d). Compared with a metal-free allylisothiocyanate (Fig. 4c), signals of H(1) and H(3) shifted upfield and a new single peak due to methoxy protons was observed at 3.97 ppm. If the difference between solvents is considered, these signals are apparently different from those of the monomer complex, suggesting that **2** retains a hexanuclear structure in solution.

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