

Simultaneous formation of both novel bis(μ -sulfur)- and bis(μ -oxo)-bridged copper(II) dimers by reaction of *N*-benzoyl-*N'*,*N'*-dimethylthiourea (HL) with CuCl₂. Syntheses, crystal structures and magnetic properties of [$\{\text{CuL}(\text{HL})\text{Cl}\}_2$] and [$\{\text{CuL}_2\}_2$][†]

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Reaction of *N*-benzoyl-*N'*,*N'*-dimethylthiourea (HL) with copper(II) chloride yielded simultaneously two novel dimers: a pale green bis(μ -sulfur) bridged copper(II) dimer **1**, [$\{\text{CuL}(\text{HL})\text{Cl}\}_2$], and a dark green bis(μ -oxo) bridged copper(II) dimer **2**, [$\{\text{CuL}_2\}_2$], instead of the mononuclear copper(II) complexes, [CuL_2], usually formed from other dialkyl-substituted benzoylthiourea ligands. The molecular structures of **1** and **2** have been established by single-crystal X-ray analyses. In dimer **1** the central copper(II) ion has a distorted tetrahedral co-ordination environment with one chloride and three sulfur atoms derived from one terminal and two bridging ligands. The two sulfur atoms of both bridging ligands with two copper(II) ions form a strictly planar Cu₂S₂ bridging core, including two short [2.330(2) Å] and two longer [2.549(2) Å] Cu–S distances. The dimer **2** may be considered as comprising two mononuclear [CuL_2] complexes bridged by one of the acyl oxygen atoms of each to the copper atom of the other, resulting in a distorted tetragonal pyramidal geometry at each copper(II) center, and forming a planar four-membered Cu₂O₂ bridging unit which consists of two short [1.944(3) Å] and two longer Cu–O distances [2.668(3) Å], bridging bond angle Cu–O–Cu* [97.9(1)°]. Magnetic measurements for both dimers showed weak antiferromagnetic coupling between the copper(II) centers through bis-sulfur or bis-oxo bridges. The best fitting of the experimental magnetic susceptibility data gave $g = 2.110$, $J = -33 \text{ cm}^{-1}$ for dimer **1** and $g = 2.107$, $J = -4.5 \text{ cm}^{-1}$ for **2**.

Much attention has been paid to the investigation of a variety of dinuclear copper(II) complexes,¹ especially those ligated by sulfur donor atoms, because of their resemblance to the active centers of some binuclear copper proteins, such as hemocyanins and tyrosinase, which mediate redox reactions and electron transfer in biological systems. Therefore, research into the synthesis, structure and properties of dinuclear copper(II) complexes of thiolate-containing ligands is expected to shed light on the structure and mechanism of action of such metalloproteins. On the other hand, magnetostructural properties of copper(II) complexes have also attracted considerable attention² due to the potential applications of magnetic exchange properties in designing new magnetic materials, such as molecular-based magnets.

In view of the versatility of co-ordination of acylthioureas with transition metals, recently we treated *N*-ferrocenecarbonyl-*N'*,*N'*-dimethylthiourea (HL') with copper(II) chloride and obtained a bis-sulfur-bridged copper(II) dimer, [$\{\text{CuL}'(\text{HL}')\text{Cl}\}_2$],³ which has a similar co-ordination configuration to that of the Cu_A site of cytochrome c oxidase and other heme copper oxidases in which two distorted tetrahedral co-ordination units are bridged by two cysteinate ligands.

We now report an extension of our prior investigations to the reaction of *N*-benzoyl-*N'*,*N'*-dimethylthiourea (HL) with copper(II) chloride. Interestingly, two novel dimers, a bis-sulfur-bridged copper(II) dimer **1**, [$\{\text{CuL}(\text{HL})\text{Cl}\}_2$], and a bis-oxo-bridged copper(II) dimer **2**, [$\{\text{CuL}_2\}_2$], were afforded simultaneously. Now we present the crystal structures of both dimers together with their magneto-structural properties.

Experimental

Reagent grade chemicals were used as received unless stated otherwise. Elemental analyses were carried out on a MOD 1106 analyzer. Infrared spectra were recorded on a Shimadzu IR-435 instrument using KBr pellets in the 400–4000 cm⁻¹ region. X-Band EPR spectra were recorded with a Bruker 200 D-SRC ESR spectrometer at room temperature. In a typical experiment the instrument settings were: modulation frequency, 100 kHz; field modulation intensity, 5 G; receiver gain, 2×10^5 ; microwave power, 10 mW.

Variable-temperature magnetic susceptibility data were obtained on a SQUID susceptometer (Quantum Design, MPMS-5) in the temperature range 4.5–300 K with an applied field of 1 T. All data have been corrected for diamagnetism by using Pascal's constants.⁴

Preparation of the ligand

N-Benzoyl-*N'*,*N'*-dimethylthiourea was prepared using a similar procedure to that reported⁵ by the reaction of benzoyl chloride with KSCN in anhydrous acetone, and then condensation with dimethylamine. The crude product was recrystallized from ethanol to obtain a white crystal, mp 146 °C (Found: C, 57.21; H, 5.64; N, 13.10. Calc. for C₁₀H₁₂N₂OS: C, 57.69; H, 5.77; N, 13.46%).

Preparation of the dimers **1** and **2**

To an ethanol solution (4 cm³) of ligand HL (0.02 mmol), copper(II) chloride (0.04 mmol) in ethanol (3.5 cm³) was added dropwise at about one drop per 2 h at room temperature. At first a pale green crystal dimer **1** began to appear within several days. After about two weeks a second dark green crystal dimer **2** was formed simultaneously. Both crystals were of adequate size and quality for X-ray studies and easily separated manually.

[†] Supplementary data available: IR and X-band EPR spectra, experimental and calculated susceptibilities. For direct electronic access see <http://www.rsc.org/suppdata/dt/1999/2683/>, otherwise available from BLDSC (No. SUP 57596, 2 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).

Dimer **1**, [$\{\text{CuL}(\text{HL})\text{Cl}\}_2$]: mp 150 °C (Found: C, 46.53; H, 4.77; N, 10.53. Calc. for $\text{C}_{20}\text{H}_{23}\text{ClCuN}_4\text{O}_2\text{S}_2$: C, 46.69; H, 4.47; N, 10.89%). Dimer **2**, [$\{\text{CuL}\}_2$]: mp 216 °C (Found: C, 49.67; H, 4.60; N, 11.44. Calc. for $\text{C}_{20}\text{H}_{22}\text{CuN}_4\text{O}_2\text{S}_2$: C, 50.20; H, 4.60; N, 11.71%).

Crystallography

Crystal intensity data were collected on a Rigaku RAXIS-IV imaging plate area detector using graphite monochromated Mo-K α ($\lambda = 0.71070$ Å) radiation for unit-cell determination and data collection. Summaries of the crystallographic data, structure solution and refinement are given in Table 1.

A total of 30 3.00° oscillation frames with an exposure time of 12.0 min for dimer **1** and 45.0 min for dimer **2** per frame were used. The structures were obtained by direct methods and expanded using Fourier techniques. The data were corrected for Lorentz-polarization effects, the non-hydrogen atoms refined anisotropically and hydrogen atoms included but not refined. The data were refined by the SHELXL 93 program⁶ using all data for dimer **1** and TEXSAN for dimer **2**.⁶

CCDC reference number 186/1545.

See <http://www.rsc.org/suppdata/dt/1999/2683/> for crystallographic files in .cif format.

Results and discussion

Formation of the dimers **1** and **2**

Recently we have found that co-ordination of the dimethyl-substituted ferrocenecarbonylthiourea HL' to copper(II) ion differs substantially from that of the corresponding diethyl-substituted analogue HL". The former yields a bis-sulfur-bridged copper(II) dimer, [$\{\text{CuL}'(\text{HL}')\text{Cl}\}_2$],³ while the latter only co-ordinates in a bidentate manner to yield a single mononuclear copper(II) complex, [CuL''].⁷

In this study, we attempted to replace the ferrocenyl in HL' by a phenyl group to minimize the steric hindrance of the acylthiourea ligand in order to realize the numerous modes of co-ordination to copper(II) ions. Just as expected, the reaction of *N*-benzoyl-*N'*,*N'*-dimethylthiourea (HL) with copper(II) chloride affords simultaneously both dinuclear copper(II) complexes with different bridging atoms (sulfur or oxygen) and different geometries (distorted tetrahedron or square pyramid). Therefore, for such metal ions as copper with remarkably flexible co-ordination and versatile ligands such as acylthioureas having both potential O/S donor atoms, decreasing the steric hindrance of the substituents in the ligand might be favorable to realize various co-ordination modes.

The synthetic methodology adopted in this work is to control the relative concentration between the reaction components by the dropwise addition of metal to ligand solution, or the reverse, to make the reaction proceed under the conditions of one component (ligand or metal) in excess. In this way, dimer **1** formed first in the presence of an excess of ligand HL; under this condition sufficient HL exists in the solution to bridge the copper(II) ions, and the dimer **2** formed subsequently only in the presence of a lower concentration of HL which is favorable to the bidentate co-ordination of HL. At the same time, the dropping method made the reaction proceed under mild conditions in favor of the formation of single crystals suitable for X-ray studies.

Molecular structures

Dimer 1, [$\{\text{CuL}(\text{HL})\text{Cl}\}_2$]. An ORTEP⁸ drawing of dimer **1** is shown in Fig. 1 together with the numbering scheme. Selected bond distances and angles are given in Table 2. Each copper(II) ion is bonded to one chloride and three sulfur atoms from one terminal and two bridging acylthiourea ligands, displaying a distorted tetrahedral geometry. The terminal ligands exhibit

Table 1 Crystal parameters, data collection and refinement for dimers **1** and **2**

	1	2
Formula	$\text{C}_{40}\text{H}_{46}\text{Cl}_2\text{Cu}_2\text{N}_8\text{O}_4\text{S}_4$	$\text{C}_{40}\text{H}_{44}\text{Cu}_2\text{N}_8\text{O}_4\text{S}_4$
<i>M</i>	1029.07	956.18
Crystal system	orthorhombic	monoclinic
Space group	<i>Pccn</i> (no. 56)	<i>P2₁/n</i> (no. 14)
<i>a</i> /Å	21.637(4)	10.19(1)
<i>b</i> /Å	26.290(5)	17.138(4)
<i>c</i> /Å	9.109(2)	12.732(2)
β /°		102.900(4)
<i>U</i> /Å ³	5181.4(18)	2166(1)
<i>Z</i>	4	2
<i>T</i> /°C	18 ± (2)	15 ± 1
<i>D_c</i> /g cm ⁻³	1.319	1.465
μ (Mo-K α)/mm ⁻¹	1.129	1.224
Reflections collected/unique	2825/2825	3764
No. observations (<i>I</i> > 3.00 σ (<i>I</i>))	None	3005
No. variables		263
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.1070, 0.1737	0.038, 0.056
(all data)	0.1635, 0.1945	

Table 2 Selected bond lengths (Å) and angles (°) for dimer **1**

Metal co-ordination sphere			
Cu(1)–S(1)	2.273(2)	Cu(1)–Cl(1)	2.331(3)
Cu(1)–S(2)	2.330(2)	Cu(1)···Cu(1*)	2.619(2)
Cu(1)–S(2*)	2.549(2)		
S(1)–Cu(1)–S(2)	112.46(10)	Cl(1)–Cu(1)–S(2*)	101.81(9)
S(1)–Cu(1)–Cl(1)	115.92(10)	S(2)–Cu(1)–S(2*)	115.24(6)
S(1)–Cu(1)–S(2*)	102.72(8)	Cu(1)–S(2)–Cu(1*)	64.76(6)
Cl(1)–Cu(1)–S(2)	108.36(9)		
Terminal ligands		Bridging ligand	
S(1)–C(3)	1.694(8)	S(2)–C(12)	1.677(9)
N(1)–C(3)	1.306(8)	N(3)–C(12)	1.334(9)
N(2)–C(3)	1.385(10)	N(4)–C(12)	1.410(10)
N(2)–C(4)	1.392(9)	N(4)–C(14)	1.379(9)
O(1)–C(4)	1.204(10)	O(2)–C(14)	1.197(8)
C(4)–C(5)	1.515(13)	C(14)–C(15)	1.518(11)
S(1)–C(3)–N(2)	118.7(5)	S(2)–C(12)–N(4)	120.8(5)
S(1)–C(3)–N(1)	122.9(6)	S(2)–C(12)–N(3)	122.7(7)
N(1)–C(3)–N(2)	118.4(7)	N(3)–C(12)–N(4)	116.5(8)
O(1)–C(4)–N(2)	122.9(8)	O(2)–C(14)–N(4)	123.4(7)
O(1)–C(4)–C(5)	120.3(7)	O(2)–C(14)–C(15)	119.9(7)
N(2)–C(4)–C(5)	116.7(8)	N(4)–C(14)–C(15)	116.6(6)

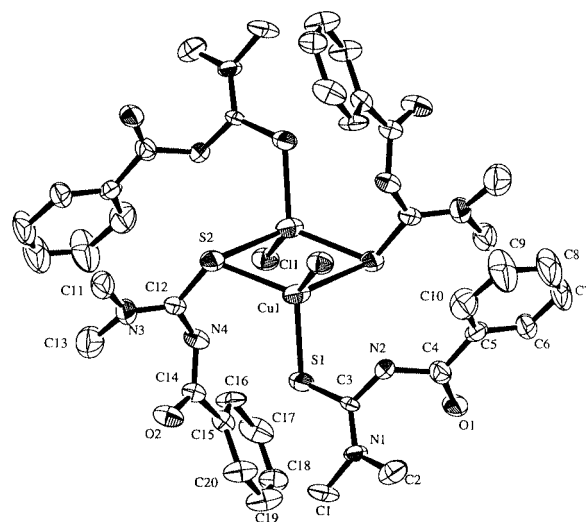


Fig. 1 An ORTEP diagram of the molecular structure of dimer **1**, showing the atomic numbering.

an ionic form (L) deprotonated from the thioamido (NHC(=S)) group and the bridged species are neutral (HL). The two copper(II) ions and the bridging sulfur atoms lie strictly in plane, forming a Cu₂S₂ core with two short (2.330(2) Å) and two longer (2.549(2) Å) Cu–S distances. The short one is nearly the same as the sum of the tetrahedral covalent radii (2.39 Å). The core also contains a relatively short Cu···Cu separation of 2.619(2) Å, a narrow bridging Cu–S–Cu* angle of 64.76(6)° and a wide S(2)–Cu–S(2)* angle of 115.24(6)°. The dihedral angle τ (56.60°) between the core and the remaining co-ordination plane, Cl(1)Cu(1)S(1) or Cl(1')Cu(1')S(1'), is smaller than the right angle (90°) of a normal tetrahedron, indicating a rather distorted tetrahedral co-ordination geometry around copper(II).

Dimer 2, [(CuL₂)₂]. Dimer **2** is built by two mononuclear [CuL₂] units related through a molecular inversion center. A

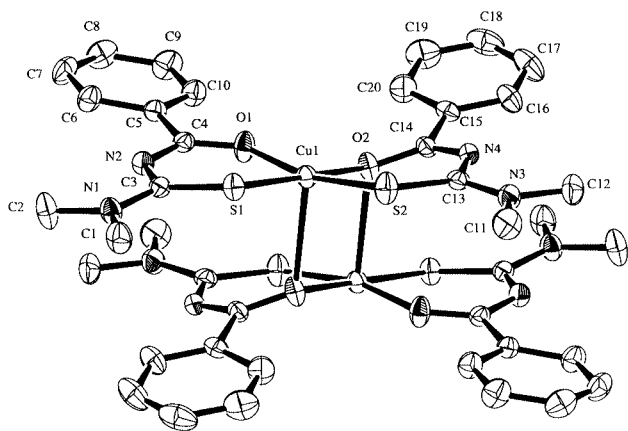


Fig. 2 An ORTEP diagram of the molecular structure of dimer **2**, showing the atomic numbering.

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

Metal co-ordination sphere			
Cu(1)–S(1)	2.245(1)	Cu(1)–O(2*)	2.668(3)
Cu(1)–S(2)	2.248(2)	Cu(1)···Cu(1*)	3.51
Cu(1)–O(1)	1.929(3)		
Cu(1)–O(2)	1.944(3)		
S(1)–Cu(1)–S(2)	89.14(7)	S(1)–Cu(1)–O(2)	177.70(8)
S(2)–Cu(1)–O(2)	93.15(10)	S(2)–Cu(1)–O(1)	167.0(1)
O(1)–Cu(1)–O(2)	84.8(1)	O(2)–Cu(1)–O(2*)	82.1(1)
O(1)–Cu(1)–S(1)	92.90(10)	Cu(1)–O(2)–Cu(1*)	97.9(1)
Ligand			
S(1)–C(3)	1.734(4)	S(2)–C(13)	1.730(4)
O(1)–C(4)	1.275(4)	O(2)–C(14)	1.278(4)
C(3)–N(2)	1.348(5)	C(13)–N(4)	1.347(5)
N(2)–C(4)	1.321(5)	N(4)–C(14)	1.315(4)
Cu(1)–O(1)–C(4)	133.3(2)	Cu(1)–O(2)–C(14)	128.8(2)
O(1)–C(4)–N(2)	129.1(3)	O(2)–C(14)–N(4)	128.9(3)
C(3)–N(2)–C(4)	124.8(3)	C(13)–N(4)–C(14)	124.9(3)
S(1)–C(3)–N(2)	128.9(3)	S(2)–C(13)–N(4)	127.8(3)
O(1)–C(4)–C(5)	114.9(3)	O(2)–C(14)–C(15)	115.7(3)
S(1)–C(3)–N(1)	116.1(3)	S(2)–C(13)–N(3)	116.8(3)

Table 4 Main characteristic IR spectral bands of HL and dimers (cm^{−1})

Compound	$\nu(\text{CH})$, $\delta(\text{NH})$	$\nu(\text{C}=\text{S})$	$\nu(\text{N}=\text{C}=\text{S})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{CH}_3)$	$\nu(\text{phenyl ring})$
HL	2900, 3200	1245, 660	1190	1685	1460, 1385	1550, 1460
Dimer 1	3457, 3110	1246, 658	1120	1690	1468, 1392	1562, 1468
Dimer 2	3456, 3108 ^a	1257, 680 ^a	1130 ^a	— ^b	1420, 1380 ^c	1574, 1498 ^c

^a Reduced in intensity. ^b Disappeared. ^c Strengthened in intensity considerably.

view of the dimeric entity is given in Fig. 2 together with the numbering scheme. Selected bond distances and angles are given in Table 3.

Each copper(II) center has an elongated square pyramidal (4+1) environment; the basal plane comprises two oxygen and two sulfur atoms in *cis* position from both quasiplanar deprotonated ligands (L[−]) and the axial co-ordination site is occupied by a second oxygen atom belonging to the other half of the dimer. The out-of-plane Cu–O distance of 2.668(3) Å is somewhat longer than the in-plane distances (bridged Cu–O 1.944(3), non-bridged Cu–O 1.929(3) Å). The bridging Cu₂O₂ unit is constrained to be planar by the presence of the crystallographic inversion center in the middle of the dimer. The intradimeric Cu···Cu distance is 3.51 Å and bridging Cu–O–Cu* angle is 97.9(1)°.

From Fig. 2, it is striking that each mononuclear moiety of the dimer is nearly planar, the greatest deviations from the mean plane being just 0.629(5) (C(18)) and 0.466(5) Å (C(7)) for the phenyl rings, while the interval (2.668(3) Å) between both moieties is large enough to form the bis-oxo-bridging bonds without steric hindrance. This may result from the substitution of planar phenyl and smaller methyl groups on the *N,N'* sites of the ligand.

IR spectroscopic properties

The characteristic IR absorption bands of ligand HL and both dimers are presented in Table 4. The broad and weak band around 2900–3200 cm^{−1} observed for free HL may be attributed to the combined $\nu(\text{CH})$ vibrations of the benzene portion and $\delta(\text{NH})$ vibration which is split into two broad bands at 3457 and 3110 cm^{−1} for both dimers. The lack of a $\nu(\text{SH})$ band around 2500 cm^{−1} and the presence of two $\nu(\text{NH})$ bands at *ca.* 3457 and 3110 cm^{−1} unequivocally confirm the S-co-ordination mode of the ligand in dimers **1** and **2**. The presence of a strong band at 1245–1257 cm^{−1} is tentatively assigned to $\nu(\text{C}=\text{S})$. The $\nu(\text{N}=\text{C}=\text{S})$ band at 1190 cm^{−1} for free HL shifts to 1120 cm^{−1} for dimer **1** and 1130 cm^{−1} for **2**; this further evidences that the ligand is co-ordinated to copper(II) *via* the sulfur atom. The strong stretch at 1685 cm^{−1} assigned to the carbonyl stretch of the C(O)NH moiety in the uncomplexed ligand is nearly unchanged at 1690 cm^{−1} for dimer **1**, because in this dimer the carbonyl group does not participate in the co-ordination. In dimer **2** this vibration virtually disappears due to the formation of bis-oxo-bridging to make the $\nu(\text{C}=\text{O})$ vibration weak.

Further characteristics of the IR spectrum of dimer **2** are the occurrence of strong and sharp bands at 1420 and 1380 cm^{−1} which are assignable to the C–CH₃ symmetric and asymmetric deformation vibrations, respectively,⁹ and other strong bands at 1574 and 1498 cm^{−1} may result from the skeletal vibrations of phenyl rings.¹⁰ These four absorption bands are strengthened considerably in intensity in comparison with those of the “free” ligand and dimer **1**. These observations are consistent with the molecular structures of dimers **1** and **2**.

EPR Spectra

The X-band (9.78 GHz) powder EPR spectra for dimers **1** and **2** have been recorded at 300 K (Fig. 3). The spectrum of **1** exhibits well resolved resonance bands in the middle magnetic

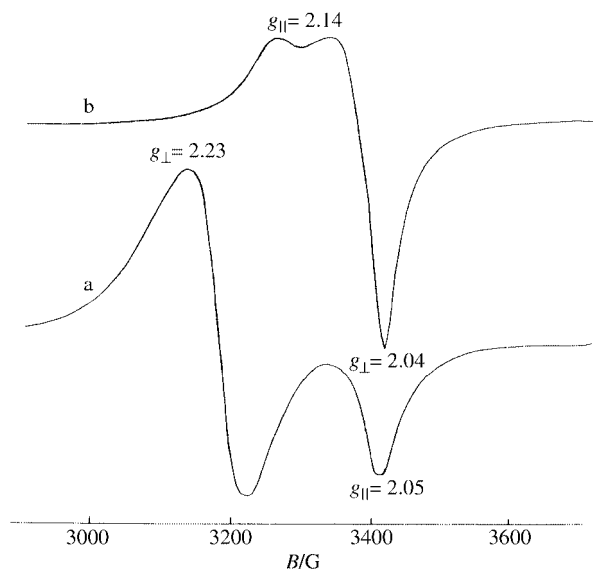


Fig. 3 X-Band EPR spectra for powdered dimers **1** (a) and **2** (b) at 300 K, $\nu = 9.78$ GHz.

field region, indicative of a typical copper(II) anisotropic (axial) g tensor, with $g_{\perp} = 2.23$ and $g_{\parallel} = 2.05$, the average value (taken as $g_{\text{av}} = (2g_{\parallel} + g_{\perp})/3$) being 2.110. These values allow us to consider the existence of a distorted four-co-ordinated geometry around the Cu^{II} ($g_{\parallel} < g_{\perp}$) in d_{xy} ground electronic state. The spectrum for dimer **2** is typical for a very weakly coupled copper(II) ion in an axially elongated square pyramidal surrounding with $g_{\perp} = 2.04$ and $g_{\parallel} = 2.14$. The average g value is 2.107. From the observed trend of g values ($g_{\parallel} > g_{\perp} > 2.0023$) the ground electronic state is suggested to be associated with the $d_{x^2-y^2}$ orbitals.

Magnetic properties

Dimer 1. In the measurements of the variable-temperature susceptibility for dimer **1**, negative diamagnetic values appeared over the temperature range 50–300 K. Further lowering the temperature (< 50 K) gave positive values which increased with temperature decrease. The χ_m vs. T curve still exhibits the feature of antiferromagnetic exchange as a whole (Fig. 4a). This situation may be attributed to the lower susceptibility of dimer **1** and the presence of a large amount of diamagnetic impurities which may stem from the reduction of Cu^{II} to Cu^{I} by the acylthiourea ligand, or to the existence of different crystal forms varying in magnetic interaction. In order to facilitate the simulation, a diamagnetic correction (χ_{impurity}) was applied to the experimental values by simple shift along the χ_m axis (Fig. 4b). However, this does not make any changes in the general trend of the magnetic response, and does not affect the magnetic parameters. The temperature dependence of the molar magnetic susceptibility $\chi_m T$ for dimer **1** in Fig. 4 illustrates that at room temperature (300 K) the value of $0.53 \text{ emu K mol}^{-1}$ ($\mu_{\text{eff}} = 2.06 \mu_B$) is near to the value of $1.9\text{--}2.0 \mu_B$ normally observed for copper(II) compounds. On lowering the temperature, the $\chi_m T$ value gradually decreases to reach a minimum at 75 K with $\chi_m T = 0.30 \text{ emu K mol}^{-1}$ ($\mu_{\text{eff}} = 1.549 \mu_B$). Such behavior reveals an intramolecular antiferromagnetic interaction between copper(II) ions with a spin-triplet ground state. However, on further decreasing the temperature below 50 K, another discontinuous $\chi_m T$ vs. T curve appears, which has a different magnetic exchange behavior. This may be due to the presence of small amounts of uncoupled paramagnetic impurity.

A preliminary analysis of the experimental susceptibility was performed by use of the modified Bleaney–Bowers eqn. (1),^{11,12}

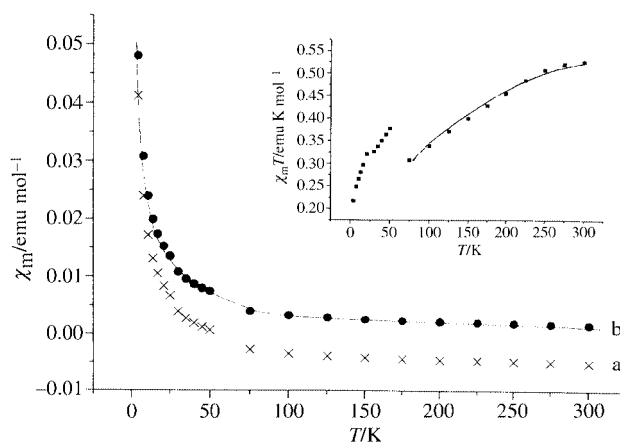


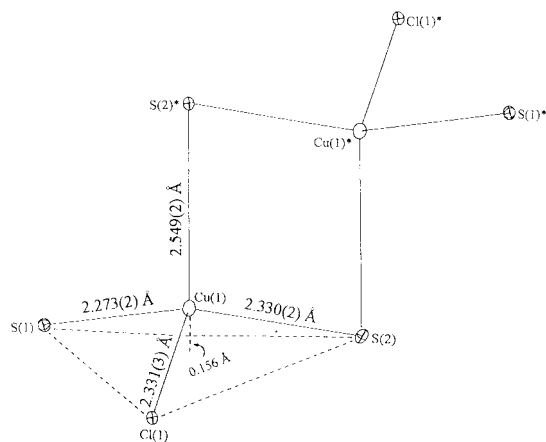
Fig. 4 Thermal variation of χ_m and $\chi_m T$ for dimer **1**. Crosses (x) represent the total susceptibility, filled circles (●) that after subtracting a diamagnetic correction (see text). Solid line (—) corresponds to the best fit.

$$\chi_m = \frac{Ng^2\beta^2}{3k(T - \theta)} \left[1 + \frac{1}{3} \exp(-2J/kT) \right]^{-1} (1 - P) + \frac{Ng^2\beta^2}{4kT} P + \chi_{\text{impurity}} \quad (1)$$

derived from the isotropic (Heisenberg) exchange Hamilton ($H = -2JS_1 \cdot S_2$) for two interacting $S = 1/2$ centers, where χ_m is expressed per mole of copper atoms, p is the fraction of monomeric impurity, and θ a corrective term for interdimer interactions, and the correction term $\chi_{\text{impurity}} = -696 \times 10^{-5} \text{ emu mol}^{-1}$. The best data fit with eqn. (1) (solid line in Fig. 4) gave $g = 2.110$, $J = -33 \text{ cm}^{-1}$, $p = 0.008$ and $\theta = -3.5 \text{ K}$. The discrepancy factor $\sigma = [\sum(\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \sum \chi_{\text{obs}}^2]^{1/2}$ in the least-squares fits was 1.57×10^{-3} .

In the literature two kinds of copper dimers with Cu_2S_2 bridging cores have been reported as: diamagnetically bis-sulfur-bridged monovalent copper(I) dimers $[\{\text{Cu}^{\text{I}}(\text{HL}^1)\text{Cl}\}_2]^{13}$ and $[\{\text{Cu}^{\text{I}}(\text{H}_2\text{L}^2)\text{Cl}\}_2]^{14}$ ($\text{HL}^1 = 2(1H)$ -pyridinethione, $\text{H}_2\text{L}^2 = 1$ -methylimidazoline-2-thione), and paramagnetic divalent copper(II) dimers, such as $[\{\text{Cu}^{\text{II}}(\text{L}^3)\text{Cl}\}_2]^{15}$ (denoted as dimer **3**) and $[\{\text{Cu}^{\text{II}}\text{L}'(\text{HL}')\text{Cl}\}_2]^3$ (denoted as dimer **4**) ($\text{HL}' = N$ -ferrocenecarboxyl- N' , N' -dimethylthiourea). To our knowledge, only dimers **3** and **4** have been studied magnetotstructurally, and can be compared with **1**.

In dimer **3** the copper(II) center has a distorted square-pyramidal (4+1) geometry, the bridging S atom is axial to one of the two Cu atoms bridged and orthogonal to the magnetic orbital ($d_{x^2-y^2}$), resulting in a weak antiferromagnetic interaction, $J = -4.7 \text{ cm}^{-1}$. In **4** the copper(II) center is in a distorted tetrahedral co-ordination geometry, the magnetic orbital (d_{xy}) is roughly toward the bridging S orbital, leading to a larger J value of -196.3 cm^{-1} . However, **1** has a similar tetrahedral co-ordination sphere, but the J value, -33 cm^{-1} , is substantially smaller than that of **4**. The weak magnetic interaction in dimer **1** may be related to the geometry of the copper co-ordination sphere as shown in Scheme 1. The apical co-ordination distance $\text{Cu-S}(2)^*$, $2.549(2) \text{ \AA}$, is apparently longer than that of three others: $\text{Cu-S}(1)$, $2.273(2)$; $\text{Cu-S}(2)$, $2.330(2)$ and $\text{Cu-Cl}(1)$, $2.331(3) \text{ \AA}$, respectively, and the copper center is only 0.156 \AA apart from the trigonal basal plane, $\text{S}(1)\text{S}(2)\text{Cl}(1)$. Apparently, the copper center is in an elongated tetrahedral environment. In addition, the dihedral angle τ between the bridging core plane Cu_2S_2 and the remaining co-ordinating plane $\text{Cu}(1)\text{S}(1)\text{Cl}(1)$ is 56.50° in dimer **1**, which is smaller than 88.55° in **4** and the normal tetrahedral τ value of 90° , consequently in **1** the distortions from idealized tetrahedral symmetry (T_d) are so great that orbital overlap is probably



Scheme 1 The geometry of bis-sulfur-bridged co-ordination sphere in dimer **1**.

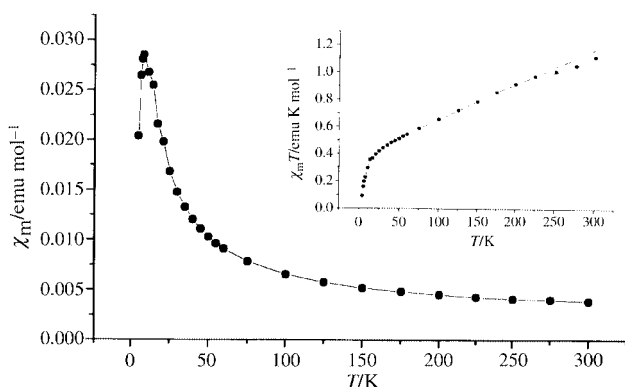


Fig. 5 Thermal variation of χ_m and $\chi_m T$ for dimer **2**. Solid line (—) corresponds to the best theoretical fit.

greatly diminished, and hence the coupling interaction is lowered.

Dimer 2. The magnetic susceptibilities were determined over the temperature range 4.5–300 K. As seen in Fig. 5 the susceptibilities increase slightly as the temperature decreases from 300 to 100 K, and then increase rapidly through a maximum at about 8 K, and eventually decrease. The shape of the plot reveals behavior typical of weakly antiferromagnetic exchange interactions. The temperature dependence of the $\chi_m T$ product for dimer **2** could be fitted very well by the Bleaney–Bowers model from the temperature 4.5 to 300 K. The $\chi_m T$ values gradually decrease from 1.104 emu K mol^{−1} ($\mu_{\text{eff}} = 2.97 \mu_B$) at 300 K to 0.095 emu K mol^{−1} ($\mu_{\text{eff}} = 0.87 \mu_B$) at 4.5 K. The feature of this curve indicates an antiferromagnetic interaction between the copper(II) centers. The magnetic data were fitted well by the Bleaney–Bowers eqn. (1) with $\theta = 0$, and $N_A = 240 \times 10^{-5}$ emu mol^{−1}, as indicated by the solid line curve in Fig. 5. The best fit parameters are $J = -4.5 \text{ cm}^{-1}$, $g = 2.107$, $p = 0.015$. The discrepancy σ in the least-square fits was 1.318×10^{-3} . The weak character of the antiferromagnetic interaction can be interpreted as due to the fact that the copper center has a distorted square pyramidal co-ordination geometry and $d_{x^2-y^2}$ ground state. The bridging Cu–O–Cu–O plane is no longer the xy plane and the orbitals containing the unpaired spins (which lie in the xy planes) overlap only very poorly with the bridging orbitals. Hence, the magnitude of J is much smaller in dimer **2**.

It should be mentioned again that the average g values resulting from these fits for both dimers agree well with the values determined from the EPR spectra.

Conclusion

Acylthiourea is a versatile complexing agent having potential O/S donor atoms bonded in mono- or bi-dentate fashion, and copper(II) is a flexible cation exhibiting plasticity of co-ordination geometry. In order to research the different possible co-ordination modes between acylthiourea and copper(II) ion, we think that diminishing the steric hindrance of the substituents at the ligand may be a crucial factor. Our recent investigations demonstrated that dimethyl-substituted ferrocenecarbonylthiourea can be co-ordinated to Cu^{II} in an unusual bis-sulfur bridged manner, while the dimethyl- and phenyl-substituted acylthioureas show a noteworthy versatility giving rise to both bis-sulfur- and bis-oxo-bridged co-ordination. Therefore, the substituent groups at the ligand play an essential role in the stereochemistry of the co-ordination compounds. These results may provide a useful channel to study the co-ordination modes of sulfur-containing binuclear copper complexes in biological systems, or to seek ferromagnetically coupled copper(II) dimers for new magnetic materials.

In respect of the methodology used in this work, a dropwise addition was adopted to make the reaction occur in a regular sequence and under mild conditions in favor of formation of different products in different concentration ranges and advantageous for the formation of single crystals suitable for X-ray studies.

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