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FULL PAPER

Synthesis, crystal structure and magnetic properties of a bis-sulfur-bridged copper(II) dimer containing *N*-ferrocenecarbonyl-*N′*,*N′*-dimethylthiourea (HL), [{CuL(HL)Cl}$_2$]†

De Ji Che,* Xiao Lan Yao, Gang Li and Yan Hong Li

Department of Chemistry, Zhengzhou University, Henan 450052, China

The bis-sulfur-bridged copper(II) dimer [{CuL(HL)Cl}$_2$] (HL = *N*-ferrocenecarbonyl-*N′*,*N′*-dimethylthiourea) has been synthesized and structurally characterized. The central copper(II) ion has a distorted tetrahedral environment with one chloride and three sulfur atoms derived from one terminal and two bridging acylthiourea ligands. The two sulfur atoms of both bridging ligands with two copper(II) ions form a strictly planar Cu$_2$S$_2$ bridging core including two short [2.3649 Å] and two longer Cu–S distances [2.4496 Å]. Dimers with this type of bridging are very scarce. Magnetic measurements showed antiferromagnetic coupling between the copper(II) centers through the sulfur bridges. The best fitting to the experimental magnetic susceptibilities gave $g = 2.06$, $J = -196.3$ cm^{-1}.

In studies of the magnetic characteristics of binuclear copper(II) complexes the main interest centers around the magnetostructural correlations.[1–3] According to the principles of superexchange, the magnetic coupling interaction between copper(II) ions is dependent on the magnetic orbital configuration (the orbital ground state) of the copper(II) ion and a good superexchange pathway provided by the orbitals of the bridging atom, *i.e.* the nature of the bridging atom or group is one of the important factors influencing the magnetic properties. However, at present, the great majority of these studies are concentrated on oxygen or halogen-bridged copper(II) complexes, and a minority on sulfur-bridged species because the latter are very scarce.

Constable[4] and Creighton[5] and co-workers have prepared bis-sulfur-bridged copper dimers through reactions of copper(II) chloride with thiones, such as 2(1*H*)-pyridinethione and imidazolethione. However, copper(II) ions are easily reduced by thiones and the latter are oxidized to disulfide,[6] and the resulting dimers consisted of copper(I) which are diamagnetic. More recently, Javier *et al.*[7] prepared two copper(II) dimers containing pyridine-2-carbaldehyde thiosemicarbazonate (L), [{CuL(X)}$_2$] (X = Cl or Br), which have a bis-sulfur-co-ordinated Cu$_2$S$_2$ core; their structural and magnetic properties show antiferromagnetic coupling between the copper(II) cations through the sulfur bridges.

Binuclear copper(II) complexes, particularly those containing sulfur-donor ligands, have drawn special attention in the past few years, due to their marked antitumor activities.[8] It has been hypothesized that the copper(II) complex *in vitro* interacts with the thiol-containing enzyme. So studies in this respect may be helpful to find new copper(II) complexes that can potentially be used as antitumor agents.

Recently, we prepared a new copper(II) dimer with a bis-sulfur-bridged Cu$_2$S$_2$ core, [{CuL(HL)Cl}$_2$], through the reaction of copper(II) chloride with the *N*-ferrocenecarbonyl-*N*,*N′*-dimethylthiourea (HL), which apparently exhibits magnetic exchange interaction through the sulfur bridging atoms. In this paper we report the synthesis, crystal structure and magnetic properties of the dimer.

Experimental

All reagents and solvents were of analytical grade, used without further purification. 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 and far-IR measurements were made with a Magna IR 750 Nicolet spectrophotometer. Variable-temperature magnetic susceptibility data were obtained on a SQUID susceptometer (Quantum Design, MPMS-5) in the temperature range 5–300 K with an applied field of 1 T. All data have been corrected for diamagnetism by using Pascal's constants.[9]

Preparation of the ligand

N-Ferrocenecarbonyl-*N′*,*N′*-dimethylthiourea (abbreviated as HL) was prepared according to the method described in the literature[10] by the reaction of ferrocenecarbonyl chloride with KSCN in anhydrous acetone, first converting it into ferrocenecarbonyl isothiocyanate and then condensing with dimethylamine. The product was orange crystals, m.p. 160 °C (Found: C, 52.85; H, 5.08; N, 8.78. Calc. for C$_{14}$H$_{16}$FeN$_2$OS: C, 53.19; H, 5.07; N, 8.86%).

Preparation of the complexes

The copper(II) dimer, [{CuL(HL)Cl}$_2$]. To an ethanol solution (4 cm^3) of the ligand HL (0.02 mmol), copper(II) chloride (0.01 mmol) in ethanol (3.5 cm^3) was added dropwise at a speed of about one drop per 2 h at room temperature for several days until good-quality single crystals were formed for X-ray structural analysis. Elemental analyses were consistent with the dinuclear stoichiometry (Found: C, 45.78; H, 4.45; N, 7.72. Calc. for C$_{28}$H$_{31}$ClCuFe$_2$N$_4$O$_2$S$_2$: C, 45.95; H, 4.38; N, 7.66%).

The nickel(II) complex [NiL$_2$]. The preparation was carried out in an analogous manner as described above by the reaction of the ligand HL with nickel(II) chloride in ethanol. Elemental analyses were consistent with the mononuclear stoichiometry (Found: C, 49.16; H, 4.56; N, 8.05. Calc. for C$_{28}$H$_{30}$Fe$_2$N$_4$NiO$_2$S$_2$: C, 48.81; H, 4.36; N, 8.13%).

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† *Supplementary data available:* IR spectra, magnetic susceptibility data. For direct electronic access see http://www.rsc.org/suppdata/dt/1998/1853/, otherwise available from BLDSC (No. SUP 57370, 4 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Table 1 Crystallographic data and parameters for [{CuL(HL)Cl}$_2$]

Empirical formula	$C_{28}H_{31}ClCuFe_2N_4O_2S_2$
M	730.38
T/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.873(2)
b/Å	10.949(2)
c/Å	13.041(2)
α/°	77.483(14)
β/°	79.866(11)
γ/°	88.092(13)
U/Å^3, Z	1492.0(5), 2
D_c/mg m^{-3}	1.627
μ/mm^{-1}	1.929
F(000)	746
Crystal size/mm	0.6 × 0.5 × 0.5
θ Range for data collection/°	1.62 to 27.5
Limiting indices	$-1 \leq h \leq 14$, $-13 \leq k \leq 13$, $-16 \leq l \leq 16$
Reflections collected	7891
Independent reflections	6814 (R_{int} = 0.0359)
Data, restraints, parameters	6814, 0, 365
Goodness of fit on F^2	0.798
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0486, 0.0981
(all data)	0.1051, 0.1105
Extinction coefficient	0.0056(5)
Largest difference peak, hole/e Å^{-3}	0.523, −0.468

Table 2 Selected bond lengths (Å) and angles (°) for [{CuL(HL)Cl}$_2$]

Metal co-ordination sphere			
Cu–S(1)	2.3649(14)	Cu–Cl	2.3452(13)
Cu–S(2)	2.2845(14)	Cu–Cu(A)	2.6316(13)
Cu–S(1A)	2.4496(14)		
S(1)–Cu–S(2)	109.78(5)	Cl–Cu–S(1A)	105.26(5)
S(2)–Cu–Cl	108.75(5)	S(1)–Cu–S(1A)	113.76(4)
Cl–Cu–S(1A)	105.26(5)	Cu–S(1)–Cu(A)	66.24(4)
S(2)–Cu–S(1A)	109.99(5)		
Ligand			
S(1)–C(22)	1.720(4)	S(2)–C(25)	1.689(5)
N(1)–C(22)	1.379(5)	N(3)–C(25)	1.392(5)
N(2)–C(22)	1.322(5)	N(4)–C(25)	1.322(5)
N(1)–C(21)	1.399(5)	N(3)–C(26)	1.385(6)
O(1)–C(21)	1.209(5)	O(2)–C(26)	1.218(5)
C(20)–C(21)	1.479(6)	C(8)–C(26)	1.482(6)
S(1)–C(22)–N(2)	120.8(3)	S(2)–C(25)–N(4)	121.8(4)
S(1)–C(22)–N(1)	120.7(3)	N(4)–C(25)–N(3)	118.9(4)
O(1)–C(21)–N(1)	121.9(4)	O(2)–C(26)–N(3)	123.4(4)
Hydrogen bonding			
O(1)···C(1)	3.221(8)	O(1)···H(1)	2.416(8)
O(1)···H(1)–C(1)	139.15		

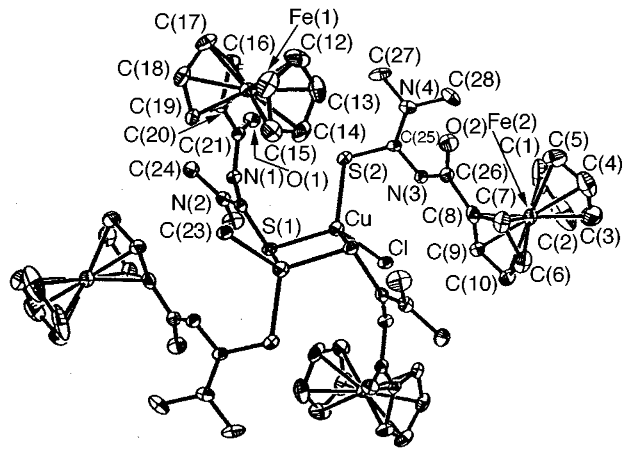

Fig. 1 An ORTEP[15] diagram of the dimer, showing the atomic numbering

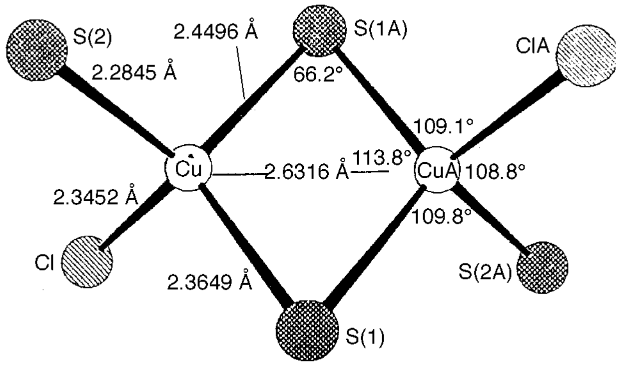

Fig. 2 Drawing of the unusual bis-sulfur-bridged Cu_2S_2 core

Crystallography

All the X-ray data were measured on a Siemens P4 diffractometer with graphite-monochromated Mo-Kα (λ = 0.710 73 Å) at ambient temperature. Unit-cell parameters were obtained from the setting angles of a minimum of 30 carefully centered reflections having $10 \leq 2\theta \leq 30°$. During the data collection, three standard reflections monitored every 97 did not show any significant intensity variation. The data were corrected for Lorentz-polarization effects, and absorption corrections were also applied using the ψ-scan techniques. The positions of all of the non-hydrogen atoms were found *via* direct methods using SHELXS 86 and were refined by full-matrix least-squares techniques (SHELXL 93).[11] Hydrogen atoms were added to the model in calculated positions. The final R value of 0.0486 was computed for 365 parameters and 3396 reflections. The structure determination is summarized in Table 1; selected bond distances and angles are listed in Table 2.

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Results and Discussion

Synthesis of the dimer

As is well known, acylthioureas usually act as bidentate ligands to transition-metal ions through the acyl oxygen and sulfur atoms.[12–14] For instance, the reaction of diethyl-substituted ferrocenecarbonylthiourea (HL′) with Cu^{II}, Ni^{II} and Co^{III} forms neutral mononuclear complexes [ML′$_2$],[12] which have been characterized by X-ray analysis. Surprisingly, we found that the reaction of the analogous ligand, dimethyl-substituted ferrocenecarbonyl thiourea (HL), with copper(II) chloride yields the bis-sulfur-bridged copper(II) dimer, [{CuL(HL)Cl}$_2$]. We also examined the reaction of HL with nickel(II) chloride, but the product is the mononuclear complex, [NiL$_2$] rather than the dimer. It is evident that the bis-sulfur-bridged copper(II) dimer could only be obtained by complexation of the dimethyl-substituted derivative with $CuCl_2$. This may be caused by the structural or steric effect of the substituents, and also by the co-ordination characteristics of the copper(II) ion. In addition, intermolecular hydrogen bonding may also play an important role in the stabilization of the dimer (see below).

Structural considerations

The molecular structure of the dimer [{CuL(HL)Cl}$_2$] is shown in Fig. 1 together with the atom numbering scheme used. Each copper(II) ion is bonded to one chloride and three sulfur atoms which come from one terminal and two bridging acylthiourea ligands, displaying a distorted tetrahedral geometry as reflected in Fig. 2. The two copper(II) ions and the bridging sulfur atoms form a strictly planar Cu_2S_2 core with two short [2.3649 Å]

Table 3 Some magnetic and structural features for copper dimers with Cu_2S_2 bridging cores

		Distance/Å							
				Bridging Cu–S					
Dimer	Geometry	Terminal Cu–S	Terminal Cu–C	Short	Long	Cu···Cu′	Bridging angle Cu–S–Cu/°	J/cm^{-1}	Ref.
1 $[\{Cu^I(HL^1)Cl\}_2]$	a	2.284		2.308	2.498	2.907	74.3	Diamagnetic	4
2 $[\{Cu^I(H_2L^2)Cl\}_2]$	a	2.271	2.360	2.301	2.572	2.914	73.3	Diamagnetic	5
3 $[\{Cu^I(HL^3)_2Cl\}_2]$	b	2.245	2.273	2.235	2.904	3.527	85.64		18
4 $[\{Cu^{II}(L^4)Cl\}_2]$	c	2.760	2.240	2.278	2.760	3.486	87.0	−4.70	7
5 $[\{Cu^{II}L(HL)Cl\}_2]$	a	2.285	2.345	2.365	2.449	2.631	66.24	−196.3	This work

HL^1 = 2(1*H*)-Pyridinethione; H_2L^2 = 1-methylimidazoline-2-thione; HL^3 = *N*-2-propenoyl-*N*′-benzylthione; HL^4 = pyridine-2-carbaldehyde thiosemicarbazone. a = Distorted tetrahedral, b = distorted trigonal pyramidal and c = distorted square pyramidal.

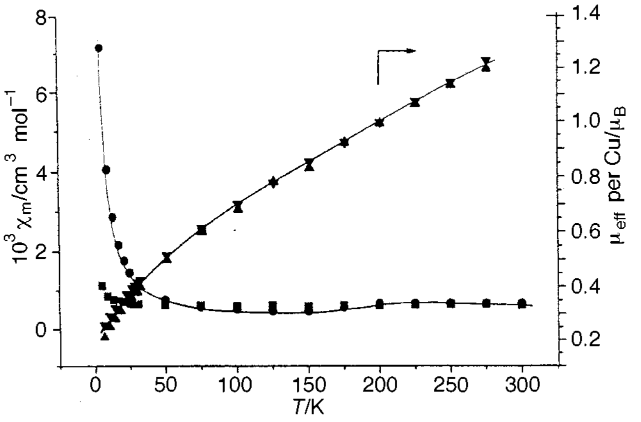

Fig. 3 Temperature dependence of χ_{Cu} and μ_{eff} for the dimer. The solid lines represent the best least-squares fitting of the data

and two longer Cu–S distances [2.4496 Å]. The short one is nearly the same as the sum of the tetrahedral covalent radii (2.39 Å).[16] The core also contains a relatively short Cu···Cu separation of 2.6316 Å, a narrow bridging Cu–S–Cu(A) angle of 66.24°, and a wide S(1)–Cu–S(1A) angle of 113.76°.

The Cu_2S_2 bridging plane with the remaining co-ordination plane, ClS(2)Cl(A)S(2A), forms a dihedral angle τ of 88.55° (Fig. 2). Both are virtually normal to each other. In the dimer the ligands L are co-ordinated to the copper(II) ions only through the unidentate S atom; the acyl oxygen atoms do not take part in co-ordination but form intermolecular hydrogen bonds C–H···O with the cyclopentadienyl ring of the other dimer (Table 2).

The terminal and bridging ligands have differences in structure, the former dissociates a hydrogen atom from the imido (NH) group and the latter connects the copper(II) centers in neutral species. The co-ordination distances S–Cu are 2.2845 Å for the terminal, 2.3649 and 2.4496 Å for the bridging ligand.

IR spectroscopic properties

The major IR activity of the dimer is consistent with the structural results. The characteristic IR bands of the ferrocenyl group have changed very little because these groups are far from the co-ordination centers. The strong absorption peak ν(C=O) at 1645 cm^{-1} of free HL shifts a little to 1685 cm^{-1}, due to the carbonyl group forming an intermolecular hydrogen bond in the dimer. The band at 3235 cm^{-1} observed for free HL may be attributed to the δ(NH) vibration which is almost absent in the complex, probably due to the deprotonation of the terminal ligands. The ν(N–C=S) stretching vibration at 1182 cm^{-1} of free HL shifts to 1130 cm^{-1} for the dimer, indicative of the co-ordination *via* the sulfur atom to copper(II). The metal–ligand stretching vibrations are identified in the low-frequency region 450–250 cm^{-1}. The absorption bands at 401–369 cm^{-1} could be assigned to the ν(Cu–S) modes and the band at 347–285 cm^{-1} may be attributed to the ν(Cu–Cl) vibration.

Magnetic properties

Variable-temperature magnetic susceptibility measurements were performed on powdered samples in the temperature range 5–300 K. The thermal variation of the molar susceptibility (χ_{Cu}) together with a plot of μ_{eff} *vs.* T is shown in Fig. 3. The decrement of the effective magnetic moments μ_{eff} from 1.22 (300) to 0.5 μ_B (50 K) as well as the shape of the susceptibility plot reveal behavior typical of antiferromagnetic exchange between the bis-sulfur-bridged copper(II) ions. The increase in χ_{Cu} with decreasing temperature at very low temperatures is due to the presence of traces of monomeric paramagnetic impurity.

Magnetic simulations were performed by use of the modified Bleaney–Bowers equation (1) for exchange-coupled pairs of

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1 + \tfrac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1 - P) + \frac{Ng_i^2\beta^2}{4kT}P + N_\alpha \quad (1)$$

copper(II) ions,[17] where each symbol has its usual meaning. However, the magnetism of the dimer could not be simulated in the region between 5 and 50 K. At this temperature the observed and calculated data diverge slightly, therefore we have concentrated our efforts in the range 50–300 K. Magnetic parameters thus determined are $g = 2.06$, $J = -196.3$ cm^{-1}, $N_\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}, $P = 0.09$. The discrepancy factor $\sigma = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}]^{\frac{1}{2}}$ in the least-squares fits was 3.27×10^{-3}.

Magnetostructural correlations

The magnetic superexchange interaction of the copper(II) dimers with Cu_2O_2 bridging cores has been extensively investigated, at the same time some empirical rules and theoretical bases for the correlation of magnetic properties and structural features have been established.[1–3] However studies of dimers with Cu_2S_2 bridging cores are still very limited, and so it is hard to establish a comparable relationship between them. A preliminary comparison can be made with other analogs as listed in Table 3.

For the dimers **1**[4] and **2**[5] the co-ordination geometry, bond distance and bridging angle in the core are similar to those of dimer **5** (this work). However, the copper(II) centers in the former are copper(I) ions reduced by the ligand thiones. So they exhibit diamagnetism. The dimer **3**[18] contains an analogous acylthiourea ligand as in the dimer **5**. But the long bridging distance Cu–S (2.90 Å) and Cu···Cu′ separation (3.527 Å) are larger than in the dimer **5** (2.449 and 2.631 Å, respectively). In fact, the former may be considered formally as a dimer; no magnetic examination has been reported. In dimer **4** the copper(II) center has a distorted square-pyramidal geometry. The bridging S atom is axial to one of the two Cu atoms bridged, and therefore almost orthogonal to the magnetic orbital ($d_{x^2-y^2}$); this will result in a weak antiferromagnetic interaction, J −4.7 cm^{-1}. However, in dimer **5** the copper(II) center is in a distorted tetrahedral co-ordination environment and the magnetic orbital (d_{xy}) may be expected to be directed roughly toward the bridging S orbital, resulting in a larger J value of −196.3 cm^{-1}.

Conclusion

The dimethyl-substituted ferrocenecarbonylthiourea acted as a unidentate ligand to the copper(II) ion, forming a bis-sulfur-bridged copper(II) dimer. Magnetic susceptibility data indicate a magnetic superexchange interaction through the sulfur bridge. The J value obtained is significantly larger than those for similar copper(II) dimers with a Cu_2S_2 bridging core.

In regard to the synthesis, the diethyl-substituted analog only forms a neutral mononuclear complex with the acyl oxygen and sulfur donor atoms. This difference may be caused by the structural or steric effect of the substituents. According to our results, the dimethyl-substituted acyl thiourea tends to form bis-sulfur-bridging copper(II) dimers. Since this type of dimer is very rare, it would be worthwhile to study further their synthesis, structural and magnetic properties.

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