Synthesis, Reactivity, Structural Studies and Magnetic Properties of 4-Amino-1,4-dihydro-3-methyl-1,2,4-triazole-5-thione Copper Complexes[†]

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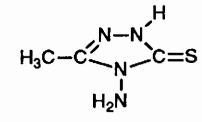
By reaction of $CuCl_2$ with 4-amino-1,4-dihydro-3-methyl-1,2,4-triazole-5-thione (HL) in a 4:1 molar ratio and in a 12 mol dm^{-3} HCl medium, at room temperature, the complex $[CuCl_2(HL)]{\cdot}H_2O$ **1** was isolated in an orthorhombic form. With an excess of $CuCl_2$ a polymeric complex $[\{Cu_2Cl_4(HL)\}_n]{\cdot}nH_2O$ **2** was isolated, while introduction of a bar of metallic copper gave a polymeric mixed-valence Cu^I–Cu^{II} (1:2) complex $[\{Cu_3Cl_5(OH_2)(HL)_2\}_n]{\cdot}2nH_2O$ **3**. Crystals of **1** are orthorhombic, space group *Pbca*, $a = 16.256(1)$, $b = 15.611(2)$, $c = 7.327(1)$ Å and $Z = 8$. Crystals of **2** are orthorhombic, space group *Pbca*, $a = 12.900(3)$, $b = 12.965(5)$, $c = 14.250(5)$ Å and $Z = 8$. Crystals of **3** are monoclinic, space group $P2_1/a$, $a = 34.099(8)$, $b = 8.704(3)$, $c = 7.163(3)$ Å, $\beta = 96.14(2)°$ and $Z = 4$. The structures have been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.0393$, 0.0582 and 0.0467 for 1132, 1346 and 3177 observed reflections respectively. In **1** the triazole acts as a chelating ligand through the sulfur and the aminic nitrogen atoms and the co-ordination of Cu^{II} is fundamentally square planar. In **2** the ligand acts in a tridentate manner, chelating and bridging through the iminic nitrogen atom. The $[Cu_2Cl_4(HL)]$ units can be considered as inner salts and are joined in a head-to-tail fashion forming zigzag polymeric chains. In **3** the two independent ligands present different behaviours; one chelates a Cu^{II} atom as in **1**, while the other acts as a μ_3 ligand chelating another Cu^{II} atom and bridging through the iminic nitrogen and the sulfur atoms two Cu^I atoms. The magnetic properties were investigated by measurements of electron paramagnetic resonance microwave absorption. For all compounds $S = \frac{1}{2}$ spectra were observed with spectroscopic g constants in the range *ca.* 2.05–2.20. The resulting single-ion g tensors are typical of a tetragonal elongated copper(II) ion where covalency plays a relevant role due to the presence of the SCNN chelating structure. The magnetic local axes deduced on this basis are strictly related to the copper co-ordination planes (obtained from the structural data) confirming the oxidation state II for all the copper atoms except for the tetrahedral Cu^I in **3**.

Investigation of the reaction chemistry of 4-amino-1,4-dihydro-3-methyl-1,2,4-triazole-5-thione (HL) with copper(II) chloride, in acidic media, shows that complexes are formed in which the organic ligand can act in a bi- or tri-dentate manner.[1a] It can be desulfurated by Cu^{II}, giving rise to the parent unsaturated triazole derivative; moreover it can stabilize mixed-valence copper complexes. Previously we published a study on the interaction of $CuCl_2$ with HL where some hypotheses about the desulfuration phenomenon were discussed, and the crystal structures of the ligand HL, of its complex $[CuCl_2(HL)]{\cdot}H_2O$ **1′** in a monoclinic form and of the complex of the parent triazole $[(CuCl_2L')_n]$ **1″** (L′ = 4-amino-3-methyl-1,2,4-triazole)[1b] were reported. Using a very strong acidic medium we have now obtained the orthorhombic form of the complex $[CuCl_2(HL)]{\cdot}H_2O$ **1**, the polymeric complex $[\{Cu_2Cl_4(HL)\}_n]{\cdot}nH_2O$ **2** in which dimeric subunits contain two copper atoms with different charge environments, and the polymeric mixed-valence Cu^I–Cu^{II} (1:2) complex $[\{Cu_3Cl_5(OH_2)(HL)_2\}_n]{\cdot}2nH_2O$ **3**.

Experimental

The ligand HL was prepared according to the reported procedure.[2]



HL

Preparation of the Copper Complexes.—$[CuCl_2(HL)]{\cdot}H_2O$ **1**. Solid HL (0.1 g, 0.8 mmol) was added to a solution (20 cm^3) of $CuCl_2{\cdot}2H_2O$ (0.6 g, 3.5 mmol) in concentrated HCl and stirred for 5 min. The green solution was left to stand at room temperature and in 1 d light green crystals of **1** were separated.

$[\{Cu_2Cl_4(HL)\}_n]{\cdot}nH_2O$ **2**. After the crystals of complex **1** had been filtered off, solid $CuCl_2{\cdot}2H_2O$ (0.3 g, 1.7 mmol) was added to the filtrate, dissolved while stirring and the resulting green solution left to evaporate to dryness. After a few days red-brown plate-like crystals of **2** were obtained together with crystals of $CuCl_2{\cdot}2H_2O$.

$[\{Cu_3Cl_5(OH_2)(HL)_2\}_n]{\cdot}2nH_2O$ **3**. A bar of metallic copper was added to a solution prepared as for complex **2** and the solution was left to evaporate to dryness. After a few days well shaped bright black crystals of **3** were formed on the bar together with $CuCl_2{\cdot}2H_2O$ and an unidentified microcrystalline product.

X-Ray Structural Analyses.—*Crystal data.* $C_3H_8Cl_2CuN_4OS$

[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

1, $M = 282.63$, orthorhombic, space group *Pbca* (no. 61), $a = 16.256(1)$, $b = 15.611(2)$, $c = 7.327(1)$ Å, $U = 1859.4(4)$ Å^3 (by least-squares refinement of diffractometer angles for 30 automatically centred reflections, $\bar{\lambda} = 1.541\ 838$ Å), $T = 295$ K, $Z = 8$, $D_c = 2.019$ Mg m^{-3}, $F(000) = 1128$. Crystal dimensions $0.01 \times 0.07 \times 0.30$ mm, μ(Cu-Kα) = 10.514 mm^{-1}.

$C_3H_8Cl_4Cu_2N_4OS$ **2**, $M = 417.09$, orthorhombic, space group *Pbca* (no. 61), $a = 12.900(3)$, $b = 12.965(5)$, $c = 14.250(5)$ Å, $U = 2383(1)$ Å^3 (by least-squares refinement as above), $T = 295$ K, $Z = 8$, $D_c = 2.325$ Mg m^{-3}, $F(000) = 1632$. Crystal dimensions $0.02 \times 0.26 \times 0.28$ mm, μ(Cu-Kα) = 14.344 mm^{-1}.

$C_6H_{18}Cl_5Cu_3N_8O_3S_2$ **3**, $M = 682.28$, monoclinic, space group $P2_1/a$ (alt. $P2_1/c$, no. 14), $a = 34.099(8)$, $b = 8.704(3)$, $c = 7.163(3)$ Å, $\beta = 96.14(2)°$, $U = 2114(1)$ Å^3 (by least-squares refinement as above), $T = 295$ K, $Z = 4$, $D_c = 2.144$ Mg m^{-3}, $F(000) = 1352$. Crystal dimensions $0.05 \times 0.13 \times 0.40$ mm, μ(Cu-Kα) = 11.550 mm^{-1}.

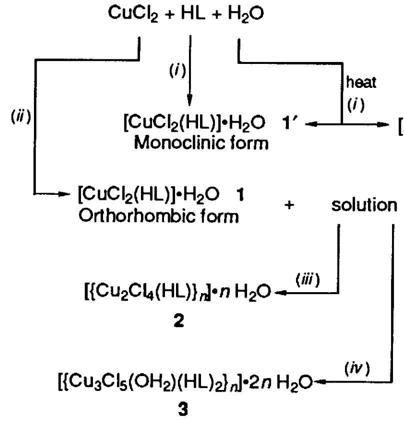
Data collection and processing. Siemens AED diffractometer, θ–2θ scan mode, scan width $1.20 + 0.142 \tan\theta$, scan speed 3–12° min^{-1}, nickel-filtered Cu-Kα radiation. 1762 Reflections (hkl) for complex **1**, 2271 for **2** and 4341 ($\pm hkl$) for **3** measured ($3 \leqslant \theta \leqslant 70°$); 1132 with $I \geqslant 2\sigma(I)$ for **1**, 1346 with $I \geqslant 3\sigma(I)$ for **2** and 4021 unique for **3** (merging $R = 0.0273$ after absorption correction) giving 3177 with $I \geqslant 2\sigma(I)$. Absorption correction applied[3] (maximum and minimum transmission factors: 1.1728, 0.8604 for **1**, 1.3338, 0.7946 for **2** and 1.1583, 0.8115 for **3**). No decay during data collection of the three specimens.

Structure analysis and refinement. Patterson method (Cu, Cl, S atoms) for the three structures followed by normal procedures. Full-matrix least-squares refinements with all non-hydrogen atoms anisotropic; hydrogen atoms refined isotropically for complexes **1** and **3**, and placed in their found positions for **2** with one overall $U_{iso} = 0.08$ Å^2. The weighting scheme $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$ ($k = 0.5423$, 1.0000, $g = 0.0013$, 0.0048 for **1** and **3** respectively) gave satisfactory agreement analyses. Unit weights were used in all stages of the refinements for **2** as a weighting scheme $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$, with k and g values to be refined, in the last cycles of refinements did not give better results. Number of refined parameters: 141 for **1**, 136 for **2** and 316 for **3**. Final R and R' $\{\Sigma|\Delta F|/\Sigma|F_o|$ and $[\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$ 0.0393, 0.0480 for **1**, 0.0582, 0.0638 for **2** and 0.0467, 0.0647 for **3**. Final atomic coordinates for non-hydrogen atoms of the three compounds are given in Tables 1–3.

The calculations were carried out on the Gould POWERNODE 6040 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma and the programs and sources of scattering factors are given in ref. 4.

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

Magnetic Analysis.—The magnetic properties of complexes **1**–**3** were examined in the temperature range 320–67 K by electron paramagnetic resonance (EPR) experiments on single crystals and powders. Derivative microwave absorption was recorded at a frequency of *ca.* 9.0 GHz (X-band) by means of a Varian E-Line EPR spectrometer, with a 100 kHz modulation frequency. Resonance fields were determined by use of a diphenylpicrylhydrazyl marker. The room-temperature powder spectra of the three compounds are given in Fig. 7. The low-temperature angular variation of the signal and the spectroscopic splitting g factor for a single crystal of **2** is shown in Fig. 8.



Scheme 1 (*i*) 6 mol dm^{-3} HCl; (*ii*) 12 mol dm^{-3} HCl; (*iii*) $CuCl_2$; (*iv*) Cu

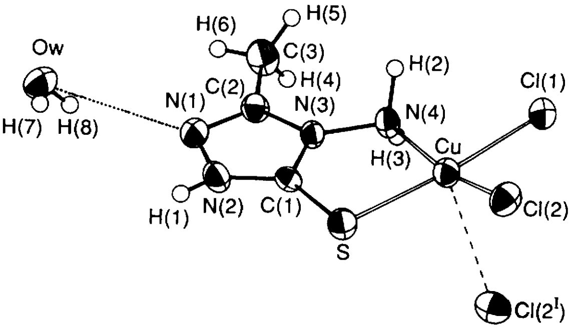


Fig. 1 Perspective view of complex **1**

Results and Discussion

The compound HL is a weak monoprotic acid which reacts as a thiol in neutral or basic solution. Reactions with $CuCl_2$ are accompanied by reduction of copper(II) to copper(I) as found for many other thiol ligands. Considering the reaction (1) of Cu^{II}

$$2Cu^{2+} + 2HSR \rightleftharpoons 2Cu^{+} + RSSR + 2H^{+} \qquad (1)$$

with thiols, in order to minimize this reduction and the formation of disulfides or other oxidation products we have to operate in an acidic medium, also to avoid the deprotonation of the ligand that could result in very insoluble salts. An acidic medium was found,[1] moreover, to influence the desulfuration processes of the ligand in the presence of $CuCl_2$ and oxygen. The syntheses of the copper complexes that we have prepared can be summarized as in Scheme 1. Compound **1** exhibits polymorphism; a monoclinic form of the same complex, $[CuCl_2(HL)]\cdot H_2O$ **1′**, was previously obtained from a milder acidic medium and characterized by X-ray structure determination.[1b]

X-Ray Structural Studies.—In complex **1** the ligand chelates the copper atom through the sulfur and the aminic nitrogen atoms (Fig. 1) forming a five-membered ring. Two chlorine atoms are also bound to the copper in a slightly distorted square-planar co-ordination. An additional weak interaction of the metal with a chlorine atom of an adjacent complex completes the co-ordination sphere as an elongated square pyramid (Table 4). In **1′** the copper co-ordination is similar but if the long contact Cu ··· Cl [3.259(2) Å] is considered the co-ordination can be described as a very elongated tetragonal bipyramid. The complexes are linked in chains running parallel to c (Fig. 2). The Cu–Cl bond distances in the basal plane are asymmetric [Cu–Cl(1) 2.291(2), Cu–Cl(2) 2.259(2) Å] and the shortest is involved in the semi-bridge. A similar trend can be pointed out for **1′** if the very long Cu ··· Cl contact is left out. It is difficult to explain this shortening in terms of electronic effects.

The packing is determined by stepped double chains with the copper atoms lying roughly in the b glide planes held together by a rich network of N–H ··· Ow, N–H ··· Cl, Ow–H ··· N and Ow–H ··· Cl hydrogen bonds. In **1′** only two hydrogen

Table 1 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms of compound **1**, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	2260(1)	2888(1)	746(1)
Cl(1)	1664(1)	1568(1)	1088(2)
Cl(2)	3274(1)	2416(1)	−1109(2)
S	2709(1)	4281(1)	502(2)
Ow	−32(3)	7244(3)	907(9)
N(1)	755(3)	5583(3)	1908(7)
N(2)	1553(3)	5517(3)	1282(8)
N(3)	1149(3)	4258(3)	1694(6)
N(4)	1182(3)	3351(3)	1743(8)
C(1)	1806(3)	4713(3)	1167(8)
C(2)	522(4)	4801(4)	2175(8)
C(3)	−297(4)	4511(5)	2853(12)

Table 2 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms of compound **2**, with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	2289(1)	5658(1)	660(1)
Cu(2)	671(1)	3684(1)	160(1)
Cl(1)	1329(2)	5066(2)	−621(2)
Cl(2)	1424(2)	4319(2)	1478(2)
Cl(3)	2805(2)	7040(2)	−196(2)
Cl(4)	3108(2)	6181(2)	1973(2)
S	−152(2)	3130(3)	−1168(2)
Ow	−1646(7)	1939(7)	−2790(6)
N(1)	−1353(7)	530(8)	−316(7)
N(2)	−1121(7)	1257(7)	−991(6)
N(3)	−445(7)	1798(7)	284(6)
N(4)	49(7)	2491(8)	897(6)
C(1)	−585(9)	2033(9)	−650(8)
C(2)	−947(8)	872(9)	469(8)
C(3)	−997(10)	388(9)	1406(8)

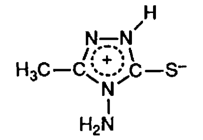
Table 3 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms of compound **3**, with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	1313(1)	2909(1)	1860(1)
Cu(2)	908(1)	5530(1)	−3327(1)
Cu(3)	2007(1)	3378(1)	−2025(1)
Cl(1)	695(1)	2222(2)	2484(2)
Cl(2)	1102(1)	5183(1)	560(2)
Cl(3)	1487(1)	4442(2)	−4124(2)
Cl(4)	1091(1)	7957(1)	−3778(2)
Cl(5)	2020(1)	815(1)	−2781(2)
S(11)	1951(1)	3530(1)	1295(2)
S(12)	283(1)	6389(1)	−2921(2)
O(1w)	1203(1)	1337(4)	−1022(5)
O(2w)	−1029(1)	1212(4)	−1069(6)
O(3w)	3124(1)	2617(5)	852(6)
N(11)	2502(1)	−365(4)	2398(6)
N(21)	2485(1)	1139(5)	1789(6)
N(31)	1921(1)	623(4)	2624(6)
N(41)	1534(1)	900(5)	3095(5)
N(12)	−271(1)	2552(5)	−2012(6)
N(22)	−243(1)	4125(5)	−2101(6)
N(32)	307(1)	3313(4)	−2718(5)
N(42)	691(1)	3341(4)	−3268(6)
C(11)	2128(1)	1752(5)	1895(6)
C(21)	2155(1)	−669(5)	2924(7)
C(31)	2028(2)	−2140(6)	3709(8)
C(12)	101(1)	4614(6)	−2567(7)
C(22)	70(1)	2073(6)	−2402(7)
C(32)	203(2)	445(7)	−2428(10)

Table 4 Selected bond distances (Å) and angles (°) in the co-ordination polyhedron of compound **1**

Cu–Cl(1)	2.291(2)	Cu–N(4)	2.033(5)
Cu–Cl(2)	2.259(2)	Cu–Cl(2$^{\text{I}}$)	2.872(2)
Cu–S	2.301(2)		
S–Cu–N(4)	87.99(14)	Cl(1)–Cu–Cl(2)	94.66(6)
Cl(2)–Cu–N(4)	163.98(17)	S–Cu–Cl(2$^{\text{I}}$)	92.11(6)
Cl(2)–Cu–S	91.74(6)	Cl(1)–Cu–Cl(2$^{\text{I}}$)	90.40(6)
Cl(1)–Cu–N(4)	85.15(15)	Cl(2)–Cu–Cl(2$^{\text{I}}$)	90.61(6)
Cl(1)–Cu–S	173.10(6)	N(4)–Cu–Cl(2$^{\text{I}}$)	105.40(17)

Symmetry operation: I $x, \frac{1}{2} - y, \frac{1}{2} + z$.



bonds, one very strong N(2)–H • • • Ow 2.702(8) Å and the other very weak Ow–H • • • Cl 3.321(7) Å, were observed and this type of packing can explain the higher density of **1** with respect to **1′** (2.019 and 1.965 Mg m^{-3}).

The structure of compound **2** (Fig. 3), obtained with an excess of $CuCl_2$, is rather unusual and consists of roughly planar Cu_2Cl_4(HL) units [maximum deviation 0.28(1) Å for N(1)] where the two copper atoms show square-planar co-ordination. Two chlorine atoms bridge the copper atoms and the co-ordination is completed for one Cu by a chelating HL ligand and for the second by two terminal chlorine atoms. The two copper atoms are unequally surrounded by chlorine atoms. Comparison of the bond distances within the free HL ligand with those in copper complexes of both the HL ligand and of the aromatic, desulfurated derivative, 4-amino-3-methyltriazole,[1] shows no significant differences, indicating an equal degree of aromaticity in both ligands. Considering the possible role of HL, it is reasonable to hypothesize a relevant percentage of a mesoionic form as shown, stabilized by the aromaticity of the ring, in agreement with the planarity of the system and the delocalization of the double bonds. The red-brown colour of the complex, characteristic of thiolcopper(II) compounds,[5] supports this hypothesis. In this context the complex behaves partially as an inner salt with the positive charge carried by the triazole ring and the negative charge localized around the Cu(1) atom, in agreement with the oxidation state II for both the copper atoms, and as confirmed by EPR spectroscopy (see below). Also in the complex [Cu_2Cl_4(L^1)][6] [L^1 = *N*,*N′*-bis(2-dimethylaminoethyl)pyridine-2,6-dicarboxamide 1-oxide] there are two copper atoms linked by two bridging chlorine atoms and unequally surrounded by negative charges, but in this case the complex is a real zwitterion with the positive charge localized on a protonated aminic nitrogen atom and the negative one on the tetrachlorocuprate moiety. Moreover the co-ordination geometry around the two copper atoms is rather different, tetrahedral for one and square-pyramidal for the other. A monomeric zwitterionic chloro complex of copper(II)[7] was obtained with thiocarbonohydrazide which is the starting material of the preparation of HL.[2]

The Cu(2)–N(4) and Cu(2)–S bond distances in complex **2** (Table 5) are comparable with those found in **1** and **1′**. The Cu–Cl distances involving the bridging chlorine atoms are slightly asymmetric and those implied in the co-ordination of the Cu(1) atom are longer than the others. A similar trend is also observed in [Cu_2Cl_4(L^1)] for the bridging chlorine atoms [Cu(2)–Cl(2) 2.389(1), Cu(1)–Cl(2) 2.306(1) Å]. Probably this lengthening is due to the different distribution of charges around the metal atoms. The dihedral angle between the planes Cl(1)Cu(1)Cl(2) and Cl(1)Cu(2)Cl(2) is 8.6(1)°, indicative of an imperfectly planar system; the bond angles Cu–Cl–Cu are

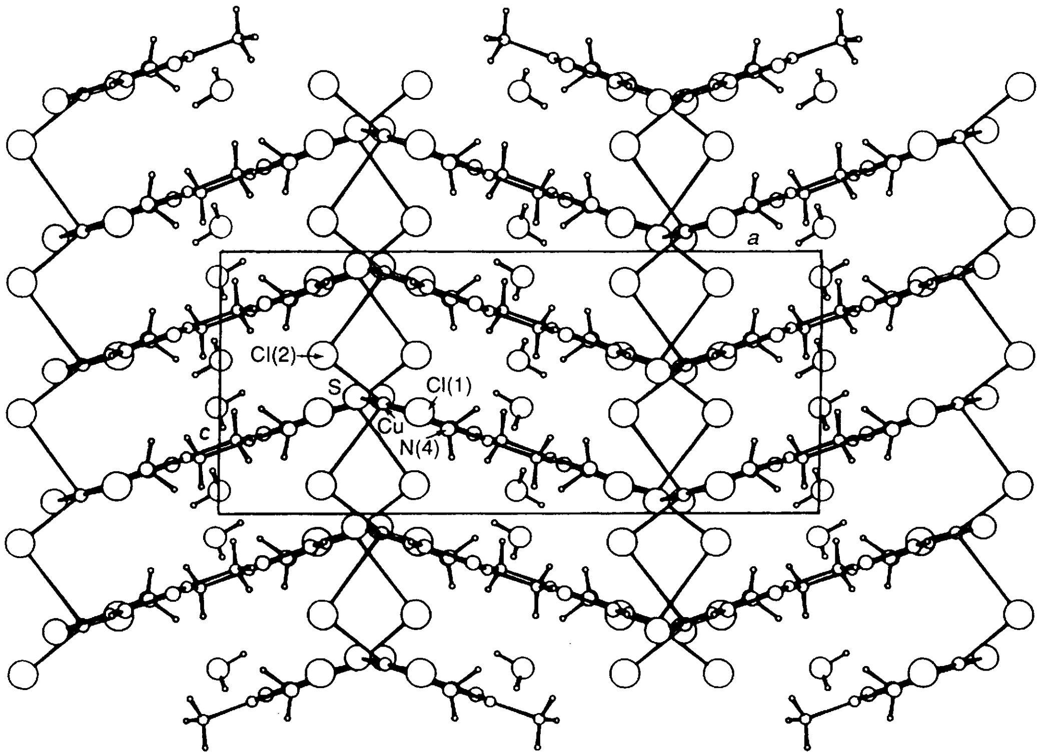


Fig. 2 Projection of the structure of complex **1** along *b* showing the polymeric chains running parallel to *c*

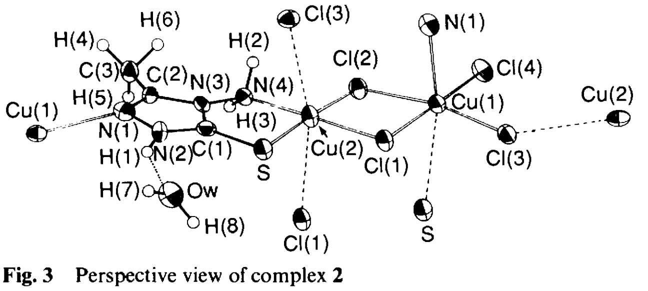


Fig. 3 Perspective view of complex **2**

Table 5 Selected bond distances (Å) and angles (°) in the co-ordination polyhedron of compound **2**

Cu(1)–Cl(1)	2.337(3)	Cu(2)–Cl(1)	2.273(3)
Cu(1)–Cl(2)	2.371(3)	Cu(2)–Cl(2)	2.270(3)
Cu(1)–Cl(3)	2.267(3)	Cu(2)–S	2.284(3)
Cu(1)–Cl(4)	2.254(3)	Cu(2)–N(4)	2.035(9)
Cu(1)–N(1^I)	2.384(10)	Cu(1) ··· Cu(2)	3.379(3)
Cl(1)–Cu(1)–Cl(2)	83.9(1)	Cl(1)–Cu(2)–Cl(2)	87.7(1)
Cl(1)–Cu(1)–Cl(3)	89.7(1)	Cl(1)–Cu(2)–S	90.9(1)
Cl(1)–Cu(1)–Cl(4)	175.2(1)	Cl(1)–Cu(2)–N(4)	177.4(3)
Cl(2)–Cu(1)–Cl(3)	169.0(1)	Cl(2)–Cu(2)–S	176.5(1)
Cl(2)–Cu(1)–Cl(4)	91.9(1)	Cl(2)–Cu(2)–N(4)	91.0(3)
Cl(3)–Cu(1)–Cl(4)	94.1(1)	S–Cu(2)–N(4)	90.3(3)
Cl(1)–Cu(1)–N(1^I)	90.9(3)	Cu(1)–Cl(1)–Cu(2)	94.3(1)
Cl(2)–Cu(1)–N(1^I)	88.5(3)	Cu(1)–Cl(2)–Cu(2)	93.4(1)
Cl(3)–Cu(1)–N(1^I)	100.6(3)		
Cl(4)–Cu(1)–N(1^I)	91.2(3)		

Symmetry operation: I $\frac{1}{2} + x, \frac{1}{2} - y, -z$.

greater than 90°, while Cl–Cu–Cl are smaller, indicative of a repulsive interaction between the two copper atoms [Cu(1) ··· Cu(2) 3.379(3) Å]. In this complex the ligand acts in a bridging tridentate manner. The Cu(1) atom is also bonded to an iminic nitrogen atom of a triazole ring of an adjacent complex so achieving a square-pyramidal co-ordination; this Cu–N bond is responsible for the head-to-tail arrangement of the units in a zigzag polymeric chain running parallel to *a* (Fig. 4). The sixth co-ordination site is occupied by a sulfur atom at a very long distance [Cu(1) ··· S(1) ($-x$, $1 - y$, $-z$) 3.254(4) Å]. The Cu(2) atom completes its co-ordination with two long contacts with chlorine atoms of adjacent complexes [Cu(2) ··· Cl(3) ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, z) 2.943(3), Cu(2) ··· Cl(1) ($-x$, $1 - y$, $-z$) 3.117(3) Å], so that an elongated octahedral co-ordination is realized. These long contacts link the polymeric chains forming layers of complexes perpendicular to *c*. Hydrogen bonds of the type N–H ··· Cl are present in the layers while the N–H ··· Ow and Ow–H ··· Cl hydrogen bonds link the layers together.

Mixed-valence copper(I)–copper(II) complexes with heterocyclic thioamide ligands which exhibit thione to thiol tautomerism are interesting as the copper centres can mimic the behaviour of a variety of biological macromolecules containing active sites.[8,9] Moreover compounds containing a metal in two valence states are interesting because of the possibility of easy electron transfer.

The structure of compound **3** (Fig. 5), obtained by introducing a bar of metallic copper into the solution, consists of mixed-valence copper complexes in an unusual 2:1 Cu^{II}:Cu^{I} molar ratio.[10] Two independent HL molecules chelate two independent copper(II) atoms through the sulfur and the aminic nitrogen atoms. One copper(II) atom [Cu(1)] completes its co-ordination sphere with a water molecule and two chlorine atoms, one terminal and one bridging in a very asymmetric way a second copper(II) atom [Cu(2)]; Cu(2), in turn, completes its five-co-ordination polyhedron with two other chlorine atoms, one terminal and one that bridges the copper(I) atom [Cu(3)]. Both the copper(II) atoms assume a square-pyramidal co-ordination but a chlorine atom of an adjacent complex [Cu(1) ··· Cl(3) (x, y, $1 + z$) 3.169(2) Å] occupies the sixth co-ordination site of Cu(1). Moreover the HL molecule which chelates Cu(1) bridges two copper(I) atoms [Cu(3)] through the sulfur and the iminic nitrogen atoms thus acting as a μ_3-HL ligand and forming helicoidal polymeric chains of complexes

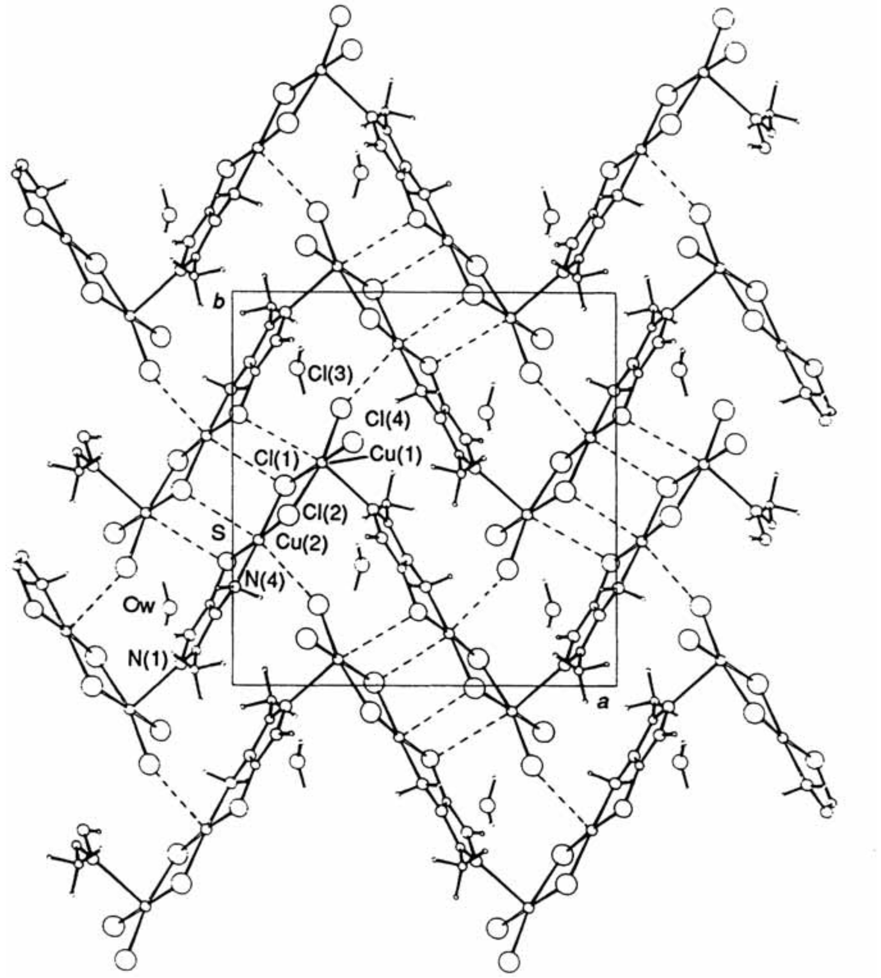


Fig. 4 Projection of the structure of complex **2** along *c* showing the zigzag polymeric chains

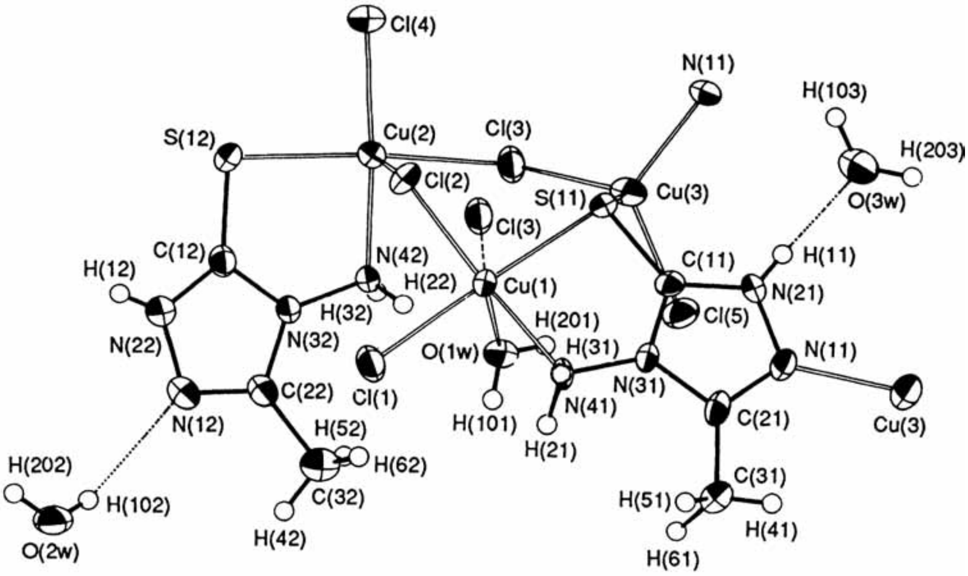


Fig. 5 Perspective view of complex **3**

running along *b* (Fig. 6). Atom Cu(3) completes its co-ordination with a terminal chlorine atom and assumes the common tetrahedral geometry of copper(I) complexes (Table 6). The Cu(2)–Cl(3)–Cu(3) bond angle is very large and is one of the greatest found in the literature for a bridging chlorine atom. The tridentate HL ligand has a μ-S atom which is co-ordinated to the metals in a quasi-tetrahedral fashion, in contrast with the formal C=S double bond. A similar behaviour is found in some copper(I) complexes with thiourea or thiourea derivatives[11,12] and in these cases a reduction of the C=S double-bond character to 40% is observed. This value implies a predominance of the resonance form **I** which can explain the different kind of co-ordination of the sulfur atom in thiourea and its derivatives. In the case of **3** the C=S bond distance of the tridentate ligand

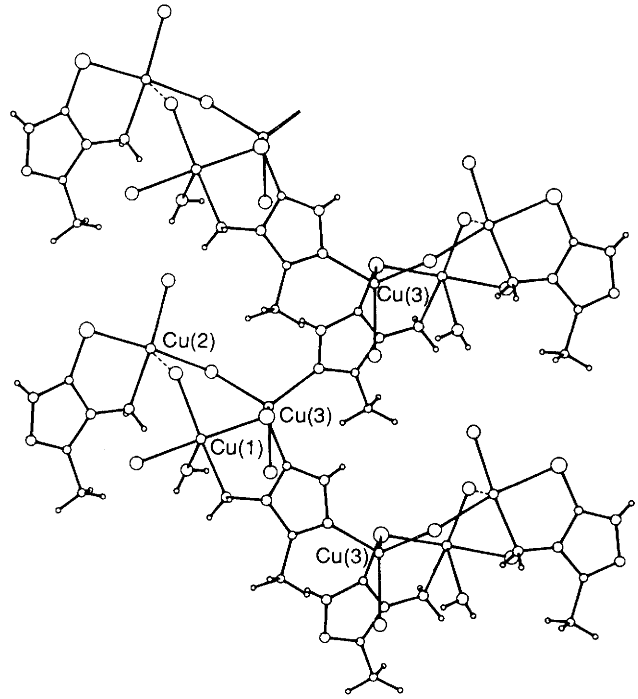


Fig. 6 Perspective view of the helicoidal polymeric chain running along *b* in complex **3**

Table 6 Selected bond distances (Å) and angles (°) in the co-ordination polyhedron of compound **3**

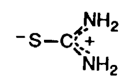
Cu(1)–Cl(1)	2.278(1)	Cu(2)–Cl(3)	2.315(1)
Cu(1)–Cl(2)	2.270(1)	Cu(2)–Cl(4)	2.235(2)
Cu(1)–S(11)	2.320(1)	Cu(2)–S(12)	2.308(1)
Cu(1)–N(41)	2.066(4)	Cu(2)–N(42)	2.046(4)
Cu(1)–O(1w)	2.472(4)	Cu(2)–Cl(2)	2.808(2)
Cu(3)–Cl(3)	2.385(1)	Cu(3)–Cl(5)	2.297(2)
Cu(3)–S(11)	2.409(2)	Cu(3)–N(11^I)	2.042(4)
Cl(1)–Cu(1)–Cl(2)	92.94(7)	Cl(3)–Cu(2)–Cl(4)	95.32(7)
Cl(1)–Cu(1)–S(11)	177.79(7)	Cl(3)–Cu(2)–S(12)	170.89(7)
Cl(1)–Cu(1)–N(41)	89.85(12)	Cl(3)–Cu(2)–N(42)	86.77(12)
Cl(2)–Cu(1)–S(11)	89.24(6)	Cl(4)–Cu(2)–S(12)	89.31(6)
Cl(2)–Cu(1)–N(41)	176.72(12)	Cl(4)–Cu(2)–N(42)	171.84(14)
S(11)–Cu(1)–N(41)	87.96(11)	S(12)–Cu(2)–N(42)	87.59(12)
Cl(1)–Cu(1)–O(1w)	87.57(10)	Cl(3)–Cu(2)–Cl(2)	94.83(6)
Cl(2)–Cu(1)–O(1w)	97.30(10)	Cl(4)–Cu(2)–Cl(2)	101.86(6)
S(11)–Cu(1)–O(1w)	92.56(10)	S(12)–Cu(2)–Cl(2)	91.88(6)
N(41)–Cu(1)–O(1w)	84.54(14)	N(42)–Cu(2)–Cl(2)	85.79(12)
Cl(3)–Cu(3)–Cl(5)	105.11(7)	Cl(5)–Cu(3)–S(11)	106.96(6)
Cl(3)–Cu(3)–S(11)	118.00(7)	Cl(5)–Cu(3)–N(11^I)	116.87(13)
Cl(3)–Cu(3)–N(11^I)	105.91(13)	S(11)–Cu(3)–N(11^I)	104.59(13)
Cu(1)–Cl(2)–Cu(2)	122.09(6)	Cu(2)–Cl(3)–Cu(3)	126.78(7)
Cu(1)–S(11)–Cu(3)	109.49(7)	Cu(3)–S(11)–C(11)	97.83(17)
Cu(1)–S(11)–C(11)	93.35(17)		

Symmetry operation: I $\frac{1}{2} - x, \frac{1}{2} + y, -z$.

Table 7 Experimental EPR data and corresponding single-ion $g_{\parallel}$, $g_{\perp}$ and 2α (°) values (e.s.d.s in parentheses), and expected values $2\alpha'$ and $2\alpha''$ (°) on the basis of the crystallographic data

Cmpd.	$g_1(g_{\perp})$	g_2	g_3	$g_{\perp}$	$g_{\parallel}$	2α	$2\alpha'$	$2\alpha''$
1	2.054(1)	2.069(1)	2.173(1)	2.054(1)	2.190(3)	40.7(3)	36.8	42.3
2	2.067(1)	2.127(1)	2.186(1)	2.067(1)	2.246(3)	70.8(1)	73.8	75.1
3	2.064(1)	2.070(1)	2.196(1)	2.064(1)	2.202(3)	23.9(4)	24.6	28.2

[1.699(5) Å] is not significantly greater than that of the other non-bridging HL [1.694(5) Å], but both are greater than in the free ligand [1.674(6) Å]. The percentage of π character of the C–S bond[13] changes from *ca.* 58% in the free HL to *ca.* 46% in the tridentate HL ligand of **3**.


$$-S-C^{+}(NH_2)_2$$

I

The intra- and inter-chain packing is determined by a rich network of N–H···Cl, N–H···Ow, Ow–H···Cl and Ow–H···Ow hydrogen bonds. The helicoidal chains are also held together by the long contact [Cu(1)···Cl(3) (*x*, *y*, 1 + *z*)].

In all these compounds unco-ordinated water molecules are present and interact with the HL ligand. Atom Ow acts as donor in a hydrogen bond with the imine nitrogen atom in **1** and in **3**, and as an acceptor with the thioamide NH group in **1′**, **2** and **3**.

The triazole molecule HL, as found in these complexes, can act (*i*) as a chelating ligand through the sulfur and the aminic nitrogen atoms, (*ii*) as in a bridging tridentate manner and finally (*iii*) as a μ_3-HL ligand. Moreover, its thiol derivatives can stabilize the low oxidation number of copper and prevent oxidation by air, a phenomenon also observed for complexes of Fe^{II} and Co^{II}.[14]

EPR Magnetic Data.—The shape of the EPR resonance signal (Figs. 7 and 8) and the measured *g* values (Table 7), the latter being substantially temperature independent, are consistent with the assumption of an effective spin $S = \frac{1}{2}$ for all the compounds examined. The powder spectra of **1** and **2** indicate a reduced *g* anisotropy, unusual for a copper(II) ion in a distorted octahedral field.[15] However, the anisotropic trend of all compounds **1**–**3** was evident in the angular variation of both the linewidth (not reported) and *g* values (Fig. 8). The singularity of the signal and the principal axes of *g*, invariably found along the bisecting directions between the local axes, strongly support the presence of inter-copper superexchange coupling.[15]

Owing to the approximate tetragonal co-ordination of the copper involved and the difficulty in predicting the local in-plane directions of *g*, we simplify the problem by assuming axially symmetric copper(II) *g* tensors (with $g_{\parallel}$ and $g_{\perp}$ principal values). Thus, in the limit of strong exchange the observed principal values are[16] as in equations (2)–(4) where 2α is the angle between the local $g_{\parallel}$ axes.

$$g_1 = g_{\min} = g_{\perp} \quad (2)$$

$$g_2 = g_{\text{med}} = g_{\parallel}\sin^2\alpha + g_{\perp}\cos^2\alpha \quad (3)$$

$$g_3 = g_{\max} = g_{\parallel}\cos^2\alpha + g_{\perp}\sin^2\alpha \quad (4)$$

Experimental values of g_1, g_2 and g_3 were deduced from the spectral angular variation with magnetic field sweeping three orthogonal planes of the crystal. They are collected in Table 7 together with the corresponding values of $g_{\parallel}$, $g_{\perp}$ and 2α obtained from equations (2)–(4). In the two last columns we also report values of the angles between the molecular planes of the symmetry-related copper units, deduced from the structural data. These were calculated by either assuming the complete set of in-plane atoms of the complex ($2\alpha'$) or taking into account only the four ligands directly bonded to the copper ion ($2\alpha''$). In both cases the Cl(2) atom was neglected in compound **1** because of the largely anomalous position related to its bridging role. For compounds **2** and **3** the $g_{\parallel}$, $g_{\perp}$ and 2α values should properly represent effective constants for the Cu(1)–Cu(2) dimeric units as a whole. However for **2**, owing to the substantial equiorientation of Cu(1) and Cu(2), they coincide with the local single-ion constants. This is only approximately the case in compound **3** where a misorientation of *ca.* 20° between Cu(1) and Cu(2) within the same dimeric unit which may slightly affect the $g_{\parallel}$ and $g_{\perp}$ values was not considered for

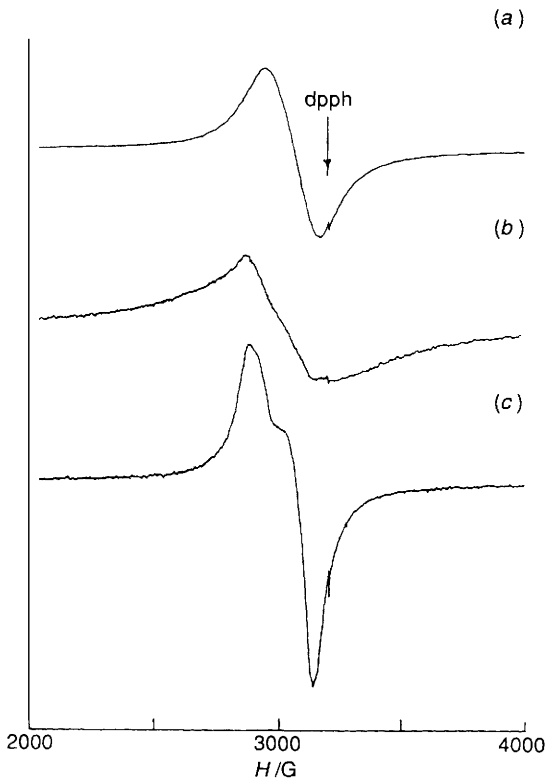


Fig. 7 X-Band EPR spectra (T = 295 K) of powders of complexes **1** (*a*), **2** (*b*) and **3** (*c*)

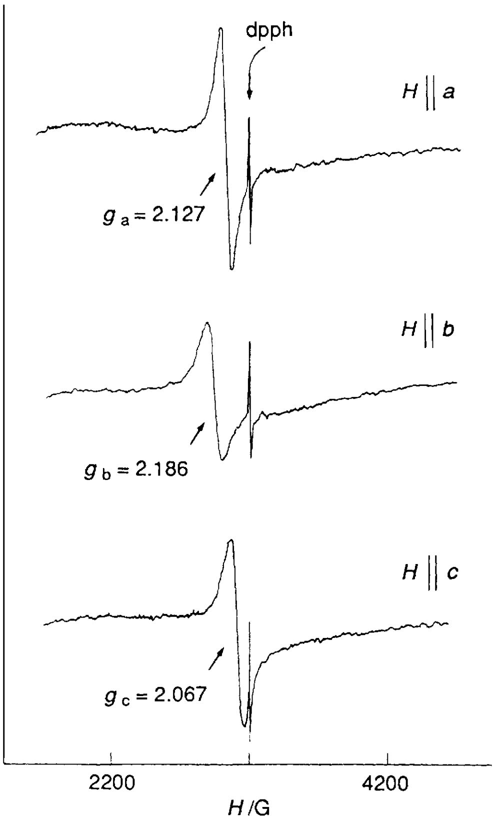


Fig. 8 The EPR signal anisotropy and measured g values of a single crystal of complex **2**

simplicity. As one can see in Table 7, in spite of the roughness of the assumption of axial local symmetry, close correspondence between the magnetically determined 2α values and the orientation of the copper ions is found. This testifies that resonating copper is not present as an impurity or defect and that the only non-magnetic copper is the tetrahedral Cu(3) ion in **3**. As a further confirmation of this, very similar values of $g_{\parallel}$ and $g_{\perp}$ are found for **1** and **3** consistently with the identical in-plane co-ordination experienced by Cu^{II} in the two compounds. For all compounds the anisotropy ($g_{\parallel} > g_{\perp}$) is indicative of $3d_{x^2-y^2}$ unpaired electron in line with the 'elongated' tetragonal co-ordination revealed by structural data. The low $g_{\parallel}$ value can be attributed to very large in-plane spin delocalization, particularly at the sulfur position in the chelating SCNN fragment. Values of the typical order $g_{\parallel}$ = 2.13 and $g_{\perp}$ = 2.03 were reported for square-planar copper complexes with 2N + 2S co-ordination resulting from the complexation of two such chelating groups.[17,18] On that basis, for the present N + S + 2Cl$^-$ square-planar co-ordination, values of the order of $g_{\parallel}$ *ca.* 2.20(2) and $g_{\perp}$ *ca.* 2.05(2) may be reasonably expected in line with our results. For compound **2**, where two copper atoms with formal in-plane co-ordinations N + S + 2Cl$^-$ and 4Cl$^-$ are magnetically coupled, somewhat larger g constants may be expected, in line with the observed $g_{\parallel}$ = 2.246 and $g_{\perp}$ = 2.067.

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