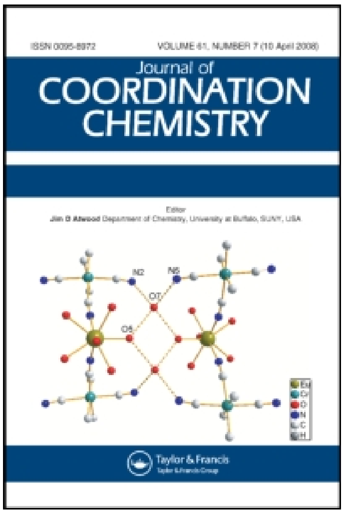

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REACTION BETWEEN $CuCl_2$ AND 2-*S*-METHYL-5,5-DIMETHYLIMIDAZOLINE-4-THIONE X-Ray Crystal Structure of *catena*-Chloro(*μ*-*N*(1), *S*(4) (2-*S*-Methyl-5,5-Dimethylimidazoline-4-Thione)) Copper(I)

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REACTION BETWEEN $CuCl_2$ AND 2-*S*-METHYL-5,5-DIMETHYLIMIDAZOLINE-4-THIONE

X-Ray Crystal Structure of *catena*-Chloro(μ-*N*(1), *S*(4) (2-*S*-Methyl-5,5-Dimethylimidazoline-4-Thione)) Copper(I)

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catena-Chloro(μ-*N*(1),*S*(4)(2-*S*-methyl-5,5-dimethylimidazoline-4-thione)) copper(I) was prepared and structurally characterized. The structure exhibits linear polymeric chains disposed parallelly to the *b* axis. The structure of each chain consists of copper(I) ions coordinated in a planar trigonal geometry by the N(1) and S(4) atoms of two different ligand molecules and one chloride. The ligand acts as an N(1), S(4) bidentate molecule and the orientation of the imidazoline rings is determined by a hydrogen bond between the NH of each ring and the coordinated chloride. The quite strong interaction between the thioether sulphur atom of one chain, S(2), and the copper(I) of the next chain [2.898(2)Å] is significant in the structure.

Keywords: copper(I) complexes; 2-*S*-methyl-5,5-dimethylimidazoline-4-thione; X-ray crystal structure

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INTRODUCTION

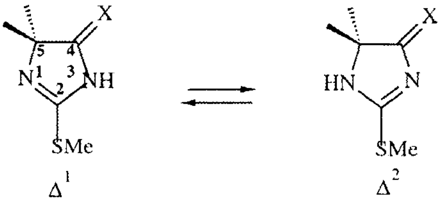
2-*S*-methyl-5,5-dimethylimidazolin-4-one (L′) and 2-*S*-methyl-5,5-dimethylimidazoline-4-thione (L) are characterized by annular desmotropy[1,2] also known as annular tautomerism[3] which consists of proton transfer between the two nitrogen atoms contained in the imidazoline ring. The equilibrium displacement depends on the polarity of the solvent, the isomer Δ^1 being favoured in apolar solvents (carbon tetrachloride or benzene) and Δ^2 in polar solvents (for example water). Mixtures of the two isomers are always present in intermediate dielectric constant solvents.

The presence of both soft and hard donor atoms[4] together with possible annular tautomerism, and the biological importance of imidazole-type heterocycles[5] makes these molecules interesting as to their coordinating properties. In view of attention to copper bio-mimetic models[6] we have recently investigated the reaction between $CuCl_2$ and L′ in alcoholic media and obtained a complex[7] having the formula $[CuL'_4(H_2O)]^{2+}$. In this complex, the copper(II) ion displays a square pyramidal coordination geometry with the square plane determined by the N(3) atoms of the four L′ molecules coordinating as Δ^2 isomers and the apex occupied by the oxygen of a water molecule. The same reaction carried out in CH_3CN, gives a copper(I) complex identified as *catena*-chloro (*μ*-*N*(1),*S*(4)(2-*S*-methyl-5,5-dimethylimidazoline-4-thione)) copper(I), $\{CuLCl\}_\infty$.

EXPERIMENTAL

Materials

2-*S*-Methyl-5,5-dimethylimidazoline-4-thione (L) was prepared as previously described[1]. The solvent and the copper(II) salt used in the synthesis were purchased from Aldrich and used without any further purification.



L′ X = O
L X = S

IR spectra were recorded in KBr (4000-400 cm^{-1}) and polyethylene pellets (400-180 cm^{-1}) using a Perkin-Elmer 983 instrument and a Perkin-Elmer 7500 Data Station.

$\{CuLCl\}_\infty$

A mixture of $CuCl_2 \cdot 2H_2O$ (18.07 mg, 0.106 mmol), 2-*S*-methyl-5,5-dimethylimidazoline-4-thione (L) (74 mg, 0.425 mmol) and CH_3CN (50 cm^3) was stirred at room temperature under N_2 for 20 m. The mixture was filtered and the solution allowed to evaporate at room temperature. Block-shaped yellow crystals of $\{CuLCl\}_\infty$ (10.5 mg, 36.24% yield) were obtained having m.p. 185-187°C with decomposition. Anal. found % (calcd. for $C_6H_{10}ClCuN_2S_2$): C, 26.65 (26.37); H, 3.79 (3.69); N, 10.23 (10.25); S, 23.34 (23.46). IR (4000-400 cm^{-1} KBr pellets): ν(CH) 2974w, 2925w; ν(NH) 2738m; ν(CN) 1564s cm^{-1}. IR (400-180 cm^{-1} polyethylene pellets): ν(CuCl) 244 cm^{-1}.

X-ray Crystal Structure Determination

Intensity data were collected at room temperature on a Enraf-Nonius CAD 4 automatic diffractometer. Details of crystal data, intensity collection, and refinement are reported in Table I. All data were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on the ψ scan was applied[8]. The reflections were processed by direct methods (program SIR 92[9]) which provided a satisfactory set of starting parameters for many of the non-hydrogen atoms. After location of the missing non-hydrogen atoms by Fourier difference syntheses, the atomic positions were refined by the SHELXL 93 program package[10]. Complex neutral atom-scattering factors[11] were employed throughout. Hydrogen atoms were treated as fixed contributors at calculated positions, assuming a temperature factor greater by 1 Å^2 than that of the attached carbon or nitrogen atom. Drawings were performed with the ORTEP[12] plotting program. Major calculations were carried out on an Alpha 3000/800S computer. Selected bond distances and angles are given in Table II. Atomic coordinates for the non-hydrogen atoms are given in Table III.

RESULTS AND DISCUSSION

As established[13,14], thioamido-group containing molecules tend to reduce Cu^{II} to Cu^{I}. It was hence easy to predict that 2-*S*-methyl-5,5-dimethylimidazoline-4-thione (L) would have reduced copper(II) chloride[15]. In fact, after slow

TABLE I Crystal data and structure refinement for $\{CuLCl\}_\infty$.

Empirical formula	$C_6H_{10}ClCuN_2S_2$
Formula weight	273.27
Temperature (K)	293(2)
Radiation (λ,Å)	MoKα(0.71069)
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a (Å)	7.942(2)
b (Å)	14.366(2)
c (Å)	9.210(2)
β (°)	102.01(2)
Volume (Å^3)	1027.8(4)
ρ_{calc} (g cm^3)	1.766
Z	4
F(000)	552
Absorption coefficient (mm^{-1})	2.738
Crystal size (mm)	0.4 × 0.3 × 0.4
θ range (°)	2.62-25.97
Index ranges	$-9 \leq h \leq 9$ $0 \leq k \leq 17$ $0 \leq l \leq 11$
Reflections collected	1792
Independent reflections (R_{int} = 0.0181)	1686
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1686/0/109
Goodness-of-fit on F^2	1.049
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.045$, $wR_2{}^b = 0.086$
R indices (all data)	$R_1{}^a = 0.0664$, $wR_2{}^b = 0.093$

[a] $R_1 = S|F_o| - |F_c|/\Sigma||F_o|$. [b] $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)2/\Sigma wF_o{}^4]^{1/2}$ with $w = 1/[\sigma^2(F_o{}^2) + (0.0394P)^2 + 0.1612P]$, where $P = [\max(F_0{}^2,0) + 2\,F_c{}^2]/3$

evaporation of the solvent, the reaction of $CuCl_2{\cdot}2H_2O$ with 4 equivalents of L in CH_3CN afforded yellow block-shaped crystals having elemental analysis in accordance with the stoichiometry CuLCl. Its IR spectrum showed as main features a broad medium band at 2738 cm^{-1}, indicative of a weak N···H bond, and a weak peak at 244 cm^{-1} attributable to a ν(Cu-Cl) stretching vibration. An X-ray crystal structure determination was undertaken in order to establish the nature of the complex.

The crystal structure consists of a polymeric $\{CuLCl\}_\infty$ chain (Figure 1), in which each L molecule acts as an *N*(1),*S*(4)-bidentate ligand, bridging two copper(I) centres. The coordination geometry around the metal ion is almost trigonal planar with a chloro ligand occupying the third coordination site (Figure 2). The copper lies 0.139(2)Å out of the plane determined by N(1), Cl, and S(4′) as a consequence of the long contact [2.898(2)Å] with the S(2) thioether sulphur atom of a ligand molecule belonging to the nearest chain. Cu-S(4′) and Cu-Cl bond lengths [2.234(1) and 2.265(2)Å] are in accordance with values reported for

TABLE II Selected Bond Lengths (Å) and Angles (°) for $\{CuLCl\}_\infty$.

Cu-N(1)	1.980(3)	Cu-S(4′)	2.234(1)
Cu-Cl	2.265(2)	S(2)-C(2)	1.738(4)
S(2)-C(8)	1.784(6)	S(4)-C(4)	1.652(4)
S(4)-Cu″	2.234(1)	N(1)-C(2)	1.263(5)
N(1)-C(5)	1.488(5)	N(3)-C(4)	1.324(5)
N(3)-C(2)	1.395(5)	C(5)-C(6)	1.513(7)
C(5)-C(7)	1.521(6)	C(5)-C(4)	1.523(6)
N(1)-Cu-S(4′)	125.0(1)	N(1)-Cu-Cl	115.1(1)
S(4′)-Cu-Cl	115.6(1)	C(2)-S(2)-C(8)	103.8(2)
C(4)-S(4)-Cu″	108.7(2)	C(2)-N(1)-C(5)	108.0(3)
C(2)-N(1)-Cu	126.6(3)	C(5)-N(1)-Cu	125.4(3)
C(4)-N(3)-C(2)	109.1(4)	N(1)-C(5)-C(6)	109.6(4)
N(1)-C(5)-C(7)	111.1(4)	C(6)-C(5)-C(7)	112.0(4)
N(1)-C(5)-C(4)	102.0(3)	C(6)-C(5)-C(4)	111.3(4)
C(7)-C(5)-C(4)	110.4(4)	N(1)-C(2)-N(3)	113.9(4)
N(1)-C(2)-S(2)	122.8(3)	N(3)-C(2)-S(2)	123.3(3)
N(3)-C(4)-C(5)	107.0(3)	N(3)-C(4)-S(4)	127.2(3)
C(5)-C(4)-S(4)	125.7(3)		

Symmetry codes: ′ = $-x + 1, y + 1/2, -z + 1/2$; ″ = $-x + 1, y - 1/2, -z + 1/2$.

TABLE III Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $\{CuLCl\}_\infty$. *U(eq)* is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor.

	x/a	*y/b*	*z/c*	*U(eq)*
Cu	5856(1)	741(1)	2183(1)	46(1)
S(2)	2497(2)	−530(1)	326(2)	47(1)
S(4)	6087(2)	−3192(1)	3821(1)	36(1)
Cl	8174(2)	1290(1)	3821(2)	62(1)
N(1)	5366(5)	−598(2)	2385(4)	28(1)
N(3)	4080(5)	−1984(2)	2051(4)	28(1)
C(2)	4078(6)	−1042(3)	1681(5)	29(1)
C(4)	5487(6)	−2171(3)	3060(5)	26(1)
C(5)	6492(6)	−1265(3)	3378(5)	28(1)
C(6)	8217(6)	−1330(3)	2932(5)	37(1)
C(7)	6675(8)	−992(3)	4998(5)	45(1)
C(8)	959(6)	−1438(4)	−204(5)	55(2)

mononuclear trigonal Cu^I complexes with thione and chloride ligands where the Cu-S bond distances have always been found shorter than those of Cu-Cl[15]. The Cu-N(1) bond length [1.980(3)Å] is in good agreement with those already reported for Cu^{II} and Cu^I complexes[14] and shorter than those observed in $[CuL'_4(H_2O)]^{2+}$[7]. The imidazoline ring is planar; however, if the bond distances and angles within the ring are compared with those found in $[CuL'_4(H_2O)]^{2+}$, the following differences (see Scheme) appear to be: (i) meaningful variations occur

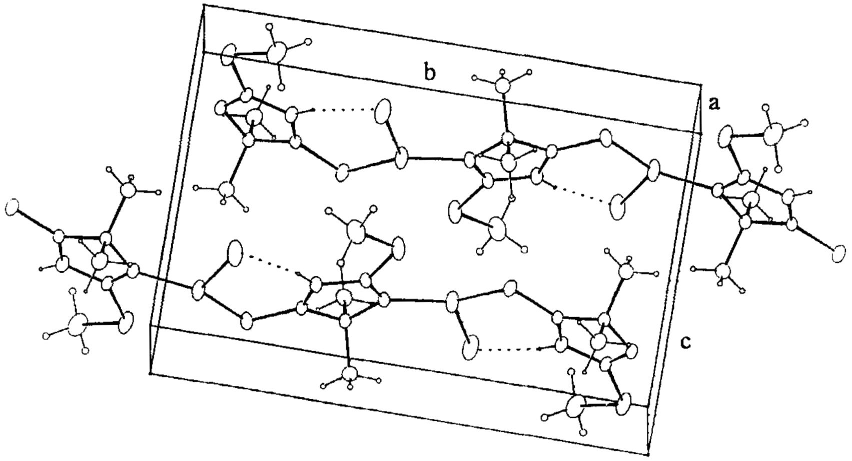


FIGURE 1 Crystal packing of *catena*-chloro (μ-*N*(1), *S*(4)(2-*S*-methyl-5,5-dimethylimidazoline-4-thione)) copper(I).

in the portion of the ring involved in π delocalization, and (ii) the imidazoline ring in $\{CuLCl\}_\infty$ is more stretched along an axis passing through the bridging atoms N(1) and S(4) with respect to what has been observed in $[CuL'_4(H_2O)]^{2+}$. The dihedral angles between the imidazoline ring planes of the two L molecules coordinated to each copper(I) ion and the coordination plane are 8.3(3)° and 16.5(5)° respectively, and the dihedral angle between the two imidazoline ring

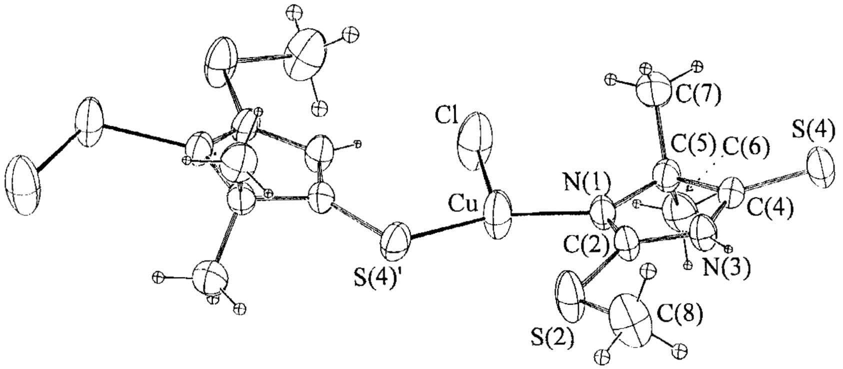
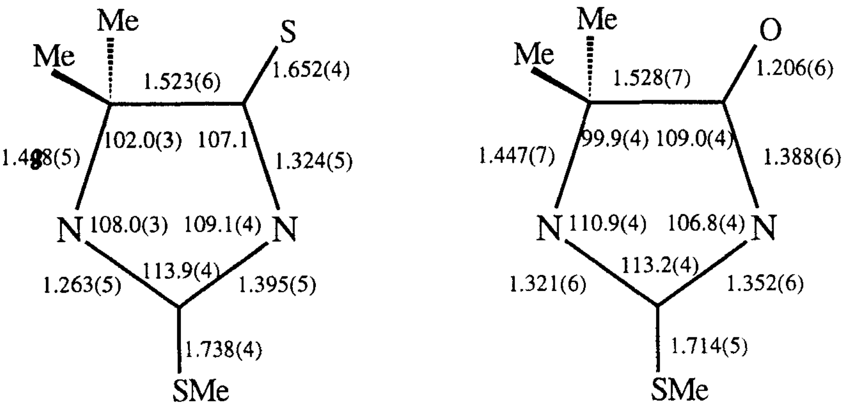


FIGURE 2 ORTEP view of *catena*-chloro (μ-*N* (1), *S*(4)(2-*S*-methyl-5,5-dimethylimidazoline-4-thione)) copper(I) showing the atom numbering scheme and thermal ellipsoids (50%). Labels of hydrogen atoms are omitted for clarity.



SCHEME Comparison between bond distances (Å) and angles (°) of the imidazoline rings in $\{CuLCl\}_\infty$ (left) and $[CuL'_4(H_2O)]^{2+}$ (right) complexes.

planes is 23.8(6)°. Intrachain hydrogen bond contacts occur between the NH group of each imidazoline molecule and the chloro ligand. The Cl···H separation is 2.24 Å and the subtended N-H···Cl angle is 162.1° [*d*(N-Cl) = 3.069(6)Å] (Figure 2). This interaction is responsible for the N-H bond length and the appearance of the ν(N-H) stretching vibration at 2738 cm^{-1} in the IR spectrum of $\{CuLCl\}_\infty$. The IR absorption fits fairly well with the correlation *d*(N···Cl) *versus* ν(N···H) reported for an N-H···Cl system[16]. A polymeric complex, $\{Cu(ss)_2Cl\}_\infty$, was obtained by reacting $CuCl_2$ and 5,5-dimethylimidazolidine-2,4-dithione (ss)[18]. In this case the complex forms a polymeric chain in which every copper(I) ion displays a tetrahedral environment; one ss molecule bridges through the two sulphur atoms between two copper centres, and the remaining two coordination sites are occupied by one chloro ligand and another ss molecule bonded to the metal ion through the S(2) sulphur atom. However, in $\{CuLCl\}_\infty$, although a strong interaction between the thioether sulphur, S(2), of one chain and the copper(I) ion belonging to the next chain is evident, the tetrahedral environment is not achieved (as in $Cu(ss)_2Cl$) probably because the coordinating ability of the thioether sulphur, $-S(2)-CH_3$, in L is lower than that of the thionic C=S(2) group in ss.

Finally, it is interesting to point out that even though the ligand should be present in polar solvents predominantly as a Δ^2 isomer and coordination through N(3) should be favoured, in this case coordination occurs through the N(1) atom, probably for structural reasons.

Supplementary Material

Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and observed and calculated structure factors are available from the authors upon request.

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