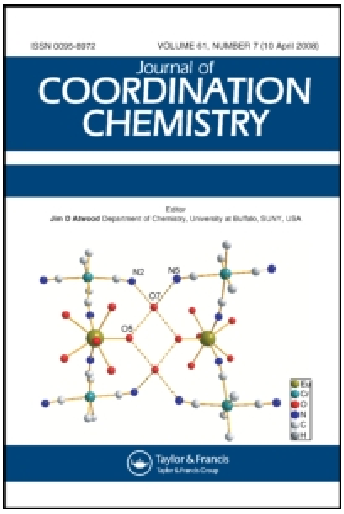

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REACTION OF CuX_2(X = Cl, Br) WITH 5,5-DIMETHYLMIDAZOLIDINE-2,4-DITHIONE (ss), AND THEIR -2-ONE-4-THIONE (oxs) AND -2-THIONE-4-ONE (sox) ISOLOGUES-CRYSTAL STRUCTURES OF $CU(oxs)_2Br$ AND $Cu(ss)_2Cl$

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REACTION OF CuX_2(X = Cl, Br) WITH 5,5-DIMETHYLMIDAZOLIDINE-2,4-DITHIONE (ss), AND THEIR -2-ONE-4-THIONE (oxs) AND -2-THIONE-4-ONE (sox) ISOLOGUES-CRYSTAL STRUCTURES OF $CU(oxs)_2Br$ AND $Cu(ss)_2Cl$

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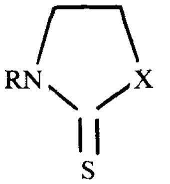
Copper(I) complexes, obtained by reacting CuX_2 (X = Cl, Br) with 5,5-dimethylimidazolidine-2-thione-4-one (sox), and its 2-one-4-thione (oxs) and 2,4-dithione (ss) derivatives, are reported. Infrared spectra show evidence for *S*-coordination in all the complexes. The crystal structure of $Cu(oxs)_2Br$ shows dimeric units, where every copper(I), practically trigonal planar, undergoes a tetrahedral distorsion by long range interactions with one bridging bromine and one bridging sulphur atom of oxs. The crystal structure of $Cu(ss)_2Cl$ is formed by a polymeric chain in which every copper has a tetrahedral environment, achieved by two ligands bridged *via* the two sulphur atoms between two coppers, one ligand bonded only through the 2-thione sulphur, and one chlorine. The distortions of the C=O and C=S groups from the symmetrical positions with respect to the other two bonds of the $C(sp^2)$ carbons, verified in the complexes and in the free ligands, are interpreted in terms of the VSEPR model.

INTRODUCTION

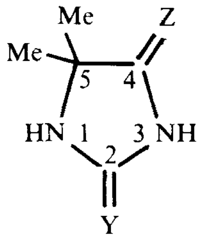
It is well known that thioamido-containing ligands reduce copper(II) salts to yield complexes of copper(I), whose stereochemistry is very flexible. We have reported several copper(I) complexes with the following heterocyclic pentaatomic rings



X = CH_2, O, S, NH, NMe, NEt
R = H, Me

prepared from different copper(II) salts.[1] The reduction rate is very fast for R = H, but for R = alkyl the reaction proceeds with such a low rate that copper(II) complexes of *N,N'*-dimethyl- and *N,N'*-diethyl-imidazolidine-2-thione have also been obtained.[2]

Recently,[3] we have prepared a new series of ligands still having the imidazolidine ring as framework and two chalcogen atoms at C-2 and C-4, as shown below.



Y \ Z	O	S	Se
O	oxox	oxs	oxse
S	sox	ss	sse
Se	seox	ses	sese

By studying the donor abilities of Y and Z towards molecular iodine,[4] we have found that for Y=Z the interaction occurs *via* Y, while for $Y \neq Z$ selenium binds I_2 more strongly than sulphur and oxygen. The comparison of the stability constants obtained for sox, oxs and ss with those obtained for the imidazolidine-2-thiones variously substituted, shows that the latter are much richer in electrons than the formes. This fact leads us to think that the reducing properties of the substituted imidazolidine-2,4-dichalcogens must be lower than those of the corresponding imidazolidines.

Nevertheless, the reaction of sox, ss and oxs with copper(II) chloride and bromide always yields copper(I) complexes.

EXPERIMENTAL

The syntheses and purification of the ligands have been described elsewhere.[3] The copper(I) complexes with sox and oxs (see Table I) were obtained by refluxing CuX$_2$ (X = Cl, Br) and the appropriate ligand (1:4 molar ratio), both dissolved in isopropanol. After cooling, chloroform was added to the solution and crystals of the complexes were obtained by slow evaporation.

TABLE I
Colours, melting points and analytical data for the copper(I) complexes.

Complex,	Colour	M.p./°C	Analysis (%)[a] C	H	N
Cu(sox)$_2$Cl·H$_2$O	yellow	154	29.8 (29.6)	4.7 (4.5)	13.8 (13.8)
Cu(sox)$_2$Br·H$_2$O	yellow	138	26.6 (26.7)	4.2 (4.0)	12.4 (12.5)
Cu$_2$(oxs)$_3$Cl$_2$	yellow	201d	28.7 (28.6)	3.6 (3.8)	13.1 (13.3)
Cu(oxs)$_2$Br	yellow	191	27.9 (27.8)	4.0 (3.7)	12.7 (13.0)
Cu(ss)Cl	yellow	174	22.9 (23.2)	3.1 (3.1)	10.7 (10.8)
Cu(ss)Br	yellow	234	19.6 (19.8)	2.7 (2.7)	9.5 (9.2)
Cu(ss)$_2$Cl	orange	230	28.6 (28.6)	3.9 (3.8)	13.2 (13.4)
Cu(ss)$_2$Br	orange	278	26.1 (25.9)	3.4 (3.5)	12.0 (12.0)

[a] Calculated values in parentheses.

The crystals of the oxs complex employed in the X-ray analysis contained isopropanol as $2Cu(oxs)_2Br \cdot C_3H_8O$. The presence of one molecule of water in the sox complexes was determined by thermogravimetric analyses and was evident by the medium band at 3536 and 3542 cm^{-1}, present in the infrared spectra of the chloro- and bromo-complexes, respectively.

Using methanol instead of isopropanol as solvent, yellow powders of Cu(ss)X (X = Cl, Br) precipitate immediately. After filtration, orange crystals of $Cu(ss)_2X$ are formed from the mother liquor by slow evaporation of the solvent. The Cu(ss)X complexes were also prepared by refluxing CuX and ss in methanol in a 1:1 molar ratio (see Table I).

The X-ray measurements were carried out as described in Table II; the lattice parameters in both cases were determined from least-squares refinement of θ values for 15 reflections accurately centred on the diffractometer. The intensity data were corrected for Lorentz and polarization effects; for $Cu(oxs)_2Br$ an empirical aborption correction was also applied.[5] The structures were solved by the Patterson and Fourier method and refined by least-squares methods using the SHELX-76 program;[6] in $Cu(ss)_2Cl$ the hydrogen atoms, located from a final ΔF map, were included in the last refinement cycle, while in $Cu(oxs)_2Br$ they were not located. In the latter compound five reflections (200, 011, 111, $\bar{1}02$, $0\bar{1}2$) which can be effected by extinction were excluded

TABLE II
Experimental data for the crystallographic analyses.

Compound	$2Cu(oxs)_2Br \cdot C_3H_8O$	$Cu(ss)_2Cl$
Formula	$C_{23}H_{40}Br_2Cu_2N_8O_5S_4$	$C_{10}H_{16}ClCuN_4S_4$
M.W.	923.76	419.50
Space group	$P1$	$P2_1/n$
a, Å	15.637(5)	11.766(12)
b, Å	13.154(5)	9.654(4)
c, Å	10.096(3)	15.018(7)
α, °	109.94(6)	90.0
β, °	80.82(5)	90.56(2)
γ, °	98.07(5)	90.0
V, Å^3	1919(1)	1706(2)
Z	2	4
D_c, g cm^{-3}	1.599	1.634
D_o, g cm^{-3}	1.57	1.65
$F(000)$	932	856
Temperature, K	293	293
Crystal size, mm^3	0.39 x 0.82 x 0.82	0.45 x 0.62 x 0.25
Diffractometer	Philips PW 1100	Siemens AED
μ, cm^{-1}	34.24	19.07
Absorption correction	1.00–1.88	
Max. scan speed, °/min	4.8	2.5
Scan width, °	1.60	$1.2 + 0.35\ \mathrm{tg}\theta$
Radiation, Å	0.71069	0.71069
θ range, °	2.5–25.0	3–24
Standard reflection	$5\ \bar{5}\ 4$	$7\ \bar{5}\ 0$
Intensity variation	0.020	0.038
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$
Measured reflections	6738	3020
Reflections used in the refinement	3936	2059
Condition of the measured reflections	$I > 3\sigma(I)$	$I > 2\sigma(I)$
No. of refined parameters	378	245
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.0593	0.0504
$R_w = [\Sigma_w(\Delta F)^2/\Sigma_w F_o^2]^{1/2}$	0.0666	0.0541
$K, g (w = K[\sigma^2(F_o) + gF_o^2])$	1.0, 0.0046	0.43, 0.0115

TABLE III
Atomic coordinates (fractional x 10^4) for $Cu(oxs)_2Br\cdot C_3H_8O$, with estimated standard deviations in parentheses.

Atom	*x/a*	*y/b*	*z/c*
Cu(1)	1315(1)	167(1)	2156(2)
Cu(2)	2901(1)	−1369(1)	1710(1)
Br(1)	2036(1)	37(1)	4050(1)
Br(2)	2159(1)	−3115(1)	1802(1)
S(1)	1368(2)	1776(2)	1790(3)
S(2)	217(2)	−1064(2)	1349(3)
S(3)	2665(2)	−785(2)	−97(3)
S(4)	4328(2)	−1026(3)	2133(3)
O(1)	3183(6)	3598(6)	5760(9)
O(2)	310(5)	−2965(6)	4823(8)
O(3)	1139(6)	−4378(5)	−2512(8)
O(4)	4083(9)	−4118(10)	3957(19)
N(1)	2316(6)	2555(6)	3984(9)
N(2)	2640(6)	4297(7)	4252(9)
N(3)	335(5)	−1873(6)	3420(8)
N(4)	1465(6)	−2852(7)	−3210(9)
N(5)	1879(5)	−2803(6)	−1180(8)
N(6)	−588(6)	−3371(6)	3040(8)
N(7)	4043(6)	−2719(8)	3019(12)
N(8)	5259(8)	−3006(8)	3559(14)
C(1)	1924(7)	2714(7)	2976(9)
C(2)	2765(7)	3530(8)	4768(11)
C(3)	2122(6)	3892(7)	3070(9)
C(4)	1300(8)	4474(9)	3432(11)
C(5)	2657(8)	3978(9)	1657(11)
C(6)	−3(5)	−1923(6)	2284(8)
C(7)	51(7)	−2775(7)	3877(10)
C(8)	−662(6)	−2905(7)	1924(9)
C(9)	−434(8)	−3655(8)	452(10)
C(10)	−1586(7)	−2578(9)	2115(12)
C(11)	2144(6)	−1808(7)	−1295(9)
C(12)	1452(7)	−3477(8)	−2372(10)
C(13)	1904(7)	−1732(7)	−2598(10)
C(14)	2705(9)	−1587(11)	−3628(14)
C(15)	1276(8)	−898(9)	−2309(12)
C(16)	4565(6)	−1953(8)	2723(10)
C(17)	4448(9)	−3371(11)	3615(17)
C(18)	5475(8)	−2091(10)	2997(13)
C(19)	6059(10)	−2303(19)	1649(17)
C(20)	5804(10)	−1037(11)	4213(18)
O(1A)	6380(12)	3871(14)	2835(19)
C(1A)	5811(18)	3565(20)	1776(26)
C(2A)	5098(18)	2827(19)	2289(26)
C(3A)	4558(18)	3627(20)	3493(27)
H(1)	2291(13)	1844(18)	4151(17)
H(2)	2878(12)	5073(18)	4638(17)
H(3)	750(11)	−1258(16)	3907(15)
H(4)	−950(12)	−4027(17)	3173(16)
H(5)	1970(12)	−3035(17)	− 371(16)
H(6)	1211(13)	−3110(17)	−4129(17)
H(7)	3417(14)	−2853(23)	2854(23)
H(8)	5706(16)	−3320(25)	3873(26)

TABLE IV

Fractional atomic coordinates (x 10^4) for $Cu(ss)_2Cl$ with estimated standard deviations in parentheses.

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Cu	5202(1)	3786(1)	6488(1)	C(10)	1029(7)	1724(8)	7106(7)
Cl	4726(1)	2757(2)	7885(1)	N(4)	2410(5)	3609(6)	6921(3)
S(1)	6658(1)	5371(2)	6644(1)	H(1)	6133(75)	4395(91)	8521(53)
C(1)	7100(5)	5404(7)	7706(4)	H(2)	6135(76)	6411(96)	9723(58)
N(1)	8012(4)	6213(5)	7983(3)	H(3)	6061(76)	5071(95)	10064(56)
S(2)	9140(1)	6971(2)	9440(1)	H(4)	6953(77)	5920(93)	10428(64)
C(2)	8196(5)	6122(6)	8867(4)	H(5)	8380(77)	3548(92)	9246(61)
C(3)	7346(5)	5078(7)	9222(4)	H(6)	7478(68)	3124(95)	9704(51)
C(4)	6589(7)	5712(11)	9919(5)	H(7)	8359(81)	4179(96)	10069(64)
C(5)	7940(8)	3798(9)	9571(7)	H(8)	8305(73)	6562(87)	7624(55)
N(2)	6711(5)	4751(6)	8407(3)	H(9)	2931(74)	3273(96)	7151(58)
S(3)	3731(1)	4764(2)	5676(1)	H(10)	34(72)	3669(82)	8181(56)
C(6)	2544(5)	4265(6)	6164(4)	H(11)	1146(73)	3499(92)	8475(64)
N(3)	1463(4)	4475(6)	5820(3)	H(12)	972(77)	4772(99)	7926(61)
C(7)	640(5)	3958(6)	6341(4)	H(13)	266(74)	1534(80)	7220(52)
T(4)	−725(1)	4021(2)	6181(1)	H(14)	1265(74)	1414(85)	6462(59)
C(8)	1233(5)	3281(7)	7127(4)	H(15)	1254(73)	1407(87)	7542(61)
C(9)	862(8)	3918(14)	7994(6)	H(16)	1301(67)	4885(91)	5348(60)

from the final refinement. The atoms of isopropanol, present in $Cu(oxs)_2Br$, show very high thermal parameters and consequently their structural parameters are effected by large errors. The atomic scattering factors for the neutral atoms were taken from reference 7; the final atomic coordinates are reported in Table III and IV. The major calculations were performed on CDC Cyber 7600 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna with financial support of the University of Parma. Observed and calculated structure factors, and anisotropic thermal parameters together with the calculated least-squares planes have been deposited with the Editor and are available on request.

RESULTS AND DISCUSSION

Infrared Spectra

The most important i.r. bands of the ligands and their complexes are reported in Table V. For the complexes of sox and oxs, the shifts of ν(NH) and ν(CO) indicate that neither nitrogen nor oxygen are involved in coordination to the copper, since the ν(NH) undergoes small displacements as a consequence of changes in hydrogen bonding and ν(CO) increases in wavenumber. Hence, coordination must occur through the sulphur atom, as confirmed by the downward shifts of the ν(CS) vibrations. The behaviour of the bands assigned to the prevailing ν(CN) contributions requires some comment. In fact, with *S*-coordination, the higher conjugation of the lone pair of the nearby nitrogens should increase the π-bond order of the CN bonds and move their infrared bands to higher wavenumbers. The increase of ν(CN) was considered an unambiguous proof of *S*-coordination in all the pentaatomic rings containing the thioamido group previously investigated by us.[8] In the present ligands, coordination through Y or Z or both heteroatoms would change the π-system within 1–4, with a consequent change in the strength of the three CN bonds. However, as one can see by examining the shifts of ν(CN), no real trends are noticed. In fact, for the complexes of sox, the band at 1290 cm^{-1} which should increase in wavenumber (see footnote in Table V), on the contrary decreases and splits in the chloro derivative, and the band at 1523 cm^{-1} of oxs

TABLE V

I.r. spectral data (cm^{-1}) for the ligands and their copper(I) complexes.

	ν(NH)	ν(CO)	ν(CN)[a]	ν(CS)	δ(CS)	Other vibrations within 600–200 cm^{-1}
sox	3220sh–3179s	1742vs	1529vs–1290vs–1132vs	495ms	351ms	586w–563ms–444w–300w–282w
$Cu(sox)_2Cl \cdot H_2O$	3230m–3161s	1769vs–1743vs	1533vs–1280ms–1268s–1125ms–1114s	485ms	347w	563w–302w
$Cu(sox)_2Br \cdot H_2O$	3230m–3164s	1769vs–1744vs	1532vs–1278vs–1125ms–1114s	485m	345w	563w
oxs	3265s–3065s	1717vsbr	1523m–1280s	507m	391mw	597m–580sh–450sh–437w–330w
$Cu_2(oxs)_3Cl_2$	3301vs–3113ms	1758vs	1478s–1284s	489s	390w–372m	568ms–450w–328w
$Cu(oxs)_2Br$	3302s–3133ms	1758vs	1475s–1281s	490s	369m	596m–566ms–325vw
ss	3180sh–3138vs		1545vs–1433vs–1271s	554m–451m	333mw	499mw
Cu(ss)Cl	3220m		1547vs–1437vs–1294s	549m–452w	341w	586w–506w
Cu(ss)Br	3224s		1545vs–1439vs–1294vs	550ms–454m	340w	506m
$Cu(ss)_2Cl$	3125vs		1527vs–1419vs–1264vs	554ms–451m	331w	498m
$Cu(ss)_2Br$	3126vs		1527vs–1419vs–1258vs	555ms–450m	333w	497m

[a] The three different ν(CN) vibrations expected for the free ligands have been assigned to the prevailing contributions of $\nu(C_2N_1)$, $\nu(C_43_d)$ and $\nu(C_2N_3)$ in decreasing wavenumbers. For oxs, see text.

undergoes a marked downward shift in its complexes. Hence, no unequivocal information about coordination can be deduced from the displacements of ν(CN). Also, for the complexes of ss, where the behaviour of ν(NH) excludes nitrogen as a coordinating atom, the bond must occur *via* sulphur. However, an inspection of the bands attributed to ν(CN) and the CS modes does not help in defining the coordination to the metal. For this reason, we have supported the infrared study with an X-ray investigation carried out on those compounds which gave suitable crystals.

Crystal Structure of Bromo-Tris(5,5-dimethylimidazolidin-2-one-4-thione)-μ-bromo-μ-S(5,5-dimethylimidazolidin-2-one-4-thione)dicopper(I).

In the structure of the title compound, depicted in Fig. 1, each copper atom is surrounded by two sulphurs and one bromine. Bond distances and angles (Table VI) involving the Cu(1) atom show that the coordination is essentially trigonal planar [116.7(2)–120.1(2)°] with much distortion to a trigonal pyramid (or tetrahedron) by the long contact Cu(1) . . . S(3) = 2.910(4) Å; the copper atom is 0.268(3) Å out of the plane

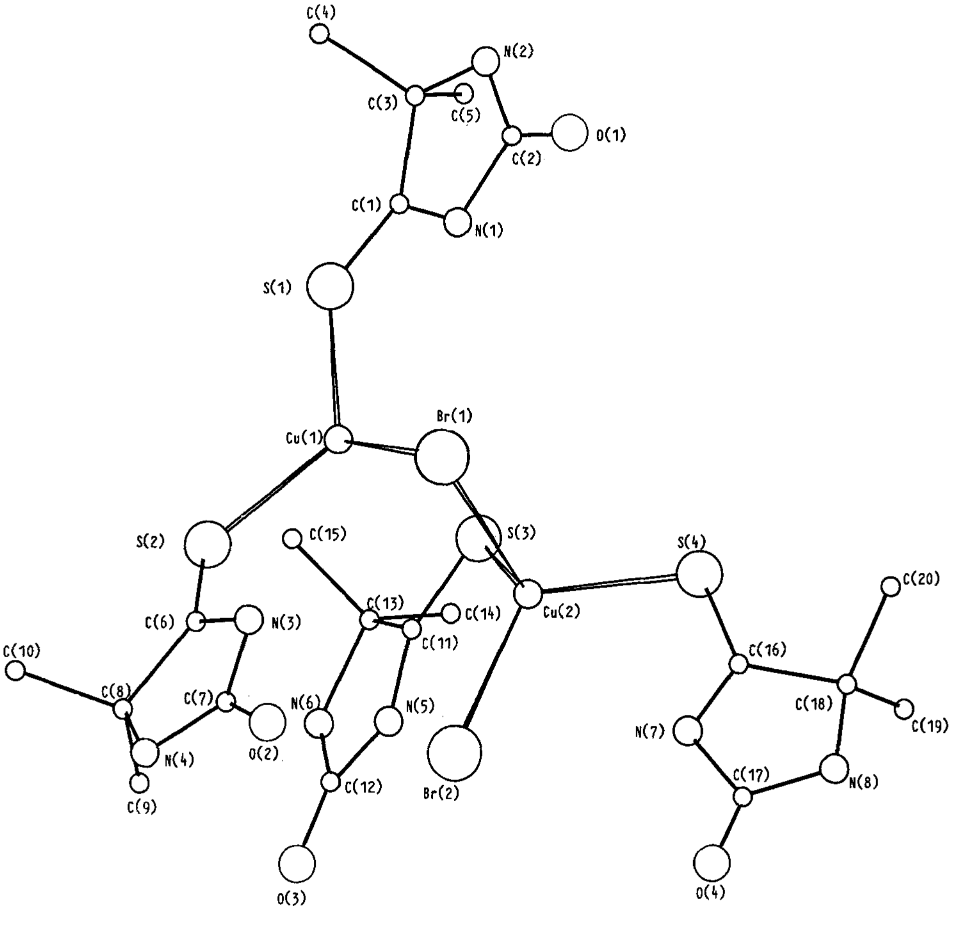


FIGURE 1 Perspective view of bromotris(5,5-dimethylimidazolidin-2-one-4-thione)-μ-bromo-μ-*S*(5,5-dimethylimidazolidin-2-one-4-thione)dicopper(I)

TABLE VI

Bond distances (Å) and angles (°) (a), contacts less than 3.60 Å (b) and hydrogen bonds (c) for $2Cu(oxs)_2Br \cdot C_3H_8O$.

(a)

Cu(1)-Br(1)	2.434(3)	Cu(2)-Br(1)	2.745(3)				
Cu(1)-S(1)	2.258(4)	Cu(2)-Br(2)	2.448(2)				
Cu(1)-S(2)	2.236(3)	Cu(2)-S(3)	2.303(4)				
Cu(1)-S(3)	2.910(4)	Cu(2)-S(4)	2.292(4)				
S(1)-C(1)	1.65(1)	S(2)-C(6)	1.67(1)	S(3)-C(11)	1.68(1)	S(4)-C(16)	1.63(1)
C(1)-C(3)	1.51(1)	C(6)-C(8)	1.51(1)	C(11)-C(13)	1.46(2)	C(16)-C(18)	1.54(2)
C(3)-C(4)	1.52(2)	C(8)-C(9)	1.50(1)	C(13)-C(14)	1.53(2)	C(18)-C(19)	1.48(2)
C(3)-C(5)	1.57(1)	C(8)-C(10)	1.53(2)	C(13)-C(15)	1.50(2)	C(18)-C(20)	1.59(2)
C(3)-N(2)	1.46(1)	C(8)-N(4)	1.48(1)	C(13)-N(6)	1.50(1)	C(18)-N(8)	1.48(2)
N(2)-C(2)	1.33(2)	N(4)-C(7)	1.39(1)	N(6)-C(12)	1.36(2)	N(8)-C(17)	1.29(2)
C(2)-O(1)	1.25(2)	C(7)-O(2)	1.21(2)	C(12)-O(3)	1.19(1)	C(17)-O(4)	1.19(2)
C(2)-N(1)	1.41(1)	C(7)-N(3)	1.41(1)	C(12)-N(5)	1.43(1)	C(17)-N(7)	1.46(2)
N(1)-C(1)	1.35(2)	N(3)-C(6)	1.32(1)	N(5)-C(11)	1.35(1)	N(7)-C(16)	1.29(1)

Br(1)-Cu(1)-S(1)	120.1(2)	Br(2)-Cu(2)-S(3)	117.7(1)
Br(1)-Cu(1)-S(2)	119.3(2)	Br(2)-Cu(2)-S(4)	116.7(2)
Br(1)-Cu(1)-S(3)	94.8(1)	S(3)-Cu(2)-S(4)	112.0(2)
S(1)-Cu(1)-S(2)	116.7(2)	Br(1)-Cu(2)-S(4)	104.3(1)
S(1)-Cu(1)-S(3)	98.0(1)	Br(1)-Cu(2)-S(3)	102.4(1)
S(2)-Cu(1)-S(3)	97.3(1)	Br(1)-Cu(2)-Br(2)	100.8(1)
Cu(1)-S(1)-C(1)	109.1(4)	Cu(2)-S(3)-C(11)	109.3(4)
Cu(1)-S(2)-C(6)	110.2(3)	Cu(2)-S(4)-C(16)	108.9(4)
Cu(1)-S(3)-C(11)	105.4(4)	Cu(1)-S(3)-Cu(2)	77.5(1)
		Cu(1)-Br(1)-Cu(2)	78.8(1)
O(1A)-C(1A)	1.42(3)	O(1A)-C(1A)-C(2A)	103(2)
C(1A)-C(2A)	1.52(4)	C(1A)-C(2A)-C(3A)	103(2)
C(2A)-C(3A)	1.53(3)		

(b)

Cu(1) . . . Cu(2)	3.296(3)
S(1) . . . S(3^{i})	3.512(3)
S(1) . . . S(4^{ii})	3.421(3)
N(3) . . . S(4^{iii})	3.441(5)
O(1A) . . . O(1^{i})	3.16(2)
O(1A) . . . O(4^{iv})	3.12(3)
O(1A) . . . N(2^{i})	3.52(2)
O(1A) . . . N(5^{v})	3.19(2)
O(1A) . . . C(11^{v})	3.58(2)
O(1A) . . . C(12^{v})	3.44(2)
C(3A) . . . N(2)	3.15(3)
C(3A) . . . O(4^{vi})	3.02(3)
C(3A) . . . O(4^{iv})	3.43(3)
C(3A) . . . N(8^{iv})	3.41(3)
O(4) . . . C(5^{vii})	3.57(2)
O(1) . . . C(10^{viii})	3.46(2)
S(2) . . . C(15^{ix})	3.51(1)

Symmetry codes for (b):
i = $1-x, 1-y, 1-z$
ii = $1-x, y, z$
iii = $\bar{x}, 1-y, 1-z$
iv = $1-x, \bar{y}, 1-z$
v = $1-x, \bar{y}, \bar{z}$
vi = $x, 1+y, z$
vii = $x, y-1, z$
viii = $\bar{x}, \bar{y}, 1-z$
ix = $\bar{x}, \bar{y}, \bar{z}$

(c)

N(1) . . . Br(1)	3.302(9)	H(1) . . . Br(1)	2.32	N(1)-H(1) . . . Br(1)	166°
N(3) . . . Br(1)	3.371(8)	H(3) . . . Br(1)	2.44	N(3)-H(3) . . . Br(1)	156
N(5) . . . Br(2)	3.277(9)	H(5) . . . Br(2)	2.30	N(5)-H(5) . . . Br(2)	166
N(7) . . . Br(2)	3.278(11)	H(7) . . . Br(2)	2.31	N(7)-H(7) . . . Br(2)	162
N(2) . . . O(4^{iii})	2.90(2)	H(2) . . . O(4^{iii})	2.16	N(2)-H(2) . . . O(4^{iii})	129
N(4) . . . O(3^{iv})	2.85(1)	H(4) . . . O(3^{iv})	1.97	N(4)-H(4) . . . O(3^{iv})	147
N(6) . . . O(2^{v})	2.85(1)	H(6) . . . O(2^{v})	1.96	N(6)-H(6) . . . O(2^{v})	147
N(8) . . . O(1^{vi})	2.91(2)	H(8) . . . O(1^{vi})	1.94	N(8)-H(8) . . . O(1^{vi})	162

Symmetry codes for (c):
iii = $x, 1+y, z$
iv = $\bar{x}, \bar{y}-1, \bar{z}$
v = $x, y, z-1$
vi = $1-x, \bar{y}, 1-z$

The hydrogen atoms are at the positions calculated 1.00 Å from their nitrogens.

determined by S(1), S(2) and Br(1). The coordination around Cu(2) resembles that found for Cu(1), but the distortion to a trigonal pyramid is more marked [bond angles 112.0(2)-117.7(1)°] since the copper lies 0.507(2) Å out of the plane passing through S(3), S(4) and Br(2), and as a consequence of the strong interaction Cu(2)-Br(1) = 2.745(3) Å. The Br(1) and S(3) atoms bridge the two metal atoms asymmetrically so that the complex must be considered a dimer. The values of the Cu(1)-S bond lengths [2.258(4)-2.236(3) Å] agree with those found in similar copper(I) complexes,[9-12], while those of Cu(2)-S are significantly greater [2.292(4)-2.303(4) Å] than the former and similar the the values reported for Cu(ss)$_2$Cl (see below). The two Cu-Br bonds [2.434(3), 2.448(2) Å] are only slightly different and compare well with the values found in several Cu(I)-Br complexes.[13-15] The Cu(1)-Br(1) bond length does not appear to be influenced by the bridging function of the bromine; the Cu(1)-Br(1)-Cu(2) angle is 78.82(8)° and the Cu(1) . . . Cu(2) separation 3.296(3) Å.

The structural features of the four ligands are very similar and agree very well with the bond distances and angles obtained for several differently substituted hydantoins.[16-18] The molecule involving S(3) and O(3) is strictly planar, except of course for the two methyl group; the others slightly deviate from planarity, but the systems of the atoms bonded to the C(sp^2) carbons are planar and form mutually dihedral angles of 1.7(3), 6.0(3), 1.1(4) and 2.9(5)° in the four ligands respectively. It is interesting to point out that in the four ligands, the C=O and C=S bonds do not lie symmetrically with respect to the other two bonds of the C(sp^2) carbons.

The whole structure is influenced in its packing arrangement by Van der Waals contacts involving several isopropanol molecules and by an extended system of hydrogen bonds between all the nitrogen, oxygen and bromine atoms (Table VI).

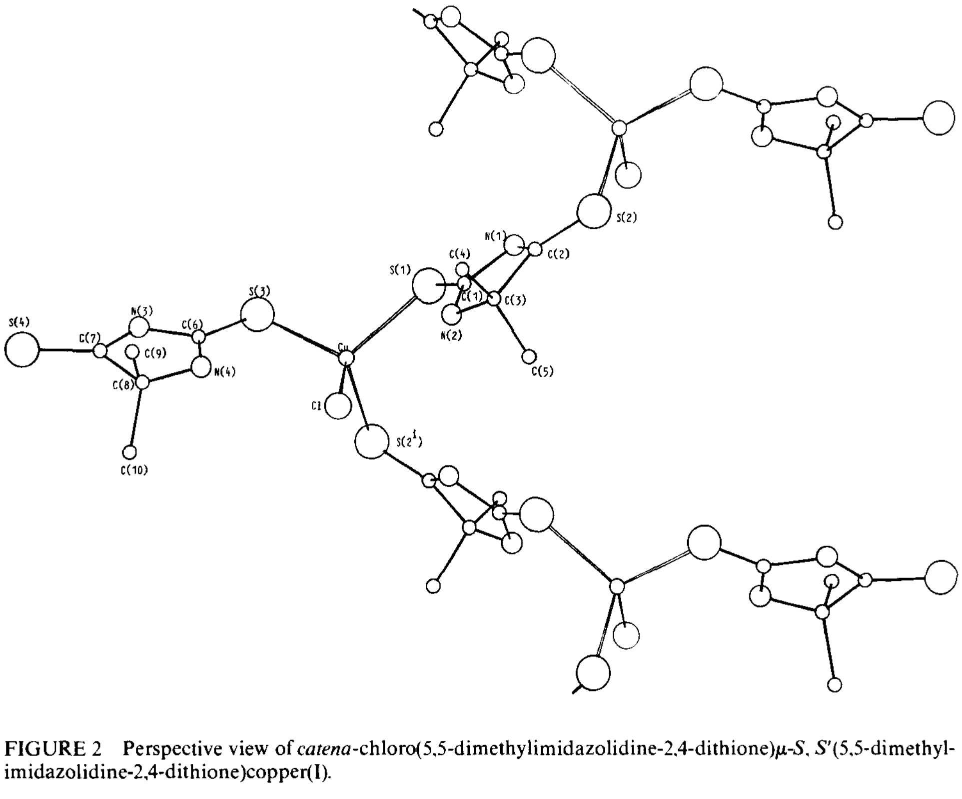


FIGURE 2 Perspective view of *catena*-chloro(5,5-dimethylimidazolidine-2,4-dithione)μ-*S*, *S*′(5,5-dimethylimidazolidine-2,4-dithione)copper(I).

Crystal Structure of Catena-Chloro(5,5-dimethylimidazolidine-2,4-dithione)-μ-S, S'(5,5-dimethylimidazolidine-2,4-dithione)copper(I).

In Cu(ss)$_2$Cl (Figure 2) the copper atom is tetrahedrally surrounded by one chlorine and three sulphur atoms from two ligand molecules, one of which acts as unidentate by the S(3) atom and the other as bridging bidentate by S(1) and S(2^i) ($i = 3/2-x, y-½, 3/2-z$), so that this molecule connects two adjacent coordination polyhedra thus generating a polymeric chain along the *b* direction. The Cu-Cl bond distance (Table VII) of 2.393(2) Å compares well with the values found in other tetrahedral copper(I) compounds.[19–20] The Cu–S(1) and Cu–S(3) bonds [2.307(2), 2.309(2) Å] are equal within experimental error, but significantly different from the Cu–S(2^i) 2.373(2) Å bond length and fall in the range of the values found for other tetrahedral copper(I) complexes,.[19,21,22] Bond angles around copper are in the range 103.8(1)–116.9(1)° and confirm the distortion of the coordination polyhedron.

Bond distances and angles in the two ligand molecules are similar and comparable with those found in the free molecule,[18] where the two thione bonds, 1.648(2)–1.641(2) Å for the 2- and 4-carbons respectively, are very similar. Under coordination, the 4-thione bond is shortened to 1.623(6) and 1.621(6) Å in the mono- and di-coordinated ligands, while the 2-thione distance becomes 1.655(6) and 1.673(6) Å, respectively. As seen in the previous structure, the directions of the S–C bonds never bisect the angles subtended at their C(sp^2) atoms, as revealed by the values of the S–C–N angles. The SCNN and SCNC groups in each molecule are planar and form dihedral angles of 3.2(2) and 1.6(2)° respectively in the di- and mono-coordinated ligands, so that, apart from the methyl groups, they are roughly planar.

The structure is packed by Van der Waals contacts and by intra- and intermolecular hydrogen bonds (Table VII).

As is well known for copper(I) complexes with soft donor ligands, no prediction about the geometry of the complex can be made on the basis of stoichiometry alone, but the coordination site of the ligand may be easily identified by infrared spectroscopy. In the present complexes, the ν(NH) and ν(CO) shifts exclude nitrogen and oxygen as coordinating atoms; consequently, coordination must occur through the sulphur atoms, as confirmed by the two reported structures, although no bands attributable to ν(CuX) (X = Cl, Br) and ν(CuS) have been identified. In addition, the anomalous behaviour of the ν(CN) bands and, for ss complexes, the absence of significant shifts of the bands attributed to the CS modes could be a consequence of their erroneous assignments; however this seems very improbable, since the CS modes were assigned on the basis of selenation[3] and the ν(CN) vibrations on the basis of their sodium salts.[23] On the other hand, for the two series of ss complexes, *i.e.* Cu(ss)X and Cu(ss)$_2$X, the ν(CN) vibrations undergo opposite shifts, although it is certain that in the Cu(ss)X complexes coordination must occur through one or both sulphur atoms. We have experienced similar difficulty in assigning the coordination site by i.r. spectra in complexes of pentaatomic rings containing the thioamido group condensed with benzene.[24] There, the large π-system was considered responsible for the very low shifts verified in the coordinated and free ligands. Here, the coupled nature of the infrared bands and the large π-system could be responsible for this behaviour. However, the structure of the oxs complex justifies the presence of only two ν(CN) vibrations. In fact, in coordinated oxs, the two bonds C2-N1* (1.29–1.39 Å) and N3-C4 (1.29–1.35 Å) are very close for all four ligands, but different from C2-N3 (1.41–1.46 Å).

On the basis of the infrared data alone, it is very difficult to predict the geometries of the other reported complexes; however, the complex Cu$_2$(oxs)$_3$Cl$_2$ could be formulated as [Cu(oxs)Cl · Cu(oxs)$_2$Cl] while the Cu(ss)X (X = Cl, Br) complexes could be polymers with bridging ligands.

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*The numbering is the one reported for the ring nomenclature.

TABLE VII

Bond distances (Å) and angles (°) (a), intermolecular contacts less than 3.6 Å (b) and intramolecular and intermolecular hydrogen bonds (Å and °) (c) for Cu(ss)$_2$Cl.

(a)

Cu-Cl	2.393(2)	Cu-S(2^{i})	2.373(2)
Cu-S(1)	2.307(2)	Cu-S(3)	2.309(2)
S(1)-C(1)	1.673(6)	S(3)-C(6)	1.655(6)
C(1)-N(1)	1.388(8)	C(6)-N(3)	1.383(8)
C(1)-N(2)	1.313(8)	C(6)-N(4)	1.312(8)
N(1)-C(2)	1.346(8)	N(3)-C(7)	1.347(8)
C(2)-S(2)	1.621(6)	C(7)-S(4)	1.623(6)
C(2)-C(3)	1.520(9)	C(7)-C(8)	1.514(9)
N(2)-C(3)	1.462(8)	N(4)-C(8)	1.457(8)
C(3)-C(4)	1.511(10)	C(8)-C(9)	1.508(12)
C(3)-C(5)	1.511(11)	C(8)-C(10)	1.522(10)
N(2)-H(1)	.78(8)	N(4)-H(9)	.77(9)
C(4)-H(2)	.91(9)	C(9)-H(10)	1.05(9)
C(4)-H(3)	.91(9)	C(9)-H(11)	.89(9)
C(4)-H(4)	.90(9)	C(9)-H(12)	.84(10)
C(5)-H(6)	.87(9)	C(10)-H(14)	1.05(9)
C(5)-H(7)	.97(10)	C(10)-H(15)	.77(9)
N(1)-H(8)	.73(8)	N(3)-H(16)	.83(9)
Cl-Cu-S(1)	111.5(1)	C(4)-C(3)-C(5)	111.4(6)
Cl-Cu-S(2^{i})	106.8(1)	C(1)-N(2)-C(3)	112.8(6)
Cl-Cu-S(3)	116.9(1)	Cu-S(3)-C(6)	106.2(2)
S(1)-Cu-S(2^{i})	107.6(1)	S(3)-C(6)-N(4)	129.3(6)
S(1)-Cu-S(3)	109.5(1)	S(3)-C(6)-N(3)	124.7(5)
S(2)-Cu-S(3)	103.8(1)	N(3)-C(6)-N(4)	106.1(6)
Cu-S(1)-C(1)	109.5(3)	C(6)-N(3)-C(7)	113.1(5)
S(1)-C(1)-N(2)	130.4(5)	N(3)-C(7)-C(8)	106.5(6)
N(1)-C(1)-N(2)	107.7(5)	C(4)-C(3)-N(2)	111.6(6)
S(1)-C(1)-N(1)	121.9(5)	N(3)-C(7)-S(4)	128.0(5)
N(4)-C(1)-N(2)	107.7(5)	S(4)-C(7)-C(8)	125.4(5)
C(1)-N(1)-C(2)	112.1(5)	C(7)-C(8)-N(4)	99.9(5)
N(1)-C(2)-S(2)	126.4(5)	C(7)-C(8)-C(10)	109.8(6)
S(2)-C(2)-C(3)	126.8(5)	C(7)-C(8)-C(9)	111.2(7)
N(1)-C(2)-C(3)	106.8(5)	C(10)-C(8)-N(4)	111.1(6)
C(2)-C(3)-N(2)	100.5(5)	C(9)-C(8)-N(4)	112.2(6)
C(2)-C(3)-C(5)	111.1(6)	C(9)-C(8)-C(10)	111.9(7)
C(2)-C(3)-C(4)	111.6(6)	C(6)-N(4)-C(8)	114.3(5)
C(5)-C(3)-N(2)	110.2(6)		

(b)

Cu . . . N(1^{i})	3.344(5)
Cu . . . C(2^{i})	3.236(6)
S(1) . . . S(3^{ii})	3.512(3)
S(1) . . . S(4^{iii})	3.421(3)
N(3) . . . S(4^{iv})	3.441(5)

Symmetry codes for (a) and (b):

i = 3/2-x, y-½, 3/2-z
ii = 1-x, 1-y, 1-z
iii = 1 + x, y, z
iv = $\bar{x}$, 1-y, 1-z

(c)

N(2)-H(1)	0.78(9)	N(2) . . . Cl	3.121(6)	Cl . . . H(1)	2.47(9)
N(2)-H(1) . . . Cl	141(8)				
N(4)-H(9)	0.77(9)	N(4) . . . Cl	3.181(6)	Cl . . . H(9)	2.43(9)
N(4)-H(9) . . . Cl	167(9)				
N(1)-H(8)	0.73(8)	N(1) . . . Cl^{i}	3.328(5)	Cl^{i} . . . H(8)	2.71(9)
N(1)-H(8) . . . Cl^{i}	145(8)				
N(3)-H(16)	0.83(9)	N(3) . . . S(4^{ii})	3.441(5)	S(4^{ii}) . . . H(16)	2.61(9)
N(3)-H(16) . . . S(4^{ii})	175(8)				

Symmetry codes for (c):

An interesting feature is the asymmetrical position of the thionic groups (see above) and their further distortions under *S*-coordination. In the structure of ss,[18] the N1-C2-S angle of 130.0(2)° is higher than N3-C2-S 124.3(1)° and this can be interpreted in terms of the VSEPR model. In fact, the bondlengths N1-C2 and N3-C2, 1.326(2) and 1.397(3) Å respectively, indicate a higher conjugation of the lone pair of N1 with respect to that of N3 towards C=S: consequently, the higher double bond character of N1-C2 increases the repulsion with the CS bond and enlarges the angle N1-C2-S. The same is true for the thione group at carbon-4, but the angle deformation is in this case very low, in consequence of the presence of the methyl groups. Under coordination, the monocoordinated ligand keeps the angles around the C2(sp^2) practically unchanged, while in the dicoordinated ligand, the 2-thione bond undergoes a remarkable lengthening from 1.648 to 1.673 Å with a consequent increase in repulsion between the two CN bonds, varying the internal angle from 105.7 to 107.7°. *Vice versa,* the changes of the angles around C4(sp^2) are very low in the monocoordinated ligand, and the 4-thione bond becomes practically symmetrical in the dicoordinated one, where the conjugation of the lone pair of N-3 towards the 4-thione bond decreases. The same considerations can be made concerning the distortions of the C=O and C=S bonds in coordinated oxs. Here, the N1-C2-O and N3-C2-O angles differ more than the corresponding angles in ss, since the conjugation of the N-3 lone pair occurs preferably towards the thiocarbonyl group, as demonstrated by the bondlengths of C2-N3 (1.41-1.46 Å) and N3-C4 (1.29-1.35 Å).

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