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Preparation and characterization of polymeric compounds of copper(I) halogenides with Et_4todit = 4,5,6,7-tetrathiocino[1,2-*b*:3,4-*b*′]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione. Crystal and molecular structures of $[Cu(I)(Et_4todit)I]_n$ and $[Cu(I)(Et_4todit)I]_n \cdot n/2Me_2CO$

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Abstract

The complexes $[Cu(II)(Et_4todit)X_2]$ (Et_4todit = title ligand, X = Cl or Br) are reduced at very positive reduction potential. Cyclic voltammograms on their CH_2Cl_2 solutions exhibit a quasi-reversible process with $E_{1/2} = 0.68$ (Cl) and 0.48 (Br) V versus SCE. The reduced species have been chemically prepared by reacting CuX_2 (X = Cl and Br) with Et_4todit in the presence of an appropriate reducing agent. When the reducing agent is hydroquinone in organic solvents, yellow products analyzed as $Cu_2(Et_4todit)X_2$ are obtained by concentration. When the reducing agent is I^- in Me_2CO, the obtained product gives instead an elemental analysis according to $Cu(Et_4todit)I$ (compound **1**), which can also crystallize with $\frac{1}{2}Me_2CO$ (compound **2**). X-ray results on crystals of compounds **1** and **2** have shown that the compounds crystallize in the orthorhombic crystal system; space group $P2_12_12_1$, $Z = 4$, with $a = 19.792(5)$, $b = 14.167(4)$, $c = 8.537(4)$ Å (compound **1**) and $a = 22.088(7)$, $b = 14.414(6)$, $c = 8.807(6)$ Å (compound **2**). The coordination around Cu(I) is trigonal in both compounds and involves the iodide ion and two S atoms of two ligand molecules related by a screw axis. Both metal and ligand are bridging and polymeric chains parallel to *b* are formed. The solvent in **2** produces a different disposition of the adjacent chains and as a consequence interactions of the type S···S between the chains are observed only in this compound. IR spectroscopic results agree with a thionic-sulfur coordination. Moreover in the low-frequency region, bands attributed to the metal–halogen vibrations are observed and their positions suggest that Cl and Br are bridging while the I atom is terminal as shown by X-ray results.

1. Introduction

The spontaneity of the reduction of copper(II) to copper(I) species is largely influenced by the ligand environment at the metal center, by the metal ion stereochemistry and by the nature of the solvent.

It is often observed that thione ligands generate a favourable situation for reduction [1]. The higher affinity of Cu(I) than Cu(II) with such ligands is explained on the basis of the hard and soft acid properties of metal ions. While Cu(II) lies on the borderline between hard and soft, Cu(I) is definitively a soft acid [2].

Also, it is observed that a tetrahedral stereochemistry around the Cu(II) facilitates the reduction to tetrahedral Cu(I) via an electron transfer process, while Cu(II) in a planar arrangement is less likely to be reduced [3].

Moreover it is known that the redox potential of Cu(II) strongly depends on the solvent, being for instance greater in acetonitrile than in other solvents, and for this reason this solvent is largely used to prepare reasonably stable Cu(I) complexes [4].

We have recently synthesized new complexes of Cu(II) [6] with Et_4todit (the title ligand [5]), drawn with the numbering scheme in Fig. 1.

Structural results on $[Cu(Et_4todit)Cl_2]_n \cdot n$THF crystals [6] showed that the coordination at the Cu(II) center is nearer to a square-planar stereochemistry

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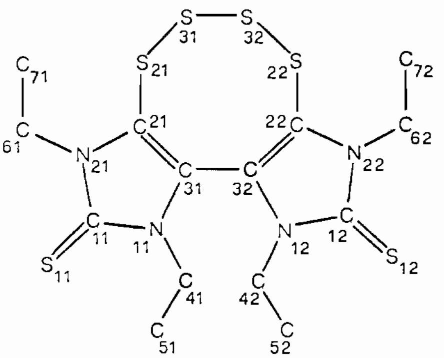


Fig. 1. Atomic numbering scheme of the ligand molecule.

than to a tetrahedral one, and that both metal and ligand are bridging and linear polymers are formed.

In this paper we report a study on the redox properties of $[Cu(Et_4todit)X_2]$, $X=Cl$ and Br, and the isolation and characterization of the reduction products.

Moreover X-ray results on crystals of $[Cu(I)(Et_4todit)I]_n$ and $[Cu(I)(Et_4todit)I]_n \cdot n/2Me_2CO$ are reported.

Experimental

Syntheses

The synthesis of Et_4todit has already been reported [5].

$Cu_2(Et_4todit)X_2$

Anhydrous CuX_2 ($X=Cl$ and Br) was dissolved in THF containing hydroquinone (Carlo Erba R.P.E.), and was added to a THF solution of the ligand in 1:1 ratio. The resulting red– (Cl) or green –brown (Br) mixture was warmed until yellow. The solution was allowed to stand at room temperature in a beaker and after a few days of slow evaporation yellow, air-stable microcrystals separated.

Anal. Calc. for $Cu_2(Et_4todit)Cl_2 \cdot \frac{1}{2}THF$: C, 28.65; H, 3.61; N, 8.35; S, 28.68. Found: C, 28.8; H, 3.6; N, 8.2; S, 28.6%. Calc. for $Cu_2(Et_4todit)Br_2$: C, 23.24; H, 2.79; N, 7.74; S, 26.59. Found: C, 23.0; H, 2.8; N, 7.0; S, 24.9%.

$Cu(Et_4todit)I$

Anhydrous $CuCl_2$ was dissolved in Me_2CO and added to a ligand solution in equimolar amounts. A Me_2CO solution of tetrabutylammonium iodide (Bu_4NI) was gradually added to the resulting red–brown solution, which became orange–yellow. A spectrophotometric titration performed at 552 nm, where only the Cu(II) complex absorbs, showed a decrease of the absorbance with increasing I^- up to 1:1 ratio. However to obtain the product the overall reaction requires two I^- ions according to the following scheme:

$$Cu(Et_4todit)Cl_2 + 2I^- \longrightarrow Cu(Et_4todit)I + \tfrac{1}{2}I_2 + 2Cl^-$$

After few days of slow evaporation, orange–yellow crystals separated from the solution. Crystals having different elemental analysis have been collected in different crystallizations.

Anal. Calc. for $Cu(Et_4todit)I$ (**1**): (Found) C, 26.81; H, 3.19; N, 8.45. Found: C, 27.1; H, 3.2; N, 8.9%. Calc. for $Cu(Et_4todit)I \cdot \frac{1}{2}Me_2CO$ (**2**): C, 28.37; H, 3.53; N, 8.54; S, 29.32. Found: C, 27.5; H, 3.3; N, 8.8; S, 30.7%.

Analyses were performed at the Dipartimento di Chimica dell'Universita' di Modena.

Electrochemical measurements

The electrochemical experiments were performed at room temperature in CH_2Cl_2 (spectroscopic grade), dried over molecular sieves, under O_2-free conditions, on a computer controlled EG&G potentiostat-galvanostat model 273. A three-electrode system was used in which the working electrode was glassy carbon and the counter electrode platinum with a standard calomel(SCE) electrode as reference. The solutions were 1.0×10^{-3} mol dm^{-3} in the complex and tetrabutylammonium perchlorate (TBAP, 0.1 mol dm^{-3}, Fluka Chemika) was used as supporting electrolyte. The measurements were performed under argon. The best combination of experimental conditions (working electrode, scan rates, solvent) was determined by preliminary experiments.

Spectroscopic measurements

Electronic spectra were performed on a UV–Vis spectrophotometer, Varian model Cary 2300. IR spectra were recorded as KBr pellets in the 4000–400 cm^{-1} range on a Perkin-Elmer model 983 spectrophotometer, and the low frequency spectra were recorded in the 400–50 cm^{-1} range as polyethylene pellets on a Bruker model 113r FT-IR spectrophotometer at the Dipartimento di Chimica dell'Universita' di Modena.

Collection and reduction of X-ray data

The representative complexes studied by X-ray analysis were $[Cu(Et_4todit)I]_n$ (**1**) and $[Cu(Et_4todit)I]_n \cdot n/2Me_2CO$ (**2**). The values of the cell parameters and the experimental conditions used during the structure determinations for both compounds are reported in Table 1. The lattice parameters were obtained from the refinement of angles of accurately centered reflections. The check of the standard reflections showed no significant decrease. Intensity data were corrected for Lorentz polarization

TABLE 1. Experimental data for the crystallographic analyses

Compound	**1**	**2**
Formula	$C_{14}H_{20}CuIN_4S_6$	$C_{14}H_{20}CuIN_4S_6\cdot\frac{1}{2}C_3H_6O$
Formula weight	627.149	656.189
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å	19.792(5)	22.088(7)
b (Å)	14.167(4)	14.414(6)
c (Å)	8.537(4)	8.807(6)
V (Å^3)	2394(1)	2804(2)
Z	4	4
D_c (Mg m^{-3})	1.740	1.554
F(000)	1240	1304
Temperature (K)	295	295
Crystal size (mm)	0.23×0.23×0.38	0.06×0.06×0.20
Diffractometer	Siemens AED	Siemens AED
μ (Mo Kα) (cm^{-1})	27.02	141.05
Scan type	$\theta/2\theta$	$\theta/2\theta$
Scan speed (° min^{-1})	2.5–12	2.5–12
Scan width (°)	1.10+0.346 tgθ	1.20+0.142 tgθ
Radiation	Mo Kα ($\bar{\lambda}$=0.71073 Å)	Cu Kα ($\bar{\lambda}$=1.541838 Å)
θ range	3–27	3–60
Reflections for lattice parameters: no., θ range	30, 8–18	29, 11–28
Standard reflections measured after every 50	334	511
Data collected	*h,k,l*	*h,k,l*
No. measured reflections	2334	1841
Condition for observed reflections	$I \geqslant 2\sigma(I)$	$I \geqslant 2\sigma(I)$
No. reflections used in refinement	1429	776
No. refined parameters	236	162
R^a ($R_w{}^a$)	3.48 (4.14)	4.57 (6.18)
k,g ($w=k/\sigma^2(F_o)+gF^2{}_o$)	0.3339, 0.002081	0.1064, 0.026604
Min./Max. height in final $\Delta\rho$ (e Å^{-3})	−0.48/0.52	−0.34/0.41

[a] $R=\Sigma|\Delta F|/\Sigma|F_o|$; $R_w=[\Sigma w(\Delta F)^2/\Sigma wF_o{}^2]^{1/2}$.

factor, and only for compound **2** for absorption (maximum and minimum values 1.11137, 0.88088) and extinction (maximum and minimum values 1.03478, 0.92284) following the empirical method of Walker and Stuart [7] by using the ABSORB [8] program.

Solution and refinement of the structures

Some peaks of the Patterson map allowed the localization of the Cu and I atoms, the subsequent Fourier syntheses revealed the remaining non-hydrogen atoms. The structures were solved by full-matrix least-squares using anisotropic thermal parameters for all the non-hydrogen atoms in **1** and only for I, Cu and S atoms in **2**. The coordinates of the hydrogen atoms placed at their geometrically calculated positions were not refined, but introduced in the final structure factor calculation with fixed isotropic thermal parameter (U=0.1912 and 0.1667 Å^2 for **1** and **2**, respectively). To define the absolute configuration of the atomic arrangement in the structure, two complete refinements corresponding to the two enantiomers were carried out and the values $R_w(xyz)=0.0414$, $R_w(\bar{x}\bar{y}\bar{z})=0.0487$ and $R_w(xyz)=0.0714$, $R_w(\bar{x}\bar{y}\bar{z})=0.1127$ for compounds **1** and **2**, respectively were reached. By applying the Hamilton's significance test [9], when compound **1** was considered, the ratio $R_w(\bar{x}\bar{y}\bar{z})/R_w(xyz)$ was calculated to be 1.1763, while the theoretical value $R_{1,1193,0.005}=1.003$, for 1429 independent F_os and 236 variables, at the half-percent confidence level. The corresponding values for compound **2** were: $R_w(\bar{x}\bar{y}\bar{z})/R_w(xyz)=1.5784$; $R_{1,614,0.005}=1.0064$, the theoretical value for 776 independent F_os and 162 variables at the half-percent confidence level. So, the *xyz* atomic coordinates of Table 2 correspond to the correct absolute configuration. In **2** a solvent molecule with s.o.f.=10.5 was clearly localized and the best result was obtained refining it with the constraints: C–O 1.25; C–C 1.45 Å. Scattering factors were taken from ref. 10. Data reduction, structure solution and refinement were carried out on a CRAY X-MP/12 computer at the Centro di Calcolo dell'Italia Nord-Orientale, Bologna and on a GOULD-SEL 32/77 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, by using the SHELX-76 system of computer

TABLE 2. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^4$)^a

	Compound 1				Compound 2			
	x/a	y/b	z/c	$U_{eq}{}^a$	x/a	y/b	z/c	$U_{eq}{}^a$
Cu	748(1)	4812(1)	24(2)	548(5)	4646(2)	2079(3)	5062(4)	567(15)
I	458(1)	5006(1)	2853(1)	910(4)	5430(1)	1945(2)	2992(3)	944(10)
S(11)	1536(1)	3772(2)	−723(3)	456(9)	3720(3)	1470(6)	4851(8)	547(27)
S(21)	2384(1)	3208(2)	5311(4)	487(10)	3522(3)	1549(5)	−1362(8)	501(28)
S(31)	3220(1)	2348(2)	5082(5)	614(12)	2632(3)	1130(5)	−1596(8)	536(27)
S(12)	−184(1)	600(2)	6817(3)	592(11)	5173(3)	−2085(5)	−2178(8)	509(25)
S(22)	2347(1)	452(2)	4253(4)	461(10)	2856(3)	−1062(5)	−687(8)	467(26)
S(32)	2930(2)	1090(2)	5971(4)	606(12)	2653(3)	−178(5)	−2489(7)	490(28)
N(11)	1284(3)	2566(5)	1685(9)	270(27)	3964(10)	336(16)	2487(26)	548(72)
N(21)	2063(4)	3582(5)	2207(10)	346(28)	3593(9)	1671(13)	1782(22)	375(56)
N(12)	592(4)	1646(5)	4822(10)	341(25)	4603(9)	−754(13)	−466(19)	325(52)
N(22)	1088(4)	377(6)	5631(10)	397(30)	3978(10)	−1679(14)	−1583(23)	509(63)
C(11)	1634(5)	3304(7)	1090(12)	317(34)	3759(10)	1152(17)	2992(30)	356(66)
C(21)	1982(5)	3034(7)	3540(12)	333(33)	3674(10)	1139(16)	475(25)	285(64)
C(31)	1498(4)	2393(6)	3199(11)	279(31)	3919(11)	341(19)	891(30)	421(75)
C(41)	799(5)	1977(7)	799(13)	405(35)	4042(15)	−506(23)	3416(38)	800(107)
C(51)	1173(7)	1255(9)	−182(17)	759(56)	4718(18)	−485(26)	4041(43)	1075(136)
C(61)	2505(5)	4404(7)	2070(15)	506(39)	3350(13)	2609(19)	1908(34)	599(87)
C(71)	3168(6)	4144(10)	1286(18)	750(53)	3841(15)	3338(22)	1637(38)	937(117)
C(12)	508(5)	872(8)	5744(12)	393(36)	4575(12)	−1491(18)	−1362(28)	478(75)
C(22)	1547(5)	856(6)	4677(12)	354(29)	3666(11)	−1075(16)	−789(26)	307(67)
C(32)	1239(4)	1623(7)	4177(11)	280(32)	4041(12)	−487(18)	−56(31)	447(78)
C(42)	89(5)	2406(7)	4681(15)	498(41)	5183(12)	−287(18)	−62(33)	518(79)
C(52)	124(7)	3073(10)	6094(17)	764(57)	5356(16)	429(23)	−1273(36)	899(106)
C(62)	1187(6)	−556(8)	6358(15)	575(43)	3728(14)	−2608(20)	−2264(35)	681(94)
C(72)	1020(8)	−1336(8)	5239(21)	909(69)	3598(22)	−2395(31)	−3861(46)	1478(175)
O(1S)					1760(42)	5791(59)	2520(139)	
C(1s)					2375(31)	4567(39)	1806(86)	
C(2s)					2291(39)	5548(45)	2163(120)	
C(3s)					2657(49)	6225(52)	1335(144)	

${}^aU_{eq}=\frac{1}{3}$trace $\tilde{U}$.

program [11] and the programs PARST [12] and PLUTO [13]. Bond distances and angles are in Table 3. See also 'Supplementary material'.

Results and discussion

A typical cyclic voltammogram of [Cu(Et$_4$todit)Cl$_2$] in CH_2Cl_2 solution, using TBAP (tetrabutylammonium perchlorate) as supporting electrolyte is shown in Fig. 2 and electrochemical data are summarized in Table 4. Both Cl and Br complexes are characterized by very positive reduction potentials, and exhibit a redox process at $E_{1/2}=0.68$ and 0.48 V (versus SCE), respectively, with the ratio I_a/I_c (calculated according to ref. 14) being approximately equal to one and E being >59 mV and increasing with increasing scan rate, as expected for a quasi-reversible process [15]. The scanning in negative direction within the -0.40 V limit does not show any additional process.

The scanning in positive direction is limited by the non-reversible waves related to the oxidation process of Br^- (~ 0.8 V) and Cl^- (~ 1.2 V).

The redox activity of these compounds can be exploited by reactions with selective reducing agents. It is sufficient to use commercial THF solvent stabilized with 0.05% hydroquinone (Carlo Erba RPE), and to warm the solutions of the [Cu(Et$_4$todit)X$_2$] complexes, prepared *in situ* for solubility reasons, to obtain a change in the colour of the solutions from red–brown (X = Cl) and green–brown (X = Br) to yellow. On standing yellow micro-crystals that analyzed as [Cu$_2$(Et$_4$todit)X$_2$] separated out. These crystals are stable on exposure to air and very slightly soluble in most solvents.

However, the reduction of [Cu(Et$_4$todit)Cl$_2$] with I^- gives as the final product orange–yellow crystals that analyse as [Cu(Et$_4$todit)I]. In both cases molecular rearrangement occurs in order to form stable copper(I) species.

TABLE 3. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

	Compound **1**[a]		Compound **2**[b]	
Coordination around metal				
Cu–I	2.498(2)		2.522(5)	
Cu–S(11)	2.238(3)		2.234(8)	
Cu–S(12′)	2.228(3)		2.255(8)	
I–Cu–S(11)	120.5(1)		122.6(3)	
I–Cu–S(12′)	120.8(1)		121.1(3)	
S(11)–Cu–S(12′)	118.6(1)		116.2(3)	
Ligand molecule				
	$i=1, j=2$	$i=2, j=1$	$i=1, j=2$	$i=2, j=1$
S(2i)–S(3i)	2.064(3)	2.074(5)	2.067(10)	2.084(10)
S(31)–S(32)	2.020(4)		2.043(10)	
S(1i)–C(1i)	1.69(1)	1.69(1)	1.70(3)	1.73(3)
S(2i)–C(2i)	1.73(1)	1.72(1)	1.75(2)	1.79(3)
N(1i)–C(1i)	1.35(1)	1.36(1)	1.34(3)	1.32(3)
N(1i)–C(3i)	1.38(1)	1.39(1)	1.41(4)	1.35(3)
N(1i)–C(4i)	1.48(1)	1.47(1)	1.47(4)	1.49(3)
N(2i)–C(1i)	1.34(1)	1.35(1)	1.35(3)	1.36(3)
N(2i)–C(2i)	1.39(1)	1.40(1)	1.39(3)	1.31(3)
N(2i)–C(6i)	1.46(1)	1.47(1)	1.46(3)	1.57(4)
C(2i)–C(3i)	1.35(1)	1.32(1)	1.32(4)	1.35(4)
C(31)–C(32)	1.47(1)		1.48(4)	
C(4i)–C(5i)	1.52(2)	1.53(2)	1.59(5)	1.53(4)
C(6i)–C(7i)	1.52(2)	1.50(2)	1.53(4)	1.47(5)
Cu–S(1i)–C(1i)	94.4(4)	97.9(4)	98.0(9)	93.2(9)
S(3i)–S(2i)–C(2i)	101.7(4)	102.6(4)	100.1(8)	100.6(8)
S(2i)–S(3i)–S(3j)	104.9(2)	106.1(2)	106.6(4)	106.0(4)
C(1i)–N(1i)–C(3i)	109.3(7)	108.8(8)	107.7(2.2)	110.2(2.1)
C(1i)–N(1i)–C(4i)	125.2(8)	123.7(8)	125.4(2.4)	123.0(2.0)
C(3i)–N(1i)–C(4i)	125.2(7)	127.3(8)	124.5(2.4)	126.8(2.0)
C(1i)–N(2i)–C(2i)	110.3(8)	110.1(8)	108.1(1.9)	107.5(2.1)
C(1i)–N(2i)–C(6i)	123.9(9)	123.3(9)	123.5(2.1)	124.5(2.2)
C(2i)–N(2i)–C(6i)	125.5(9)	126.5(8)	128.3(2.0)	125.8(2.2)
S(1i)–C(1i)–N(1i)	125.9(8)	126.6(8)	125.0(2.1)	127.5(2.0)
S(1i)–C(1i)–N(2i)	127.5(8)	127.5(8)	126.5(1.9)	125.6(1.9)
N(1i)–C(1i)–N(2i)	106.6(8)	105.9(9)	108.4(2.2)	106.9(2.2)
S(2i)–C(2i)–N(2i)	125.8(7)	124.0(7)	123.5(1.7)	123.9(1.9)
S(2i)–C(2i)–C(3i)	127.7(8)	129.2(8)	128.8(1.9)	125.6(2.0)
N(2i)–C(2i)–C(3i)	106.3(9)	106.8(8)	107.6(2.1)	110.4(2.2)
N(1i)–C(3i)–C(2i)	107.4(8)	108.4(8)	108.0(2.3)	104.9(2.2)
N(1i)–C(3i)–C(3j)	123.9(8)	121.9(7)	123.0(2.3)	123.3(2.3)
C(2i)–C(3i)–C(3j)	128.7(9)	129.5(8)	128.3(2.4)	131.6(2.4)
N(1i)–C(4i)–C(5i)	110.3(9)	110.9(9)	106.6(2.6)	110.6(2.2)
N(2i)–C(6i)–C(7i)	111.1(9)	111.3(1.1)	111.4(2.3)	104.9(2.6)

[a](′): $-x, \frac{1}{2}+y, \frac{1}{2}-z$. [b](′): $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

The most significative IR bands are listed in Table 5. Modest shifts of ν(CN) to higher and of ν(CS) to lower wavenumbers are observed. Even though these vibrations are strongly coupled with other modes in thioamide ligands [16], the observed behaviour can be indicative of an S-thioamide binding. X-ray results on $[\mathrm{Cu(Et_4todit)I}]_n$ (this work), $[\mathrm{Cu(Et_4todit)Cl_2}]_n \cdot n\mathrm{THF}$ [6], $[\mathrm{Cd(Et_4todit)Cl_2}]_n$ [17] and $(\mathrm{Et_4todit}) \cdot 2\mathrm{I_2}$ [18] crystals, where similar shifts of IR bands under discussion were observed, confirmed the thione coordination. Also, they showed that the bond distances of the free ligand are slightly modified on coordination, thus explaining the observed modest shifts of the IR bands. In the low frequencies region new bands appear on coordination. All complexes have absorptions near 270 cm^{-1}, which are likely due to ν(CuS) [19] and, while the Cl and Br derivatives have a single band, the I one shows two absorptions. Inversely in the Cu–halogen vibrations region two absorptions can be attributed to

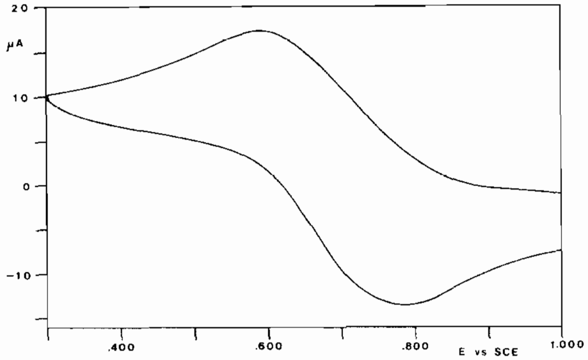
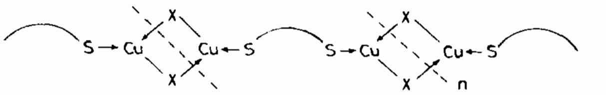


Fig. 2. Cyclic voltammogram recorded at a glassy-carbon electrode on deaerated CH_2Cl_2 solutions containing TBAP (0.1 mol dm^{-3}) and $Cu(Et_4todit)Cl_2$ (1.0×10^{-3} mol dm^{-3}), scan rate 200 mV.

TABLE 4. Significant electrochemical parameters for the redox change Cu(II)–Cu(I) of the complexes $[Cu(Et_4todit)X_2]$ (X = Cl, Br) in CH_2Cl_2/TBAP

Complex	$E_{1/2}$ (V, vs. SCE)	E (mV)	I_a/I_c	Scan rate (mV s^{-1})
$[Cu(Et_4todit)Cl_2]$	0.68	130	1.0	20
	0.69	150	1.1	60
	0.69	165	1.1	100
	0.69	178	1.2	150
	0.69	191	1.1	200
$[Cu(Et_4todit)Br_2]$	0.48	113	1.0	20
	0.48	152	1.1	60
	0.47	190	1.1	100

CuCl and CuBr vibrations while a single band appears in the CuI complex. Moreover the low values of the ν(CuCl) and ν(CuBr) bands suggest halogen bridging, and are in accordance with previously reported values [20]. Given the structure of the ligand (see 'Introduction'), which can act as an S,S-bridging ligand, the IR and analytical results, we propose the following polymeric structure for$[Cu_2(Et_4todit)X_2]$, X = Cl and Br.



Surprisingly the iodide derivative does not show a bridging halogen atom, as suggested by the IR low frequency spectra, and demonstrated by X-ray results reported below.

The coordination around Cu is trigonal in both compounds (Figs. 3 and 4) and involves the iodide ion and two S atoms of the thionic group of two ligand molecules related by a screw axis. As the metal and ligand are bridging, polymeric chains parallel to *b* are formed, as already found in $[Cu(Et_4todit)Cl_2]_n \cdot n$THF [6], while in the corresponding $[Cd(Et_4todit)Cl_2]_n$ [17], the whole structure consists of a three-dimensional network as a Cl anion is also bridging.

The solvent produces a different disposition of the adjacent chains: in fact they are mutually slipped along *b* in compound **1** with respect to those of compound **2**. Consequently interactions of the type S...S between the chains are observed only in **2** (S(11)...S(21)(x, y, $1+z$) 3.366(10); S(22)...S(32)-($\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$) 3.520(10); S(11)...S(22)($\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$) 3.562(10) Å). The other contacts between the chains are of the type: I...CH_2(or CH_3)$_{ethyl}$, S...CH_2(or CH_3)$_{ethyl}$, CH_2(or CH_3)$_{ethyl}$...CH_2(or CH_3)$_{ethyl}$. The Cu–I distance (2.498(2) and 2.522(5) Å for **1** and **2**, respectively) and the Cu–S distances (2.238(3), 2.228(3) Å and 2.234(8), 2.255(8) Å for **1** and **2**, respectively), are appropriate for trigonally coordinated Cu(I). The metal is −0.046(2) and 0.049(4) Å out of the plane containing the coordinated atoms in **1** and **2**, respectively. The structural data of the ligand molecule are similar to those observed in the uncomplexed molecule [5], in its bis-diiodine adduct [18] and in its complexes with $CuCl_2$ and $CdCl_2$. The analogies comprise the presence of a pseudo two-fold axis, the orientation of the two imidazoline rings (N(11)–C(31)–C(32)–N(12) −73(1) and −82(3)° for **1** and **2**, respectively), which is determined by the perpendicular and mutual opposite disposition of the ethyl groups with respect to the corresponding ring plane, and the chair conformation of the eight-membered ring.

TABLE 5. Selected IR absorptions of ligand and complexes, ν(cm^{-1})

Compound	ν(CN)^a	ν(CS)^a	ν(CuX)^b	ν(CuS)^b
Et_4todit	1435s	821m 810ms		
$[Cu_2(Et_4todit)Cl_2]_n$	1446ms	810w	273s 222m	264m
$[Cu_2(Et_4todit)Br_2]_n$	1443ms	810w	199m 164s	266m
$[Cu(Et_4todit)I]_n$	1440ms	805w	168s	278ms 258ms

^{a}KBr pellets. ^{b}Polyethylene pellets.

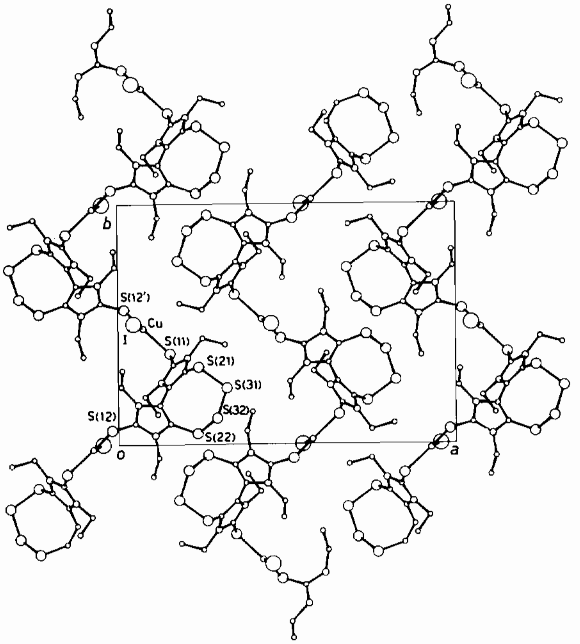


Fig. 3. Projection of the structure $[Cu(Et_4todit)I]_n$ (1) along [001].

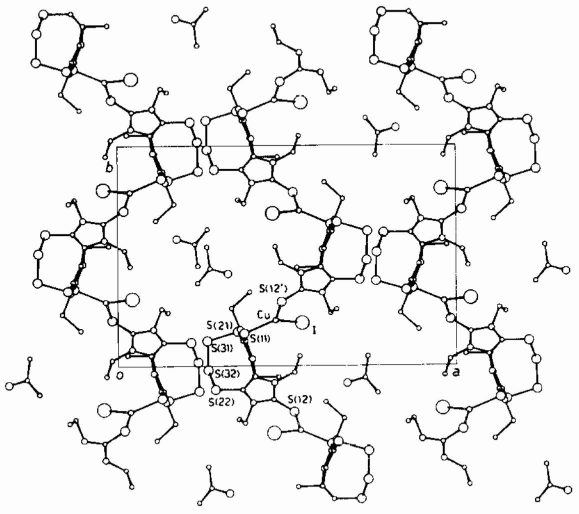


Fig. 4. Projection of the structure $[Cu(Et_4todit)I]_n \cdot n/2Me_2CO$ (2) along [001].

Supplementary material

Additional data available from the Cambridge Crystallographic Data Center comprises H atom coordinates, thermal parameters, and observed and calculated structure factors.

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