Inorganica Chimica Acta, 204 (1993) 9–13

Synthetic, structural and spectroscopic studies of the donating properties of sulfur-rich molecules: X-ray structure of [copper(I)chloride-(1,3-dithiolane-2-thione)(2/1)]$_n$

Francesco Bigoli, M. Angela Pellinghelli
Istituto di Chimica Generale ed Inorganica dell'Università, Centro di Studio per la Strutturistica Diffrattometrica del CNR, viale delle Scienze 78, I-43100 Parma (Italy)

Paola Deplano*, M. Laura Mercuri and Emanuele F. Trogu
Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche dell'Università, via Ospedale 72, I-09124 Cagliari (Italy)

(Received July 3, 1992)

Abstract

The preparation of the following compounds is reported: $Cu_2(dtt)Cl_2$, Cu(dtt)X (X = Cl, Br, I; dtt = 1,3-dithiolane-2-thione). The compounds are diamagnetic and stable to aerial oxidation at room temperature. IR spectroscopic results suggest that the thione-sulfur is involved in the coordination, and that a higher donation of this atom occur in $Cu_2(dtt)Cl_2$. Crystals of $[Cu_2(dtt)Cl_2]_n$ are monoclinic, space group $P2_1/c$ with $a=10.970(6)$, $b=13.274(6)$, $c=5.952(5)$ Å, $\beta=92.71(2)°$, $Z=4$. The structure consists of two distinct polymeric chains ···Cu–Cl–Cu–Cl··· held together by bridging thionic sulfur atoms of the ligand. The Cu atoms in the two chains are different, having a distorted tetrahedral and trigonal coordination, respectively.

Introduction

It is known that sulfur donors are soft bases and form stable complexes with soft acids. Consequently they may generate a favourable thermodynamic situation for the spontaneity of reduction of Cu(II) to Cu(I), Cu(I) being a soft acid while Cu(II) is a borderline hard acid. Moreover these ligands can coordinate with a combination of terminal or bridging sulfur, and when halides are involved in the coordination, they can also act as terminal or bridging ligands, giving rise to a variety of mononuclear or polynuclear complexes [1].

We are extensively investigating the donating properties of potentially polyfunctional thione ligands towards I_2 [2] and transition metals. In the case of a donor having two thione groups forced at a very distant position and of metal halides, new ligand- and halogen-bridged polymeric complexes having a three-dimensional structure [3], and ligand-bridged polymers having chain structures have been characterized [4, 5].

The donor under investigation in this paper is 1,3-dithiolane-2-thione (dtt), which is a potentially polyfunctional ligand through either the exo- or/and endocyclic sulfur atoms [6] and it has been allowed to react with CuX_2 (X=Cl and Br).

Experimental

Materials and methods

The starting materials and solvents were supplied by the Aldrich Chemical Company. THF was +99%, inhibited with 0.025% buthylated hydroxytoluene. In a typical reaction anhydrous CuX_2 (2.0 mmol) (X=Cl or Br) was allowed to react with dtt (4.0 mmol) in refluxing THF for 20 min. The solution turned from yellow to orange–red and on standing orange to dark brown crystals precipitated. The products were washed with MeOH and dried. These products give analytical results according to the following formulations: $Cu_2(dtt)Cl_2$ and Cu(dtt)Br. *Anal.* Found: C, 10.8; H, 1.3; S, 28.1 Calc. for $C_3H_4S_3Cu_2Cl_2$: C, 10.78; H, 1.21; S, 28.78%. Found: C, 12.8; H, 1.4; S, 35.6 Calc. for $C_3H_4S_3CuBr$: C, 12.88; H, 1.44; S, 34.40%. In the case of the Cl derivative a second darker fraction was obtained on further concentration of the mother solution. Analytical results suggest the Cu(dtt)Cl formulation. *Anal.* Found C, 15.2; H, 1.7; S, 41.5. Calc. for $C_3H_4S_3CuCl$: C, 15.32; H, 1.71; S, 40.89%. As yet

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

the oxidation product has not been identified. Cu(dtt)I was obtained by addition of Bu_4NI to a $CuCl_2$ and dtt mixture in refluxing THF. The solution turned from red to orange and on addition of MeOH an orange–brown crystalline product was obtained. This solid on standing loses some ligand, and analytical results give a ratio dtt/CuI lower than 1 (0.8). However IR spectra on freshly prepared samples are in accordance with those of the other Cu(dtt)X derivatives.

Analyses were performed by means of a Carlo Erba CHNS-O elemental analyzer model EA1108. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. UV–Vis spectra were recorded on a Cary 5 spectrophotometer. Magnetic susceptibilities were measured by the Faraday method on an Oxford Instruments magnetometer. Conductance measurements were obtained using an Analytical Control Model 120 microprocessor conductivity meter.

X-ray data collection and refinement

Crystal data and the most relevant parameters adopted in the X-ray data collection and refinement are reported in Table 1.

TABLE 1. Experimental data for the X-ray analysis

Formula	$C_3H_4Cl_2Cu_2S_3$
M_r	334.243
Space group	$P2_1/c$
a (Å)	10.970(6)
b (Å)	13.274(6)
c (Å)	5.952(5)
β (°)	92.71(2)
V (Å^3)	851.5(9)
Z	4
D_c (Mg m^{-3})	2.607
Crystal data: radiation, wavelength	Cu Kα, 1.541838
Reflections for lattice parameters	
No.	30
θ Range (°)	21/40
$F(000)$	648
Temperature (K)	295
Crystal size (mm)	$0.05 \times 0.16 \times 0.34$
Diffractometer	SIEMENS-AED
μ (cm^{-1})	182.11
Scan speed (° min^{-1})	2.5–12
Scan width (°)	$1.20 + 0.142 \tan\theta$
θ Range for intensity collection	3/70
Data collected	$\pm h\ k\ l$
Standard reflection	−6 4 2
Scan mode	θ–2θ
No. measured reflections	1875
Condition for observed reflections	$I \geqslant 2\sigma(I)$
No. of observed reflections (N)	1316
Min./max. height in final $\Delta\rho$ map (e Å^{-3})	−2.39/1.25
No. of refined parameters (P)	92
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0651
$R_w = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{1/2}$	0.0935
k, g ($w = k[\sigma^2(F_o) + gF_o^2]$)	1.5669, 0.003178

TABLE 2. Fractional atomic coordinates ($\times 10^4$) and thermal parameters (Å$^2 \times 10^4$) of non-hydrogen atoms

	x/a	y/b	z/c	U_{eq}^{a}
Cu(1)	8055(1)	2715(1)	1509(2)	506(5)
Cu(2)	4993(1)	3036(2)	5318(3)	739(6)
Cl(1)	9182(2)	3415(1)	−1199(3)	391(5)
Cl(2)	4186(2)	3361(2)	8600(3)	469(6)
S(1)	6678(2)	3515(1)	3683(3)	376(6)
S(2)	8553(2)	5133(1)	3606(3)	321(5)
S(3)	6650(2)	5216(1)	6919(3)	388(6)
C(1)	7285(5)	4609(5)	4699(12)	275(18)
C(2)	8516(7)	6283(5)	5235(14)	376(24)
C(3)	7974(6)	6035(6)	7467(13)	398(25)

$^a U_{eq} = 1/3$ trace $\tilde{U}$.

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

Cu(1)–Cl(1)	2.264(2)	S(1)–C(1)	1.69(7)
Cu(1)–Cl(1^i)	2.331(2)	S(2)–C(1)	1.69(6)
Cu(1)–S(1)	2.279(2)	S(3)–C(1)	1.72(7)
Cu(1)–S(1^{ii})	2.732(2)	S(2)–C(2)	1.81(7)
Cu(2)–Cl(2)	2.218(3)	S(3)–C(3)	1.81(7)
Cu(2)–Cl(2^{ii})	2.271(3)	C(2)–C(3)	1.51(11)
Cu(2)–S(1)	2.196(3)		
Cl(1)–Cu(1)–Cl(1^i)	113.5(1)	Cu(1)–S(1)–Cu(2)	133.8(1)
Cl(1)–Cu(1)–S(1)	126.8(1)	Cu(1)–S(1)–C(1)	110.5(2)
Cl(1)–Cu(1)–S(1^{ii})	95.8(1)	Cu(1^i)–S(1)–Cu(2)	89.5(1)
Cl(1^i)–Cu(1)–S(1)	107.7(1)	Cu(1^i)–S(1)–C(1)	95.9(2)
Cl(1^i)–Cu(1)–S(1^{ii})	103.2(1)	Cu(2)–S(1)–C(1)	113.9(3)
S(1)–Cu(1)–S(1^{ii})	106.1(1)	S(1)–C(1)–S(2)	121.4(4)
Cl(2)–Cu(2)–Cl(2^{ii})	113.4(1)	S(1)–C(1)–S(3)	121.0(4)
Cl(2)–Cu(2)–S(1)	134.5(1)	S(2)–C(1)–S(3)	117.5(4)
Cl(2^{ii})–Cu(2)–S(1)	110.2(1)	C(1)–S(2)–C(2)	95.9(4)
Cu(1)–Cl(1)–Cu(1^{ii})	82.5(1)	C(1)–S(3)–C(3)	94.6(3)
Cu(2)–Cl(2)–Cu(2^i)	94.6(1)	S(2)–C(2)–C(3)	107.8(5)
Cu(1)–S(1)–Cu(1^i)	73.8(1)	S(3)–C(3)–C(2)	107.9(5)

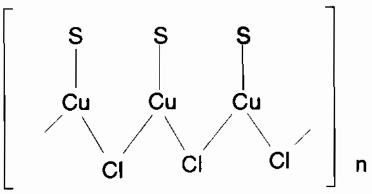
^{a}Key to symmetry operations: (^{i}): x, $1/2-y$, $1/2+z$; (^{ii}): x, $1/2-y$, $z-1/2$.

The lattice parameters were obtained by least-squares analysis of the setting angles of 30 carefully centered reflections chosen from diverse regions of reciprocal spaces. The check of the standard reflection showed no significant decrease. Intensity data were corrected for Lorentz and polarization effects and for absorption (maximum and minimum values, 1.3223 and 0.7202) and extinction (maximum and minimum values, 1.1801 and 0.9431) following the empirical method of Walker and Stuart [7] by using the ABSORB [8] program at the end of the isotropic refinement. The structure was solved by Patterson and Fourier methods and refined by full matrix least-squares using anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms, placed at their geometrically calculated positions (d(C–H) = 1.08 Å) were refined riding on the corresponding atoms with a unique refined isotropic thermal parameter ($U = 0.0623(147)$ Å^2). Scattering factors were taken from ref. 9.

The calculations were performed on the GOULD-SEL 32/77 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, by using the SHELX-76 system of computer program [10] and the programs PARST [11] and PLUTO [12]. Final atomic coordinates for the non-hydrogen atoms are given in Table 2, bond distances and angles are in Table 3.

Results and discussion

As described in 'Experimental' by reacting CuX_2 (X = Cl and Br) with dtt in refluxing THF, the crystalline compounds $[Cu_2(dtt)Cl_2]_n$ (red–brown), Cu(dtt)Cl and Cu(dtt)Br are obtained. Cu(dtt)I is prepared by addition of Bu_4NI to a $CuCl_2$/dtt mixture in refluxing THF. The colour of the Cu(dtt)X complexes varies from orange to dark–brown, depending on the size of crystals. Magnetic susceptibilities show that the compounds are diamagnetic, supporting that they are Cu(I) derivatives. The complexes are air stable (a partial decomposition of the Cu(dtt)I is observed), and are soluble with dissociation in CH_3CN. In fact the UV–Vis spectra of their solutions show the characteristic free-ligand absorptions. The molar conductances of 10^{-3} mol dm^{-3} CH_3CN solutions of the complexes, ranging between 67 and 80 Ω^{-1} cm^2 mol^{-1}, (value expected for 1:1 electrolytes [13]: 120–160 Ω^{-1} cm^2 mol^{-1}) suggest that partial liberation of the halide occurs. The principal IR bands with the corresponding assignments [14] are reported in Table 4. The very strong band found in the free ligand at 1065 cm^{-1}, due to ν (C=S) shows a shift to lower wavenumbers in the complexes. A simultaneous shift of the bands mainly attributed to ν_{as}(SCS) and ν_s(SCS) to higher wavenumbers is observed. These results suggest that a lowering of the exocyclic C=S and a simultaneous increase of the C–S endocyclic bond orders as a consequence of S–thione coordination occur [6]. The shift of these bands is much higher in $[Cu_2(dtt)Cl_2]_n$ than in the other complexes, indicating a higher donation of the thione-sulfur. The stoichiometry of this complex and IR findings suggest, and X-ray results confirm, that thione-sulfur is bridging among Cu centres. The observed shifts of the above mentioned bands of the Cu(dtt)X derivatives are instead very similar to those of $Cd(dtt)Cl_2$ [6], where the ligand is terminal. These complexes could either be two-coordinate monomers with terminal halogen and ligand, or more plausibly, three-coordinate halogen-bridging polymers. Unfortunately, the low IR region does not allow unambiguous attributions. In fact the bands of the complexes are obscured by the ligand bands. Only in the case of the chloride complexes some absorptions are strongly reinforced. In the case of Cu(dtt)Cl the reinforced bands, which are broad, fall at 297 and 218 cm^{-1}. We tentatively suggest that these bands could be attributed to the CuCl vibrations in a trigonal planar arrangement of the type (S is the thionic sulfur of the ligand)



The band at 300 cm^{-1} disappears in the spectrum of $[Cu_2(dtt)Cl_2]_n$, while a band at ≈ 270 cm^{-1} is strongly reinforced. This band may also be attributed to CuCl vibrations. These values could seem too high for bridging CuCl. However structural results on $[Cu_2(dtt)Cl_2]_n$ show that short CuCl distances comparable with those generally found in terminal CuCl are observed [15]. The short CuCl distances are presumably a reflection of

TABLE 4. IR spectral data for dtt and its Cu(I)–halogeno complexes

Assignments	dtt	$[Cu_2(dtt)Cl_2]_n$	Cu(dtt)Cl	Cu(dtt)Br	Cu(dtt)I
νC=S, ν_sSCS (ν_6)	1065vs	1010vs	1050vs	1042vs	1044vs
ν_{as}SCS (ν_{18})	882s	910sh (covered)	908s	903s	915s
ν_{as}SCS (ν_{19})	830s	840ms	843s	835s	834s
ν_sCH$_2$S (ν_9)	672m	663mw	672m	665m	665m
νC=S, ν_sSCS (ν_{10})	502ms	518mw	515m	510m	515m
CS$_3$ group	478w		480w		
Def. vibrations	383s	388ms	390ms	385ms	387ms
Ring vibrations	454m	450ms	458ms	450ms	447ms
νMS		n.o.[a]	n.o.	n.o.	n.o.
νMCl		268s,br	297s,br 218m	n.o.	n.o.

[a] n.o. = not observed.

the low total electronic contribution from the weakly bonded ligand. Distortions in the mixed tetrahedral and trigonal geometry make little meaningful predictions about the expected vibrations in $[Cu_2(dtt)Cl_2]_n$ (see structural results below). No other unambiguous bands have been recognized in this region.

Description of the structure of $[Cu_2(dtt)Cl_2]_n$

A perspective view of the polymer running parallel to *c* is reported in Fig. 1. The structure consists of two different···Cl–Cu–Cl–Cu···chains held together by bridging ligands. The coordination of the two independent metal atoms is different. For Cu(1) it is a distorted tetrahedron, whose vertices are occupied by two chlorine atoms related by a glide and a sulfur atom (S(1)), with usual bond distances and angles of coordination, and by S(1^{ii}) at a longer distance. The metal atom deviates 0.459(2) Å from the mean plane Cl(1)Cl(1^{i})S(1) toward S(1^{ii}). The Cu(2) atom shows a trigonal coordination involving, similarly to Cu(1), two chlorine atoms and a sulfur atom (Cl(2), Cl(2^{ii}) and S(1)) but with slightly shorter bond distances. An additional long contact Cu(2)···S(3) (1 − *x*, 1 − *y*, 1 − *z*) (3.174(3) Å) is present. The metal is −0.174(2) Å out of the mean plane containing the coordinated atoms. The electron delocalization within the planar CS_3 group of the free ligand [16] undergoes a modification as a consequence of the coordination. Instead, the formation of an adduct with diiodine [17] does not produce appreciable changes. The exocyclic C(1)–S(1) bond longer than in the free ligand (1.642(2) Å), is similar to that observed in the corresponding complex with CdI_2 [6] (1.685(6) Å). However the increase of the double bond character concerns only the endocyclic C(1)–S bonds, and is smaller than that observed in the CdI_2 derivative (1.668(6), 1.655(6) Å). In the last compound the electron delocalization involves also the other endocyclic C–S bonds (1.730(8), 1.781(9) Å). The five-membered ring presents a twist conformation (asymmetry parameter: Δ*C2*(C(1)) 0.0175(20) [18]). The value of the S(2)–C(2)–C(3)–S(3) torsion angle is −43.3(6)°.

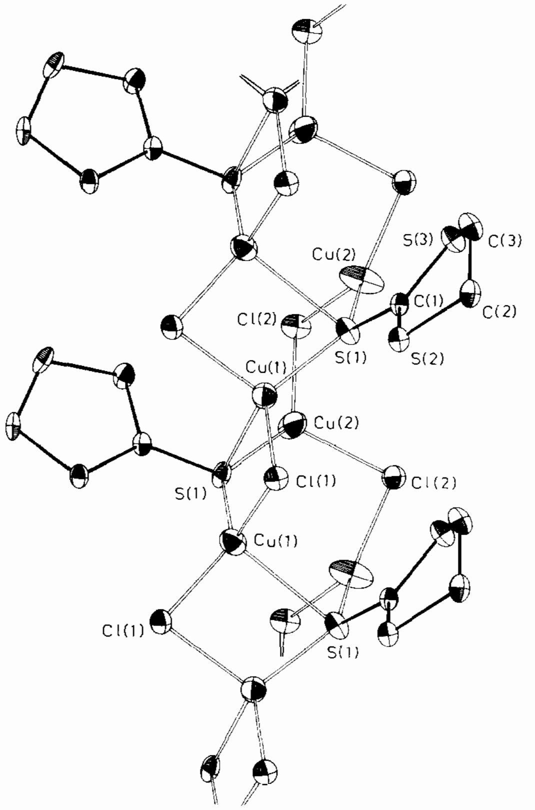
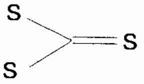


Fig. 1. Perspective view of the chain running parallel to *c*.

As the metal atoms, chlorine atoms, and the ligand (through S(1)) are bridging, polymeric chains parallel to *c* are formed. The bond distances involving each chlorine and the corresponding Cu atoms are asymmetric; the coordination polyhedron of S(1) is a distorted tetrahedron, where the metal atom at a longer distance is roughly perpendicular to the plane C(1)Cu(1)Cu(2); the S(1) atom is −0.156(2) Å out of this plane toward Cu(1^{i}). Figure 1 shows the presence in the chain of a concatenation of six-membered rings (S(1)–Cu(1)–S(1)–Cu(2)–Cl(2)–Cu(2)) held together through the S(1)–Cu(2) bond and having a twist-boat conformation (asymmetry parameters Δ*C2*(S(1) 0.1045(8), Δ*C2*(Cu(1)–S(1)) 0.0798(9). In addition each six-membered ring is fused to a four-membered ring (Cu(1)–Cl(1)–Cu(1)–S(1)) approximately planar (max. deviation 0.041(2) Å for Cl(1), through the Cu(1)–S(1) bond. As consequence Cu(1) and S(1) atoms are involved in forming both types of rings; Cl(1) is present only in the four-membered ring, Cu(2) and Cl(2) only in the six-membered ring.

The most relevant contacts determining the packing are: the above cited Cu(2)···S(3) (1 − *x*, 1 − *y*, 1 − *z*), Cl(1)···S(2)(2 − *x*, 1 − *x*, −*z*) 3.474(3) Å, Cl(2)···S(3) (1 − *x*, 1 − *y*, 2 − *z*) 3.424(3) Å, and Cl(2)···C(3) (1 − *x*, 1 − *y*, 2 − *z*) 3.474(8) Å. These contacts are responsible for the orientation of the organic molecule. The dihedral angle between the two planes for the trigonal coordination around the metal atoms is 102.4(1)°, that between each of these planes and



69.7(1) and 10.0(1)°, respectively.

The above described structure may explain the fact that the ligand bridging polymer has been isolated in the X = Cl case only. In the X = Br and I cases, following the hypothesis that the halogens are still bridging between the copper atoms, the distance of the metal centers is too large to allow coordination with the same ligand.

Supplementary material

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

Acknowledgements

We thank the CNR and the MURST 40%, Progetto 'Reattività e Catalisi' for financial support.

References

1 G. Wilkinson (ed.), *Comprehensive Coordination Chemistry,* Vol. 5, Pergamon, Oxford 1987, p. 594 and following.
2 D. Atzei, F. Bigoli, P. Deplano, M. A. Pellinghelli, A. Sabatini, E. F. Trogu and A. Vacca, *Can. J. Chem., 67* (1989) 1416, and ref. therein.
3 F. Bigoli, P. Deplano, M. A. Pellinghelli and E. F. Trogu, *Inorg. Chim. Acta, 170* (1990) 245.
4 F. Bigoli, P. Deplano, M. A. Pellinghelli, A. Sabatini, E. F. Trogu and A. Vacca, *Inorg. Chim. Acta, 180* (1991) 201..
5 F. Bigoli, P. Deplano, M. A. Pellinghelli and E. F. Trogu, *Inorg. Chim. Acta, 182* (1991) 33.
6 A. Castineiras, C. F. Vidal, R. Bastida, A. Macias and H. Hiller, *Polyhedron, 7* (1988) 2503.
7 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.
8 F. Ugozzoli, *Comput. Chem., 11* (1987) 109.
9 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch, Birmingham, UK, 1974, pp. 99, 149.
10 G. Sheldrick, *SHELX-76,* a program for crystal structure determination, University of Cambridge, UK, 1976.
11 M. Nardelli, *Comput.Chem., 7* (1983) 95.
12 W. D. Motherwell, *PLUTO,* University of Cambridge, UK, 1986.
13 W. J. Geary, *Coord. Chem. Rev., 7* (1971) 81.
14 G. Borch, L. Henriksen, P. H. Nielsen and P. Klaboe, *Spectrochim. Acta, Part A, 29* (1973) 1109.
15 G. A. Bowmaker, J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.,* (1987) 1089.
16 B. K. Klewe and H. M. Seip, *Acta Chem. Scand., 26* (1972) 1860.
17 F. Bigoli, P. Deplano, M. L. Mercuri, M. A. Pellinghelli and E. F. Trogu, *Phosphorus Sulfur Silicon, 70* (1992) 175.
18 M. Nardelli, *Acta Crystallogr., Sect. C, 39* (1983) 1141.