metal-organic compounds

catena-Poly[[cyclo-tetra-μ-chloro-tetracopper(I)]-bis{μ-3-[(2-morpholino-4-oxo-4,5-dihydro-1,3-thiazol-5-ylidene)methylphenoxy]propene}-2κN,1'η²;1η²,2'κN]

Evgeny Goreshnik,[a]* Volodymyr Karpyak[b] and Marian Mys'kiv[b]

[a]Department of Inorganic Chemistry and Technology, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia, and [b]Department of Chemistry, Ivan Franko National University of L'viv, Kyryla and Mefodia Str. 8, 79005 L'viv, Ukraine
Correspondence e-mail: evgeny.goreshnik@ijs.si

Crystals of a new copper(I) π complex of composition $[Cu_4Cl_4(C_{17}H_{18}N_2O_3S)_2]_n$ have been obtained by alternating-current electrochemical synthesis. In the crystal structure, the Cu and Cl atoms form a chair-like Cu_4Cl_4 cyclic fragment. The organic ligand acts as a bridge, being connected via the C=C bond of the allyl group to a Cu atom from one inorganic cycle and via the N atom of the thiazole ring to a Cu atom of another copper–chloride fragment. The geometry of the π center indicates that the Cu—(C=C) interaction is moderately effective.

Comment

The catalytic properties of copper(I) halides and the possibility of their olefin π-adduct separation were the basis for early studies of the structural chemistry of copper(I) π complexes (Herberhold, 1972). Such interest has led to the investigation of metal adducts with aliphatic olefin derivatives, whereas copper(I) π complexes with heterocyclic ligands have been poorly investigated. We have therefore focused on the structural investigation of copper(I) π complexes with the allyl derivatives of heterocyclic compounds.

Our recent studies of these compounds have shown some interesting peculiarities with respect to stereochemistry. Sharply defined differences in three-dimensional structure are observed between small monocyclic aromatic and non-aromatic derivatives [such as morpholine (Goreshnik & Mys'kiv, 2003) or aminopyridine (Goreshnik et al., 2005a)] on the one hand, and between bicyclic aromatic compounds [derivatives of benzotriazole (Goreshnik et al., 1999) or benzimidazole (Goreshnik et al., 2000, 2002)] on the other. As a logical extension of this chemistry, we chose to use more voluminous heterocyclic derivatives, including the 3-[(2-

morpholino-4-oxo-4,5-dihydro-1,3-thiazol-5-ylidene)methyl-phenoxy]propene ligand, L, of the title compound, (I).
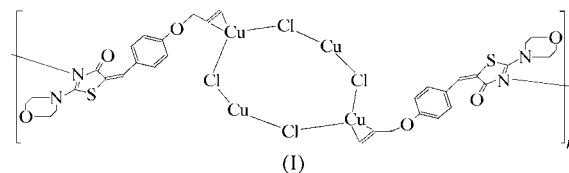
The Cu and Cl atoms in (I) form chair-like Cu_4Cl_4 cycles (Fig. 1). Similar eight-membered rings have been reported in the structures of $2CuCl(dibenzocyclooctatetraene)$ (Mak et al., 1983), CuCl(allyl alcohol) (Zavalij et al., 1983), 2CuCl(1,5-hexadien-3-ol) (Oliinik et al., 1987) and $2CuCl(C_3H_5—N=CH—R)$ (R = 2-furyl and phenyl; Filinchuk & Mys'kiv, 1998). The ligand L acts as a bridge between two Cu_4Cl_4 cycles, being coordinated to atom Cu1 of one copper–chloride cycle via π interaction with the C4=C5 bond of the allyl group and to atom Cu2 from another inorganic fragment via the N atom of the thiazole ring. Ligand L is essentially planar; the benzene and thiazole aromatic rings, the non-H atoms of the allyl group, and atom N1 of the morpholine ring are coplanar. Each bridge actually consists of a pair of organic moieties oriented in a 'head-to-tail' manner (Fig. 2). The aromatic rings within the bridge exhibit a stacking interaction with a parallel mutual orientation and typical ring–ring distances of 3.6 Å. In turn, each Cu_4Cl_4 ring is bonded to four ligands, resulting in two such bridges which connect two neighboring inorganic rings, thus forming infinite zigzag organic–inorganic chains oriented along the [111] direction. These chains are interconnected by weak interactions only.

The $Cu^I—(C=C)$ π interaction in (I) appears to be of moderate effectiveness, as indicated by the slight elongation of the C4=C5 bond [to 1.351 (8) Å] compared with a free C=C double bond (1.33 Å). In addition, the value of 37.5 (3)° for the C4—Cu—C5 angle, being an important reference of copper(I)–olefin interaction efficiency, is comparable to the value of 38.0 (8)° in $C_7H_5N_2S(C_3H_5)CuCl$ (Goreshnik et al., 2002) with the same 2Cl + C=C Cu^I atom arrangement. The π-coordinated Cu-atom environment in (I) is essentially planar (the sum of the ligand–copper–ligand angles is 359.9°), which is likewise typical for effective π interaction. On the other hand, the combination of a large inorganic fragment and a large organic ligand hinders achievement of the most suitable mutual orientation of the C=C group and metal center for effective Cu—(C=C) interaction. Consequently,
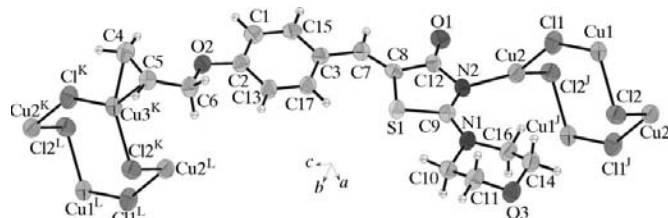

Figure 1
The ligand and copper–chloride rings in (I). [Symmetry codes: (J) $-x + 2$, $-y + 1$, $-z$; (K) $x - 1$, $y + 1$, $z + 1$; (L) $-x + 1$, $-y + 2$, $-z + 1$.]
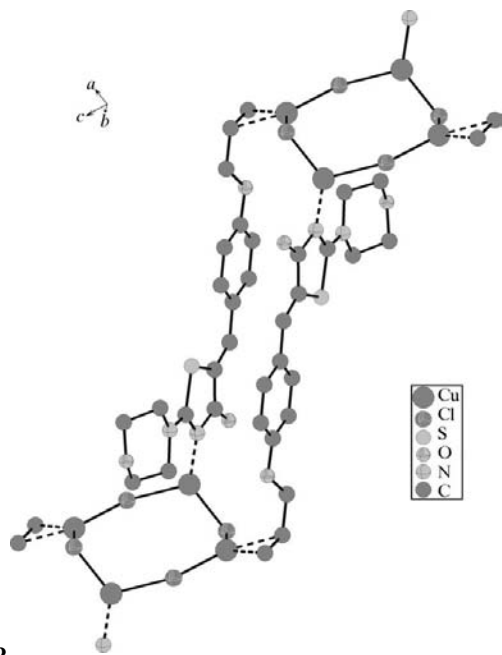
Figure 2
The bridging function of the ligands in (I).

the Cu—m distance in (I) [1.977 (7) Å; m is the mid-point of the C4=C5 bond] is slightly longer than those found in $C_7H_5N_2S(C_3H_5)CuCl$ [1.95 (2) Å] and $C_6H_4N_3(OC_3H_5)_2$-(CuCl)$_2$ [1.936 (6) Å] (Goreshnik *et al.*, 2005*b*).

The Cu—Cl distances lie in a rather narrow range, with the exception of the noticeably elongated Cu2—Cl1 bond (Table 1). Possibly, the presence of a Cl1···H14 contact (Cl···H = 2.864 Å) formally increases the coordination number of atom Cl1 and, consequently, leads to lengthening of the Cu—Cl distance. A tetrahedral coordinating sphere is the most suitable for σ-coordinated Cu^I atoms. However, in the case of (I), atom Cu2 occupies a trigonal environment consisting of the N atom of the thiazole ring and two Cl atoms. The large size of the rigid organic ligand may spatially hinder any additional donor atoms from entering the metal coordination sphere. On the other hand, the neutral status of the ligand limits the number of chloride anions in the formula that can be involved in the metal coordination environment. Both factors result finally in the trigonal–planar arrangement of atom Cu2.

Experimental

Ligand *L* was obtained by refluxing a mixture of 4-allyloxybenzal-rhodanine and morpholine in ethanol (2 h), cooling to room temperature and recrystallizing from ethanol (m.p. 486–487 K). Good quality crystals of (I) were obtained using the alternating-current electrochemical technique (Mykhalichko & Mys'kiv, 1998) starting from an ethanol solution containing copper(II) chloride and *L*. Because of low ligand solubility, the reaction was performed at 323 K. The starting mixture was placed in a small test tube and heated to dissolve the ligand. Copper-wire electrodes in cork were then inserted, and an alternating current of 0.30 V tension (frequency 50 Hz) was applied. After heating at 323 K for 9 h, the reactor was

allowed to stand at 293 K (under tension) for a few days, during which time yellow crystals of the title compound appeared on the copper electrodes.

Crystal data

$[Cu_4Cl_4(C_{17}H_{18}N_2O_3S)_2]$	$D_m = 1.9$ Mg m^{-3}
$M_r = 1056.8$	D_m measured by flotation in a
Triclinic, $P\bar{1}$	chloroform–bromoform mixture
$a = 8.7940$ (4) Å	Mo $K\alpha$ radiation
$b = 9.2890$ (4) Å	Cell parameters from 55
$c = 12.7670$ (13) Å	reflections
$\alpha = 81.47$ (2)°	$\theta = 1.6$–29.1°
$\beta = 86.40$ (2)°	$\mu = 2.68$ mm^{-1}
$\gamma = 65.79$ (2)°	$T = 200$ K
$V = 940.66$ (19) Å^3	Prism, yellow
$Z = 1$	0.15 × 0.05 × 0.02 mm
$D_x = 1.865$ Mg m^{-3}	

Data collection

Rigaku Mercury CCD (2 × 2 bin mode) diffractometer	3730 independent reflections
	2552 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.015$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{max} = 29.1°$
	$h = -12 \rightarrow 5$
$T_{min} = 0.814$, $T_{max} = 0.95$	$k = -12 \rightarrow 11$
4221 measured reflections	$l = -17 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.055$	$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2]$
$wR(F^2) = 0.161$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
3719 reflections	$\Delta\rho_{max} = 1.45$ e Å^{-3}
262 parameters	$\Delta\rho_{min} = -0.79$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—C4	2.085 (6)	Cu2—Cl2^{ii}	2.207 (4)
Cu1—C5^i	2.111 (6)	Cu2—Cl1	2.369 (2)
Cu1—Cl1	2.2399 (19)	S1—C9	1.747 (6)
Cu1—Cl2	2.268 (3)	S1—C8	1.750 (5)
Cu2—N2	1.951 (5)		
C4^i—Cu1—C5^i	37.7 (2)	N2—Cu2—Cl2^{ii}	134.15 (15)
C4^i—Cu1—Cl1	108.76 (18)	N2—Cu2—Cl1	116.33 (17)
C5^i—Cu1—Cl1	146.41 (17)	Cl2^{ii}—Cu2—Cl1	109.05 (14)
C4^i—Cu1—Cl2	135.52 (16)	Cu1—Cl1—Cu2	145.23 (9)
C5^i—Cu1—Cl2	97.94 (18)	Cu2^{ii}—Cl2—Cu1	89.38 (9)
Cl1—Cu1—Cl2	115.52 (11)		

Symmetry code: (i) $1 + x, y - 1, z - 1$; (ii) $-x + 2, -y + 1, -z$.

An orientation matrix and unit-cell parameters were obtained by indexing with the *CrystalClear* software (Rigaku, 1999). A number of unindexed reflections remained after the indexing procedure. These reflections were subsequently indexed with the *TWINSOLVE* software implemented in the *CrystalClear* program package. It was found that the twin subunits mutually tilted on some degrees, *i.e.* the crystal demonstrates epitaxic twinning with a rather small volume of second twin component. The HKLF5 file was created and reflections with batch numbers 2 and −2 (reflections belonging to the second twin component and overlapped reflections, respectively) were excluded from the refinement (resulting in a decrease in data completeness to 90% at 25° in θ).

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for

metal-organic compounds

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Altomare, A., Cascarano, M., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Filinchuk, Ya. E. & Mys'kiv, M. G. (1998). *Russ. J. Coord. Chem.* **24**, 337–340.

Goreshnik, E., Schollmeyer, D. & Mys'kiv, M. (2005a). *Acta Cryst.* C**61**, m127–m129.

Goreshnik, E. A. & Mys'kiv, M. G. (2003). *Russ. J. Coord. Chem.* **29**, 505–511.

Goreshnik, E. A., Pavlyuk, A. V., Schollmeyer, D. & Mys'kiv, M. G. (1999). *Russ. J. Coord. Chem.* **25**, 653–657.

Goreshnik, E. A., Schollmeyer, D. & Mys'kiv, M. G. (2000). *Z. Anorg. Allg. Chem.* **626**, 1016–1019.

Goreshnik, E. A., Schollmeyer, D. & Mys'kiv, M. G. (2002). *Z. Anorg. Allg. Chem.* **628**, 2118–2122.

Goreshnik, E. A., Schollmeyer, D. & Mys'kiv, M. G. (2005b). *J. Chem. Crystallogr.* **35**, 573–581.

Herberhold, M. (1972). *Metal π-Complexes*. Amsterdam: Elsevier.

Mak, T. C. W., Wong, H. N. C., Sze, K.-H. & Book, L. (1983). *J. Organomet. Chem.* **225**, 123–134.

Molecular Structure Corporation (1999). *TEXSAN for Windows*. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Mykhalichko, B. M. & Mys'kiv, M. G. (1998). Ukraine Patent UA 25450A, Bull. No. 6.

Oliinik, V. V., Zavalij, P. Yu., Mys'kiv, M. G. & Fundamensky, V. S. (1987). *Koord. Khim.* **13**, 255–259.

Rigaku (1999). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Zavalij, P. Yu., Fundamensky, V. S., Mys'kiv, M. G. & Gladyshevsky, E. I. (1983). *Kristallographiya*, **28**, 662–666.