catena-Poly[[aqua(1,10-phenanthroline-κ^2N,N')-copper(II)]-μ-1,3,4-thiadiazol-2,5-diyl-dithiodiacetato]

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In the title one-dimensional coordination polymer, [Cu(tdzdta)(phen)(H$_2$O)]$_n$ [where tdzdta^{2-} is the 1,3,4-thiadiazole-2,5-diyldithiodiacetate dianion (C$_6$H$_4$N$_2$O$_4$S$_3$$^{2-}$) and phen is 1,10-phenanthroline (C$_{12}$H$_8$N$_2$)], the Cu^{II} atom displays an elongated square-pyramidal coordination geometry with the base capped by one very long semicoordinate Cu—O$_{carboxylate}$ bond [2.842 (2) Å]. The Cu^{II} ions are bridged by tdzdta^{2-} groups, resulting in a one-dimensional chain structure. The intrachain Cu$\cdots$Cu separation is 9.112 (4) Å. Furthermore, the chains are linked into a three-dimensional supramolecular network *via* hydrogen bonds and π–π stacking interactions.

Comment

We have studied metal complexes of dicarboxylic acids having two –X—CH$_2$CO$_2$H arms (where X is O or S) on an aromatic unit, such as benzenedioxyacetic acid (Gao *et al.*, 2004*a*,*b*) and 4-(carboxymethoxy)phenylsulfanylacetic acid (Gao, Su *et al.*, 2005; Huo *et al.*, 2005). 1,3,4-Thiadiazolyl-2,5-dithioacetic acid (tdzdtaH$_2$) is also a multidentate flexible aromatic carboxylic acid having two –S—CH$_2$CO$_2$H arms, and it can be considered as a potential candidate for the construction of supramolecular complexes. Recently, we reported the crystal structure of a mononuclear Cu^{II} complex based on the tdzdtaH$^-$ ligand, namely [Cu(tdzdtaH)(C$_{10}$H$_8$N$_2$)$_2$](tdzdtaH)·2H$_2$O (Gao, Huo *et al.*, 2005), in which the tdzdtaH$^-$ ligand shows monodentate coordination. We have now synthesized the title new one-dimensional chain Cu^{II} coordination polymer, [Cu((tdzdta)-(phen)(H$_2$O)]$_n$, (I), and report its crystal structure here.

(I)
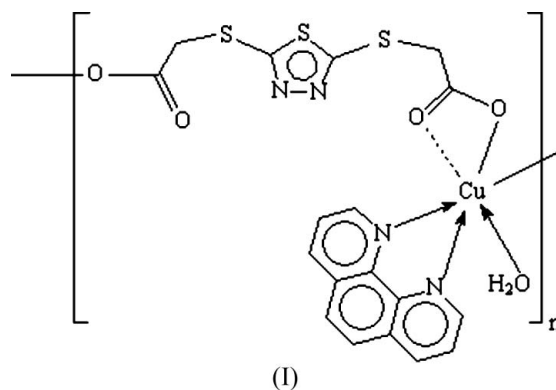
The Cu^{II} atom in (I) is coordinated by three carboxylate O atoms from two different tdzdta^{2-} groups, two N donors from the phen ligand and one water molecule, displaying an elongated square-pyramidal coordination geometry, with the base capped by one very long semicoordinate Cu1—O2 bond
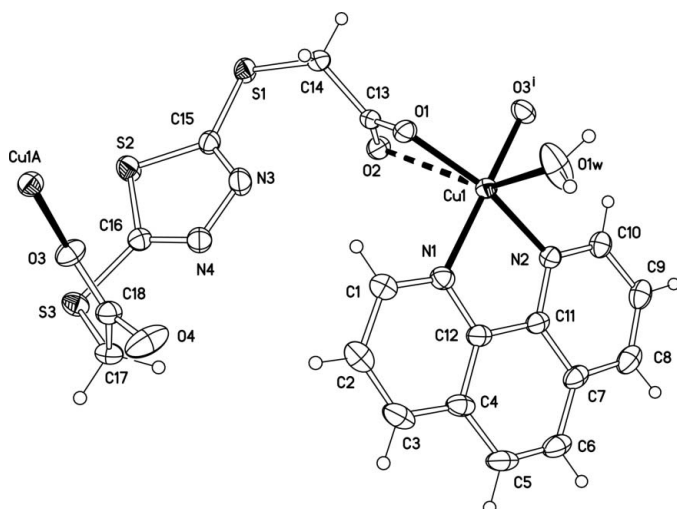
Figure 1
A plot of the title complex, with 30% probability displacement ellipsoids. The semicoordinate bond is shown as a dashed line. [Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (A) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.]

distance of 2.842 (2) Å (Sieroń *et al.*, 2002) (Fig. 1). Atoms N1, N2, O1 and O3^i [symmetry code: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$] define the basal plane [r.m.s. deviation 0.053 (3) Å]. The Cu^{II} atom is displaced from the mean basal plane by 0.19 (4) Å. Atom O1W occupies the apical site, with the Cu—O1W bond distance being 2.210 (3) Å. Both thioacetate groups are twisted out of the 1,3,4-thiadiazole ring plane, with torsion angles of 64.8 (3)° (C15—S1—C14—C13) and 64.5 (3)° (C16—S2—C17—C18), respectively. This demonstrates their obvious conformational flexibility.

The O1—C13 and O3—C18 distances are longer than those of O2—C13 and O4—C18, in agreement with the greater double-bond character of the latter bonds. Each tdzdta^{2-} ligand serves as a bis-monodentate bridging group to link two Cu^{II} ions, giving rise to a one-dimensional chain structure (Fig. 2). The antiparallel phen ligands lie on alternate sides of the chain. The polymeric chains run along the *c* axis of the unit cell and show a corrugated arrangement. The shortest adjacent intrachain Cu···Cu distance is 9.112 (4) Å.

The polymeric chains are connected *via* hydrogen bonds between the carboxylate O atoms and the water molecule (Table 2), leading to a two-dimensional hydrogen-bonding layer architecture along the crystallographic *ac* plane. Individual layers are stacked in an offset manner through π–π stacking interactions between adjacent phen molecules at 3.432 (3) Å. With the help of the hydrogen-bonding and π–π stacking interactions, a three-dimensional supramolecular network structure is constructed, as shown in Fig. 3.

Experimental

1,3,4-Thiadiazolyl-2,5-dithioacetic acid (tdzdtaH$_2$) was prepared from 2,5-dimercapto-1,3,4-thiadiazole, using the method for synthesis of benzene-1,4-dioxyacetic acid reported by Liu *et al.* (2004). The copper complex was obtained from the reaction of copper dinitrate hexahydrate (1.43 g, 5 mmol), 1,10-phenanthroline (1.99 g, 10 mmol)
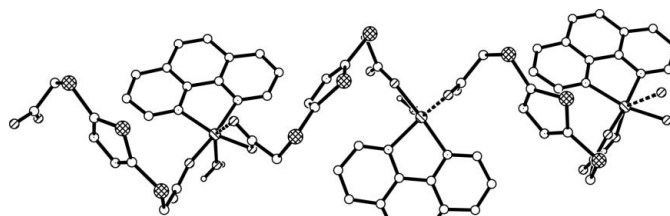

Figure 2
The one-dimensional chain structure of the title complex. The semicoordinate bond is shown as a dashed line. H atoms have been omitted.
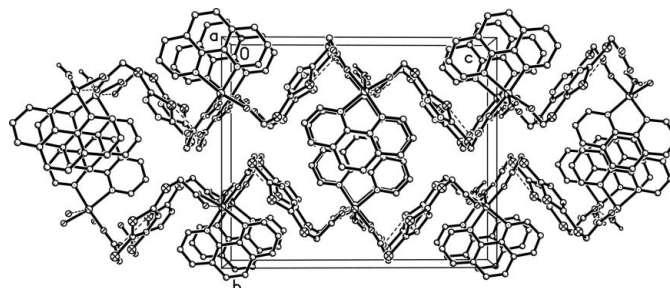

Figure 3
A packing diagram of the title complex, viewed along the *a* axis. Hydrogen bonds and the semicoordinate bond are shown as dashed lines (the H atoms on C atoms have been omitted).

and tdzdtaH$_2$ (2.66 g, 10 mmol) in water (40 ml), and then the pH was raised to about 6 with 0.2 *M* sodium hydroxide. The hot solution (333 K, 30 min) was filtered and yielded blue crystals of (I) when left aside for several days. CHN analysis, calculated for C$_{18}$H$_{14}$N$_4$O$_5$S$_3$Cu: C 41.10, H 2.68, N 10.65%; found: C 41.13, H 2.71, N 10.69%.

Crystal data

[Cu(C$_6$H$_4$N$_2$O$_4$S$_3$)(C$_{12}$H$_8$N$_2$)(H$_2$O)]	$D_x = 1.744$ Mg m^{-3}
$M_r = 526.09$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 16825
$a = 7.226$ (1) Å	reflections
$b = 15.230$ (3) Å	$\theta = 3.3$–27.5°
$c = 18.222$ (4) Å	$\mu = 1.44$ mm^{-1}
$\beta = 92.19$ (3)°	$T = 295$ (2) K
$V = 2003.9$ (7) Å^3	Prism, blue
$Z = 4$	$0.39 \times 0.28 \times 0.21$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	4590 independent reflections
	4016 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.062$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$\theta_{max} = 27.5°$
	$h = -8 \rightarrow 9$
$T_{min} = 0.623$, $T_{max} = 0.737$	$k = -19 \rightarrow 19$
17853 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.119P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 1.1283P]$
$wR(F^2) = 0.171$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
4590 reflections	$\Delta\rho_{max} = 0.55$ e Å^{-3}
286 parameters	$\Delta\rho_{min} = -0.50$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cu1—O3^i	1.955 (2)	Cu1—O1W	2.210 (3)
Cu1—O1	1.958 (2)	O1—C13	1.277 (4)
Cu1—O2	2.842 (2)	O2—C13	1.228 (4)
Cu1—N1	2.038 (3)	C18—O4	1.225 (4)
Cu1—N2	2.051 (3)	C18—O3	1.257 (4)
O3^i—Cu1—O1	89.54 (10)	N1—Cu1—O1W	95.57 (13)
O3^i—Cu1—N1	171.01 (11)	N2—Cu1—O1W	95.42 (16)
O1—Cu1—N1	92.89 (11)	O2—Cu1—O1	51.39 (11)
O3^i—Cu1—N2	94.37 (11)	O2—Cu1—O1W	147.86 (12)
O1—Cu1—N2	164.76 (10)	O2—Cu1—N1	97.97 (10)
N1—Cu1—N2	81.12 (12)	O2—Cu1—N2	115.36 (10)
O3^i—Cu1—O1W	92.59 (12)	O2—Cu1—O3^i	76.89 (11)
O1—Cu1—O1W	99.11 (15)		

Symmetry code: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
O1W—H1W1$\cdots$O2^{ii}	0.85 (3)	1.90 (4)	2.745 (4)	176 (6)
O1W—H1W2$\cdots$O4^i	0.85 (6)	2.00 (4)	2.749 (5)	146 (6)

Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x - 1, y, z$.

C-bound H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C), and were refined in the riding-model approximation. The H atoms of the water molecule were located in a difference Fourier map and refined with O—H and H$\cdots$H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and U_{iso}(H) = 1.5U_{eq}(O).

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