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catena-Poly[[[aqua(ethylenediamine-κ^2N,N')(nitrato-κO)copper(II)]-μ-4,4′-dithiodipyridine-κ^2N:N'] nitrate monohydrate]

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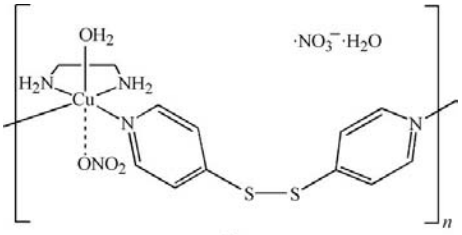
The title compound, $\{[Cu(NO_3)(C_2H_4N_2)(C_{10}H_8N_2S_2)(H_2O)]\text{-}NO_3\cdot H_2O\}_n$, is composed of a one-dimensional linear coordination polymer involving *cis*-protected copper(II) ions and a 4,4′-dithiodipyridine bridging ligand. The polymeric chains run along the *c*-axis direction. N—H···O and O—H···O hydrogen bonds involving the coordinating amine groups, nitrate ions and water molecules, as well as cocrystallized noncoordinating nitrate ions and water molecules, generate a three-dimensional structure.

Comment

Since Fujita's pioneering work on the molecular square with M_4L_4 topology, derived from $Pd(NO_3)_2(en)$ (en is ethylenediamine) and 4,4′-bipyridine (Fujita *et al.*, 1990), ethylenediamine has frequently been used to protect *cis*-coordination sites at Pd^{2+} and Pt^{2+} metal corners in discrete two- and three-dimensional metallosupramolecular assemblies, in particular with pyridine-based bridging ligands (Fujita, 1998; Navarro & Lippert, 2001; Fujita *et al.* 2005; Fujita & Yoshizawa, 2008). Not surprisingly, a related chemistry based on ethylenediamine complexes of divalent metal ions from the first-row transition metals is much less developed with respect to the lability of these metal ions. Two coordination polymers based on $Cu(en)^{2+}$ and 4,4′-bipyridine were reported by Chawla *et al.* (2001), but the solid-state structures were not determined. To the best of our knowledge the title compound, $\{[Cu(NO_3)(en)(\mu_2\text{-dtdp})(H_2O)]NO_3\cdot H_2O\}_n$ (dtdp is 4,4′-dithiodipyridine), (I), is the first structurally studied coordination polymer comprising $Cu(en)^{2+}$ units and a bridging ligand of the 4,4′-bipyridine type. The dtdp ligand has, inevitably, an ideal 90° bent structure and exhibits axial chirality. Because the barrier of rotation is relatively low, it exists as an equilibrium mixture of both enantiomeric conformers in solution (Kessler & Rundel, 1968).

The dtdp ligand has frequently been used in metallosupramolecular assemblies. A wide variety of coordination polymers are known in the literature, including double chains (Kondo *et al.*, 2000; Luo *et al.*, 2003; Horikoshi & Mikuriya, 2005*a*; Suen *et al.*, 2005; Manna *et al.*,2005; Gosh *et al.*, 2006; Suen & Wang, 2006; Carballo *et al.*, 2007), zigzag chains (Horikoshi *et al.*, 2001, 2002, 2005; Ng *et al.*, 2004; Horikoshi & Mikuriya, 2005*b*), helices (Tabellion *et al.*, 2001; Horikoshi *et al.*, 2001, 2002), arched chains (Lai & Tiekink, 2004; Carballo *et al.*, 2006; Manna *et al.*, 2007) and two-dimensional networks (Luo *et al.*, 2003). Achiral (Tabellion *et al.*, 2001) and chiral (Yu *et al.*, 2002; Horikoshi *et al.*, 2005) metallamacrocycles with M_2L_2 topology have also been reported. The coordination chemistry of the dtdp ligand was reviewed by Horikoshi & Mochida (2006). Essentially, three different products of self-assembly can be expected from the 1:1 combination of μ_2-bridging dtdp and *cis*-configured square-planar or octahedrally coordinated metal ions, namely infinite chiral helices or arched chains and discrete M_2L_2 metallamacrocycles (Fig. 1).



(I)

Compound (I) crystallizes in the monoclinic space group $P2_1/c$ with all atoms on general positions and exhibits the arched chain motif depicted in Fig. 1(*c*). A diagram of the repeat unit is shown in Fig. 2. The coordination polymer is generated by translational symmetry in the [001] direction (Fig. 3), with a period corresponding to the crystallographic *c*

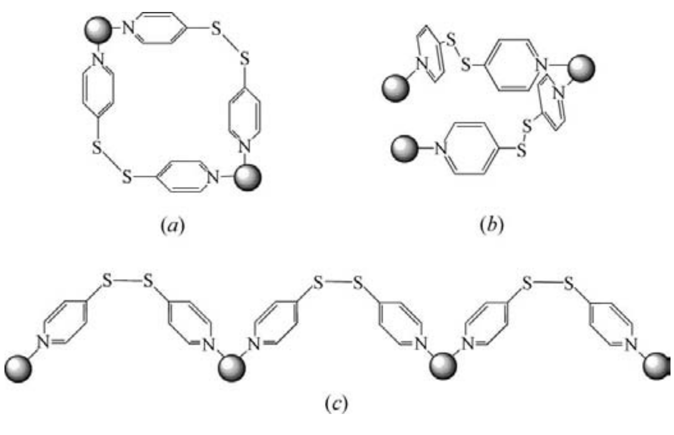


Figure 1
Topological isomers in the self-assembly of dtdp with *cis*-configured square-planar or octahedrally coordinated metal ions (large grey spheres) in a 1:1 molar ratio, showing (*a*) a discrete metallamacrocycle, (*b*) an infinite helix and (*c*) an infinite arched chain.

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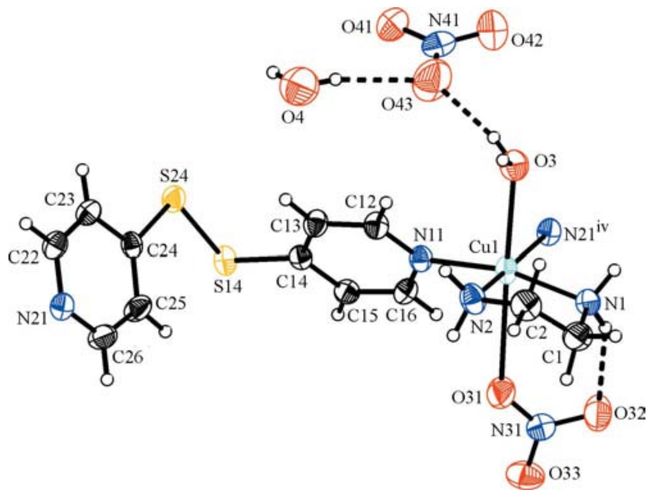

Figure 2
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are represented by dashed lines. [Symmetry code: (iv) *x*, *y*, $-1 + z$.]

axis [11.092 (5) Å]. In each polymeric chain, there is only one crystallographically independent Cu^{2+} ion. The dtdp ligand connects the Cu^{2+} ions in a μ_2-bridging mode. The coordination environment about the Cu^{2+} ion is essentially an elongated octahedron with some deviations of the angles. Two equatorial *cis* coordination sites are occupied by ethylenediamine. The two remaining equatorial *cis* sites are occupied by pyridine moieties of dtdp. The coordination geometry parameters about the Cu^{2+} ion and the equatorial N donors exhibit typical values. A water molecule is in an axial position, with a Cu1—O3 distance of 2.532 (2) Å. The coordination environment is completed by a weaker *O*-bonded NO_3^- anion with a considerably longer bond length of 2.751 (2) Å. In contrast, in *trans*-$Cu(NO_3)_2(en)_2$ this distance is 2.566 (4) Å (Manríquez *et al.*, 1996). A known example for Cu^{2+} with *trans*-configured H_2O and NO_3^- in an equatorial four *N*-ligand donor set is $Cu(nic)(NO_3)(dien)(H_2O)$ [dien is bis(2-aminoethyl)amine and nic is pyridine-3-carboxylate; Palicová *et al.*, 2000]. Interestingly, in this complex the bonding situation of the axial ligands is quite different from that observed in (I); the Cu—O distances are 2.716 (2) and 2.457 (2) Å for H_2O and NO_3^-, respectively. The molecular geometry parameters of the dtdp ligand in (I) are within the expected ranges (Tabellion *et al.*, 2001; Horikoshi & Mochida, 2006). The S—S bond length is 2.032 (1) Å. The C—S—S—C torsion angle [98.4 (1)°] is considerably larger than the ideal value of 90°.

The coordinated NO_3^- anion accepts an intrachain hydrogen bond from an amino group of the ethylenediamine ligand with a graph-set motif of *S*(6) (Bernstein *et al.*, 1995). The asymmetric unit additionally contains a noncoordinating NO_3^- anion and a cocrystallized water molecule. The crystal packing is achieved *via* N—H···O and O—H···O hydrogen bonds (Table 1), which link the coordination polymer chains into a three-dimensional framework structure, in which adjacent chains form a centrosymmetric $R_2^2(8)$ motif by means of N—H···O hydrogen-bonding interactions between atoms N1 and O3.

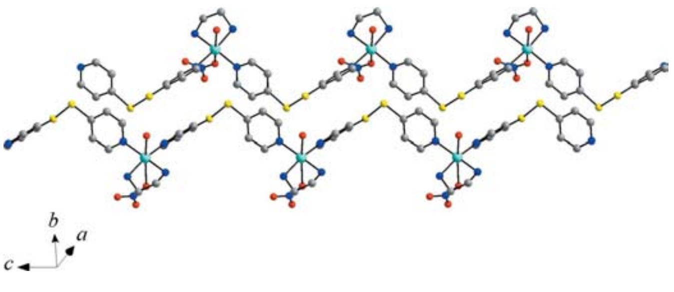

Figure 3
The compact arrangement of two polymeric chains of opposite chirality in the crystal structure of (I). H atoms and noncoordinating nitrate anions and water molecules have been omitted for clarity.

The polymeric chains in compound (I) are composed of only one enantiomeric conformer of the dtdp ligand and the $Cu(en)^{2+}$ unit, respectively. The right-handed *P* form of dtdp forms a chain with the right-handed δ conformer of the $Cu(en)^{2+}$ unit and *vice versa*. Thus, the chains exhibit chirality, although the crystal structure contains both enantiomeric forms with respect to the centrosymmetric space group. The compact arrangement is achieved by the interlocking of chains of opposite chirality.

It is notable that compound (I) was obtained from a mixture which contained Cu^{2+}, ethylenediamine and dtdp in a 1:2:1 molar ratio. This means that $Cu(en)_2^{2+}$ was the precursor in solution from which the title coordination polymer has self-assembled. Indeed, the major product in the crystallization vessel was *trans*-$Cu(NO_3)_2(en)_2$. Attempts to allow the components to react in a 1:1:1 molar ratio under the same conditions led immediately to a light-blue powder, the elemental analysis and powder X-ray diffraction analysis of which were not consistent with the calculated values for the structure of (I).

In summary, this work has shown that the $Cu(en)^{2+}$ unit can be principally functionalized as a *cis* metal corner in metallosupramolecular chemistry, although its reactivity is difficult to control.

Experimental

$Cu(NO_3)_2{\cdot}3H_2O$ (22 mg, 0.091 mmol) was dissolved in methanol (3 ml), followed by ethylenediamine (12 µl, 0.182 mmol) and dtdp (20 mg, 0.091 mmol). The solution was allowed to evaporate slowly to dryness at ambient temperature. Blue crystals of the title compound were formed, accompanied by a major component of violet crystals of *trans*-$Cu(NO_3)_2(en)_2$ which were identified from the dimensions of the unit cell (Komiyama & Lingafelter, 1964; Manríquez *et al.*, 1996).

Crystal data

$[Cu(NO_3)(C_2H_4N_2)(C_{10}H_8N_2S_2)$-
$(H_2O)]NO_3{\cdot}H_2O$
$M_r = 504.00$
Monoclinic, $P2_1/c$
$a = 8.5762$ (11) Å
$b = 21.844$ (2) Å
$c = 11.092$ (5) Å
$\beta = 110.512$ (17)°
$V = 1946.2$ (10) $Å^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.39$ mm^{-1}
$T = 294$ K
0.49 × 0.20 × 0.20 mm

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
N1—H1$A$$\cdots$O32	0.90	2.25	3.052 (4)	149
N1—H1$B$$\cdots$O3$^{\rm i}$	0.90	2.17	3.006 (3)	154
N2—H2$A$$\cdots$O33$^{\rm ii}$	0.90	2.56	3.143 (4)	123
N2—H2$A$$\cdots$O33$^{\rm iii}$	0.90	2.49	3.347 (4)	160
N2—H2$B$$\cdots$O31$^{\rm ii}$	0.90	2.36	3.114 (3)	141
O3—H3$A$$\cdots$O32$^{\rm iii}$	0.84 (3)	2.15 (4)	2.950 (4)	158 (3)
O3—H3$A$$\cdots$O33$^{\rm iii}$	0.84 (3)	2.42 (3)	3.053 (4)	133 (3)
O3—H3$B$$\cdots$O43	0.82 (3)	1.95 (3)	2.759 (4)	169 (3)
O4—H4$A$$\cdots$O42$^{\rm iv}$	0.85 (3)	2.10 (3)	2.936 (5)	169 (5)
O4—H4$B$$\cdots$O43	0.84 (3)	2.09 (3)	2.907 (5)	163 (4)

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

Data collection

Siemens *P*4 four-circle diffractometer
Absorption correction: ψ scan (ABSPSISCAN in *PLATON*; Spek, 2009)
$T_{\rm min} = 0.543$, $T_{\rm max} = 0.761$
4383 measured reflections
3419 independent reflections
2847 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
3 standard reflections every 97 reflections intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.088$
$S = 1.03$
3419 reflections
274 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}

H atoms attached to C or N atoms were treated as riding atoms in geometrically calculated positions, with C—H = 0.93–0.97 Å and N—H = 0.90 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N). The water H atoms were located in difference maps and then refined subject to restraints [O—H = 0.82 (2) Å, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O)], giving O—H distances in the range 0.82 (3)–0.85 (3) Å.

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3289). Services for accessing these data are described at the back of the journal.

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