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catena-Poly[[bis(α -thenoyltrifluoroacetonato- κ^2 0,0')copper(II)]- μ -1,4-di-3-pyridyl-2,3-diaza-1,3-butadiene- κ^2 N:N']

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Perkins et al. • $[Cu(C_8H_4F_3O_2S)_2(C_{12}H_{10}N_4)]$

metal-organic papers

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Key indicators

Single-crystal X-ray study T = 294 K Mean σ (C–C) = 0.004 Å Disorder in main residue R factor = 0.045 wR factor = 0.131 Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

catena-Poly[[bis(α -thenoyltrifluoroacetonato- $\kappa^2 O, O'$)copper(II)]- μ -1,4-di-3-pyridyl-2,3-diaza-1,3-butadiene- $\kappa^2 N:N'$]

The title compound, $[Cu(C_8H_4F_3O_2S)_2(C_{12}H_{10}N_4)]_n$ or $[Cu(tta)_2(L2)_2]_n$ (L2 = 1,4-di-3-pyridyl-2,3-diaza-1,3-butadiene and tta = α -thenoyltrifluoroacetonate), consists of undulating chains containing two crystallographically distinct Cu^{II} centers that are each located on inversion centers. Each Cu^{II} center exhibits distorted octahedral coordination provided by two pyridyl N atoms from two equivalent L2 ligands and four O atoms from two equivalent tta ligands. The chains interact through weak $C-F \cdots H-C$ contacts.

Comment

The synthesis of coordination polymers is of current interest due to their potential applications in a variety of areas, including catalysis, gas storage and nonlinear optics (Chin et al., 1993; Kitagawa et al., 2004; Janiak, 2003). Our group has been interested in utilizing N,N'-bipyridine-type ligands for the construction of new inorganic-organic coordination polymers, and we have synthesized several Schiff base ligands such as 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L1) and 1,4-bis (3-pyridyl)-2,3-diaza-1,3-butadiene (L2) for this purpose (Ciurtin et al., 2001; Dong et al., 2000). These efforts have resulted in the generation of many new coordination polymers (Perkins et al., 2005; Davis et al., 2004; Khalil et al., 2005; Dong et al., 2000a,b) including the title compound, (I), which is an example of a one-dimensional coordination polymer that utilizes L2 and tta (tta = α -thenoyltrifluoroacetonate) in its construction.



The structure of (I) contains two distinct Cu^{II} centers that

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metal-organic papers



Figure 1

The structure of (I), with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Cu atom shown in turquoise; O, red; N, blue; F, green; S, yellow; C, black. H atoms have been omitted. Only the major disorder component is shown. [Symmetry code: (i) -x, 1 - y, -z, (ii) 1 - x, -y, 1 - z.]



Figure 2 View of the crystal packing in (I).

hedrally coordinated by donor atoms from L2 and tta. For each center (Fig. 1), the axial positions are occupied by two pyridyl nitrogen donors from two equivalent L2 ligands, and the equatorial positions are occupied by four oxygen donors from two chelating and equivalent tta ligands. The Cu-N and Cu-O bond distances as well as the angles are all normal (Table 1), and the two independent Cu centers display only minor differences in their corresponding values. For the two centers combined, the average distances are 2.0984 (1) Å for Cu-N and 2.0850 (1) Å for Cu-O. Successive Cu1···Cu2 centers are bridged by L2 to form one-dimensional, undulating chains running in the crystallographic $[2\overline{12}]$ direction. The packing arrangement (Fig. 2) depicts this undulating pattern that arises by virtue of the two pyridyl N atoms occupying the 3-positions on the two pyridyl rings of L2. In comparison, linear chains are observed in an analogous crystal structure (Perkins et al., 2005) employing L1 instead, with its two pyridyl N atoms located in the 4-positions of the two pyridyl rings. As expected in (I), the intrachain Cu···Cu separation of 11.3376 (3) Å is shorter than the corresponding distance of 15.4463 (12) Å that is observed in the aforementioned crystal structure where the Cu centers within a chain are spaced by the L1 isomer.

In the crystal structure of (I), the individual chains are connected through weak $C-H \cdots F-C$ contacts involving H11 and F1 (F1···H11 = 2.54 Å, C11-H11··· F1 = 143°). Such interactions are known to exist (Perkins et al., 2005; Dong et al., 1999; Choudhury et al., 2002; Prasanna & Row, 2001) in a variety of crystal structures. In the case of (I), the $H \cdots F$ distance is less than the sum of the van der Waals radii

of F and H (2.67 Å; Bondi, 1964). Hence, this interaction may help to organize and stabilize the packing of the chains in the crystal structure.

Experimental

All chemicals and solvents were purchased from commercial sources and used without further purification. The L2 ligand (Dong et al., 2000) and Cu(tta)₂ (Perkins et al., 2005) were prepared as previously described. The title compound was obtained by slow diffusion of a solution containing 0.10 mmol of L2 dissolved in ethanol (8 ml) into a solution of 0.10 mmol of Cu(tta)₂ dissolved in dichloromethane (8 ml). Emerald-green crystals formed at the interface of the two solutions after several weeks.

Crvstal data

•	
$[Cu(C_8H_4F_3O_2S)_2(C_{12}H_{10}N_4)]$	V = 1490.19 (13) Å ³
$M_r = 716.12$	Z = 2
Triclinic, P1	$D_x = 1.596 \text{ Mg m}^{-3}$
a = 9.7970 (5) Å	Mo $K\alpha$ radiation
b = 12.5007 (6) Å	$\mu = 0.95 \text{ mm}^{-1}$
c = 13.9823 (7) Å	T = 294 (1) K
$\alpha = 98.453 \ (1)^{\circ}$	Prism, green
$\beta = 105.171 \ (1)^{\circ}$	$0.42 \times 0.28 \times 0.16 \text{ mm}$
$\gamma = 110.736 (1)^{\circ}$	
•	

Data collection

Bruker SMART APEX CCD diffractometer ω scans Absorption correction: multi-scan (SADABS; Bruker, 2001)

 $T_{\rm min}=0.816,\;T_{\rm max}=1.000$ (expected range = 0.700-0.859)

16194 measured reflections 6101 independent reflections 4938 reflections with $I > 2\sigma(I)$ $R_{\rm int} = 0.027$ $\theta_{\rm max} = 26.4^\circ$

Refinement

5	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0817P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	+ 0.2214P]
$wR(F^2) = 0.131$	where $P = (F_0^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{\rm max} < 0.001$
6101 reflections	$\Delta \rho_{\rm max} = 0.45 \ {\rm e} \ {\rm \AA}^{-3}$
435 parameters	$\Delta \rho_{\rm min} = -0.34 \text{ e } \text{\AA}^{-3}$
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Cu1-O1	2.0225 (19)	Cu2-O4	2.0108 (18)
Cu1-N1	2.111 (2)	Cu2-N4	2.086 (2)
Cu1-O2	2.1426 (18)	Cu2-O3	2.164 (2)
O1 ⁱ -Cu1-N1	88.71 (8)	O4-Cu2-N4	89.81 (8)
$O1^i - Cu1 - O2^i$	88.10 (7)	O4 ⁱⁱ -Cu2-N4	90.19 (8)
$O1-Cu1-O2^{i}$	91.90 (7)	O4-Cu2-O3	88.84 (7)
N1-Cu1-O2 ⁱ	91.14 (7)	O4 ⁱⁱ -Cu2-O3	91.16 (7)

Symmetry codes: (i) -x, -y + 1, -z; (ii) -x + 1, -y, -z + 1.

H atoms were placed in geometrically idealized positions and included as riding atoms with C–H distances fixed at 0.93 Å. Both independent thiophene rings were found to be rotationally disordered about the *ipso* carbon bonds (C16–C17 and C24–C25). The disorder components of each ring lie essentially in the same plane. For each ring, the geometry of the minor component (C17*B*–C20*B*/S1*B* and C25*B*–C28*B*/S2*B*) was restrained to be similar to that of the major (C17*A*–C20*A*/S1*A* and C25*A*–C28*A*/S2*A*). The pivot atom C10(*A*/*B*) is common to both components, and atoms less than 0.5 Å from their disorder counterparts were assigned equal displacement parameters. The total occupancy was restrained to sum to unity. The final refined occupancies are C17–C20/S1 (*A*/*B*) = 0.776 (4)/0.224 (4) and C25–C28/S2 (*A*/*B*) = 0.818 (4)/0.182 (4).

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-Plus-NT* (Bruker, 2001); data reduction: *SAINT-Plus-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

molecular graphics: *SHELXTL* (Sheldrick, 2000) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

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