

1-12-2007

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

William J. Perkins
Francis Marion University

Tamar Maxwell
Francis Marion University

Ken B. Williams
Francis Marion University

Andrea M. Goforth
University of South Carolina - Columbia

Mark D. Smith
University of South Carolina - Columbia, mdsmith3@mailbox.sc.edu

See next page for additional authors

Follow this and additional works at: https://scholarcommons.sc.edu/chem_facpub

 Part of the [Chemistry Commons](#)

Publication Info

Published in *Acta Crystallographica Section E*, Volume 63, Issue 2, 2007, pages m423-m425.

© *Acta Crystallographica Section E* 2007, International Union of Crystallography.

Publisher's version available [here](#).

This Article is brought to you by the Chemistry and Biochemistry, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact digres@mailbox.sc.edu.

Author(s)

William J. Perkins, Tamar Maxwell, Ken B. Williams, Andrea M. Goforth, Mark D. Smith, LeRoy Peterson Jr., and Hans-Conrad zur Loye

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Editors: W. Clegg and D. G. Watson

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

William J. Perkins, Tamara Maxwell, Ken B. Williams, Andrea M. Goforth, Mark D. Smith, LeRoy Peterson Jr and Hans-Conrad zur Loye

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site provided that this cover page is retained. Republication of this article or its storage in electronic databases or the like is not permitted without prior permission in writing from the IUCr.

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

William J. Perkins,^a Tamara Maxwell,^a Ken B. Williams,^a Andrea M. Goforth,^b Mark D. Smith,^b LeRoy Peterson Jr^a and Hans-Conrad zur Loye^{b*}

^aChemistry Department, Francis Marion University, Florence, South Carolina 29501, USA, and ^bDepartment of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, USA

Correspondence e-mail: lpeterson@fmarion.edu

Key indicators

Single-crystal X-ray study
 $T = 294\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 Disorder in main residue
 R factor = 0.045
 wR factor = 0.131
 Data-to-parameter ratio = 14.0

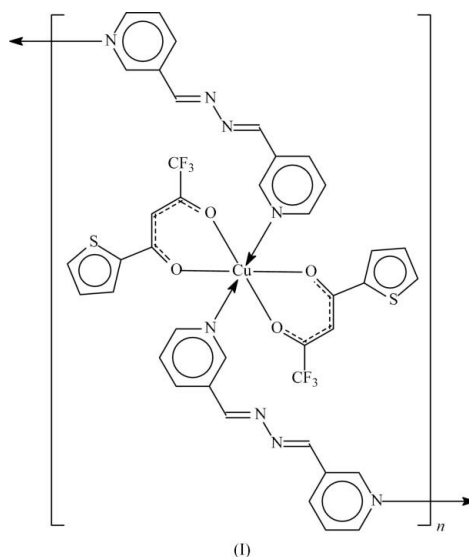
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Received 20 December 2006
 Accepted 4 January 2007

The title compound, $[\text{Cu}(\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S})_2(\text{C}_{12}\text{H}_{10}\text{N}_4)]_n$ or $[\text{Cu}(\text{tta})_2(\text{L}2)]_n$ ($\text{L}2 = 1,4\text{-di-3-pyridyl-2,3-diaza-1,3-butadiene}$ and $\text{tta} = \alpha\text{-thenoyltrifluoroacetate}$), 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 $\text{L}2$ ligands and four O atoms from two equivalent tta ligands. The chains interact through weak $\text{C}-\text{F}\cdots\text{H}-\text{C}$ 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 ($\text{L}1$) and 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene ($\text{L}2$) 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.*, 2000*a,b*) including the title compound, (I), which is an example of a one-dimensional coordination polymer that utilizes $\text{L}2$ and tta ($\text{tta} = \alpha\text{-thenoyltrifluoroacetate}$) in its construction.



The structure of (I) contains two distinct Cu^{II} centers that are both located on inversion centers and both are octa-

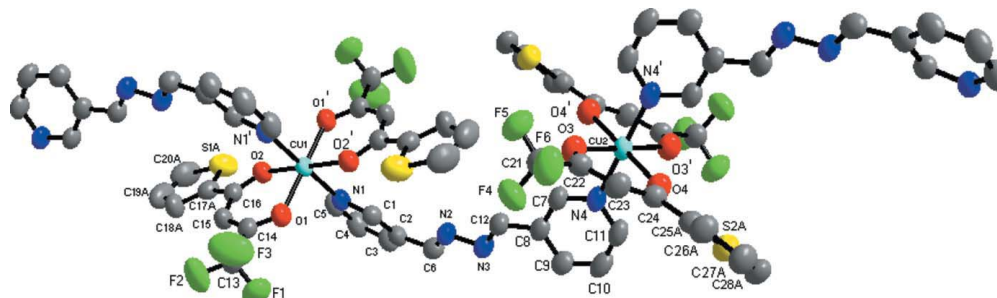


Figure 1

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) $1-x, -y, 1-z$.]

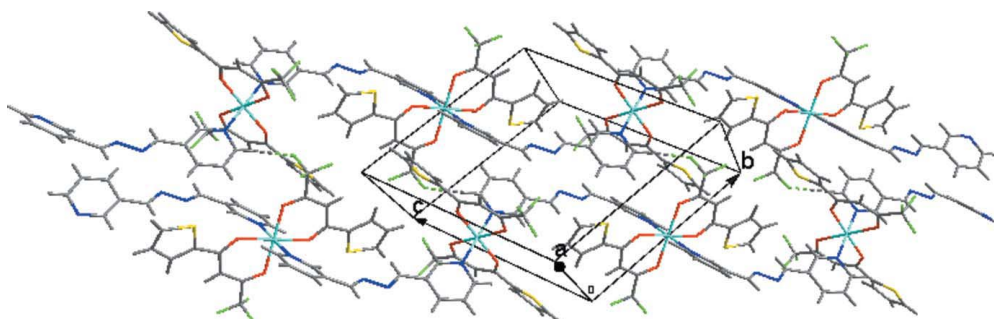


Figure 2

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 $[2\bar{1}2]$ 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...F–C contacts involving H11 and F1 ($F1\cdots H11 = 2.54$ Å, $C11-H11\cdots F1 = 143^\circ$). 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...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.

Crystal data

[Cu(C₈H₄F₃O₂S)₂(C₁₂H₁₀N₄)]
 $M_r = 716.12$
 Triclinic, $P\bar{1}$
 $a = 9.7970$ (5) Å
 $b = 12.5007$ (6) Å
 $c = 13.9823$ (7) Å
 $\alpha = 98.453$ (1) $^\circ$
 $\beta = 105.171$ (1) $^\circ$
 $\gamma = 110.736$ (1) $^\circ$

$V = 1490.19$ (13) Å³
 $Z = 2$
 $D_x = 1.596$ Mg m^{−3}
 Mo $K\alpha$ radiation
 $\mu = 0.95$ mm^{−1}
 $T = 294$ (1) K
 Prism, green
 $0.42 \times 0.28 \times 0.16$ mm

Data collection

Bruker SMART APEX CCD
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2001)
 $T_{\min} = 0.816$, $T_{\max} = 1.000$
 (expected range = 0.700–0.859)

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

Refinement

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

Table 1

Selected geometric parameters (\AA , $^\circ$).

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 (C17B—C20B/S1B and C25B—C28B/S2B) was restrained to be similar to that of the major (C17A—C20A/S1A and C25A—C28A/S2A). 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*.

Financial support from the National Science Foundation, awards CHE-0314164 and CHE-0315152, is gratefully acknowledged.

References

- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 Brandenburg, K. (2005). *DIAMOND*. Version 3.0e. Crystal Impact GbR, Bonn, Germany.
 Bruker (2001). *SMART-NT* (Version 5.625), *SAINT-Plus-NT* (Version 6.45) and *SADABS* (Version 2.05). Bruker AXS Inc., Madison, Wisconsin, USA.
 Chin, C., Suslick, K. S. & Kenneth, S. (1993). *Coord. Chem. Rev.* **128**, 293–322.
 Choudhury, A. R., Urs, U. K., Guru Row, T. N. & Nagarajan, K. (2002). *J. Mol. Struct.* **605**, 71–77.
 Ciurtin, D. M., Dong, Y.-B., Smith, M. D., Barclay, T. & zur Loye, H.-C. (2001). *Inorg. Chem.* **40**, 2825–2834.
 Davis, H., Peterson, L. Jr, Goforth, A. M., Smith, M. D., Zhang, P. & zur Loye, H.-C. (2004). *J. Chem. Crystallogr.* **34**, 299–306.
 Dong, Y.-B., Smith, M. D., Layland, R. C. & zur Loye, H.-C. (1999). *Inorg. Chem.* **38**, 5027–5033.
 Dong, Y.-B., Smith, M. D., Layland, R. C. & zur Loye, H.-C. (2000). *Chem. Mater.* **12**, 1156–1161.
 Dong, Y.-B., Smith, M. D. & zur Loye, H.-C. (2000a). *Inorg. Chem.* **39**, 4927–4935.
 Dong, Y.-B., Smith, M. D. & zur Loye, H.-C. (2000b). *J. Solid State Chem.* **155**, 143–153.
 Janiak, C. (2003). *Dalton Trans.* pp. 2781–2804.
 Khalil, S., Peterson, L. Jr, Goforth, A. M., Hansen, T. J., Smith, M. D. & zur Loye, H.-C. (2005). *J. Chem. Crystallogr.* **35**, 405–411.
 Kitagawa, S., Kitaura, R. & Noro, S. (2004). *Angew. Chem. Int. Ed. Engl.* **43**, 2334–2375.
 Perkins, W. J., Maxwell, T., Goforth, A. M., Smith, M. D., Peterson Jr, L. R. & zur Loye, H.-C. (2005). *Acta Cryst. E* **61**, m2047–m2049.
 Prasanna, M. D. & Row, T. N. G. (2001). *J. Mol. Struct.* **562**, 55–61.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Sheldrick, G. M. (2000). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.