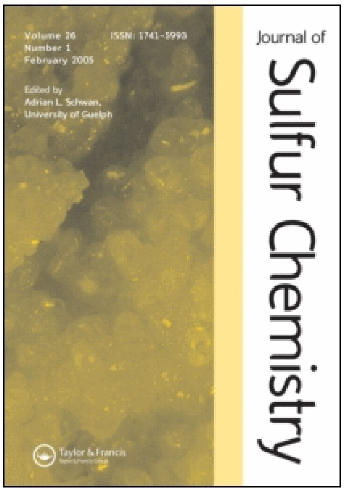
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



**Journal of Sulfur Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

# Metallopolymer formation from the interaction of a hydrolyzed dithiolane-carboxylate ligand with Ag(I)

Sudershan R. Gondi[a]; Hongming Zhang[a]; David Y. Son[a]
[a] Department of Chemistry, Southern Methodist University, Dallas, USA

Online publication date: 28 January 2011

**To cite this Article** Gondi, Sudershan R. , Zhang, Hongming and Son, David Y.(2011) 'Metallopolymer formation from the interaction of a hydrolyzed dithiolane-carboxylate ligand with Ag(I)', Journal of Sulfur Chemistry, 32: 1, 17 — 21
**To link to this Article: DOI:** 10.1080/17415993.2010.542154
**URL:** http://dx.doi.org/10.1080/17415993.2010.542154

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*Journal of Sulfur Chemistry*
Vol. 32, No. 1, February 2011, 17–21

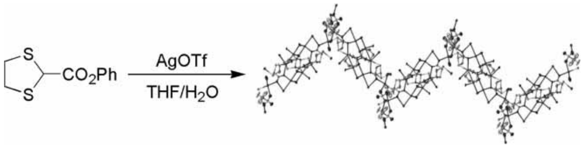
# Metallopolymer formation from the interaction of a hydrolyzed dithiolane-carboxylate ligand with Ag(I)

Sudershan R. Gondi, Hongming Zhang and David Y. Son*

*Department of Chemistry, Southern Methodist University, PO Box 750314, Dallas, TX 75275-0314, USA*

(*Received 22 April 2010; final version received 18 November 2010*)

On reaction with Ag(I), phenyl 1,3-dithiolane-2-carboxylate undergoes hydrolysis and assembles into a metal–organic coordination polymer. Crystals of the polymer were characterized by X-ray crystallography. The metallopolymer exists as a sheet-like structure consisting of twisted strands. An additional structural feature is an apparent Ag–Ag interaction (3.0679 Å) supported by the thiolane sulfur atoms. Carboxyl and triflate oxygen atoms are also key donors to the Ag(I) centers.



**Keywords:** dithiolane; coordination; supramolecular; silver; metallopolymer

Downloaded At: 13:00 30 January 2011

## 1. Introduction

Sulfur-containing heterocycles are useful ligands for the construction of supramolecular complexes and coordination polymers. Among the smaller ring systems, six-membered rings such as 1,3-dithiane (*1*–*3*), 1,4-dithiane (*3*–*5*), and 1,3,5-trithiane (*3*, *6*, *7*) have been successfully utilized in the construction of supramolecular structures when combined with various transition metal ions. A notable omission in the application of small sulfur heterocycles is 1,3-dithiolane and its derivatives. Save for some NMR studies of Pd(II) and Pt(II) complexes (*8, 9*), the coordination chemistry of these smaller ring compounds has been largely unexplored. In an earlier paper, we reported the self-assembly of a linear polymer from the interaction of 1,3-dithiolan-2-ylmethanol with silver nitrate (*10*). In this paper, we describe the synthesis of a new coordination polymer from the interaction of 1,3-dithiolane-2-carboxylic acid with AgOTf. The 1,3-dithiolane-2-carboxylic acid was generated from the unexpected *in situ* hydrolysis of phenyl 1,3-dithiolane-2-carboxylate.

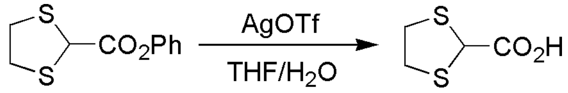
---

*Corresponding author. Email: dson@smu.edu

ISSN 1741-5993 print/ISSN 1741-6000 online
© 2011 Taylor & Francis
DOI: 10.1080/17415993.2010.542154
http://www.informaworld.com

## 2. Results and discussion

The original goal of our investigation was to examine steric effects in the coordination of different 1,3-dithiolane-2-carboxylic acid *esters* with Ag(I). Thus, one dithiolane we chose as a ligand was phenyl 1,3-dithiolane-2-carboxylate, synthesized by a procedure reported in this journal (*11*). Using the crystallization conditions described in this paper, we were surprised to see that the ester hydrolyzed to give the corresponding carboxylic acid as follows:



(1)

A subsequent literature search revealed that hydrolysis of esters can be catalyzed by metal ions such as Ag(I), presumably through initial coordination of the metal to the substrate (*12, 13*). Thus, the coordination polymer **1-OTf** was obtained from silver triflate and phenyl 1,3-dithiolane-2-carboxylate by layering a THF solution of the ligand over an aqueous solution of the salt. After several days in the dark, colorless needles were obtained in 55% yield. These crystals were insoluble in common organic solvents such as chloroform and acetone so NMR spectral data could not be obtained. Single crystal X-ray analysis revealed an asymmetric unit consisting of two molecules of 1,3-dithiolane-2-carboxylic acid, three silver ions, and a coordinating triflate anion. The asymmetric unit of **1-OTf** is shown in Figure 1(a), and an expanded structure is shown in Figure 1(b). Selected bond length and angle data are provided in Table 1. As seen in the expanded

Downloaded At: 13:00 30 January 2011

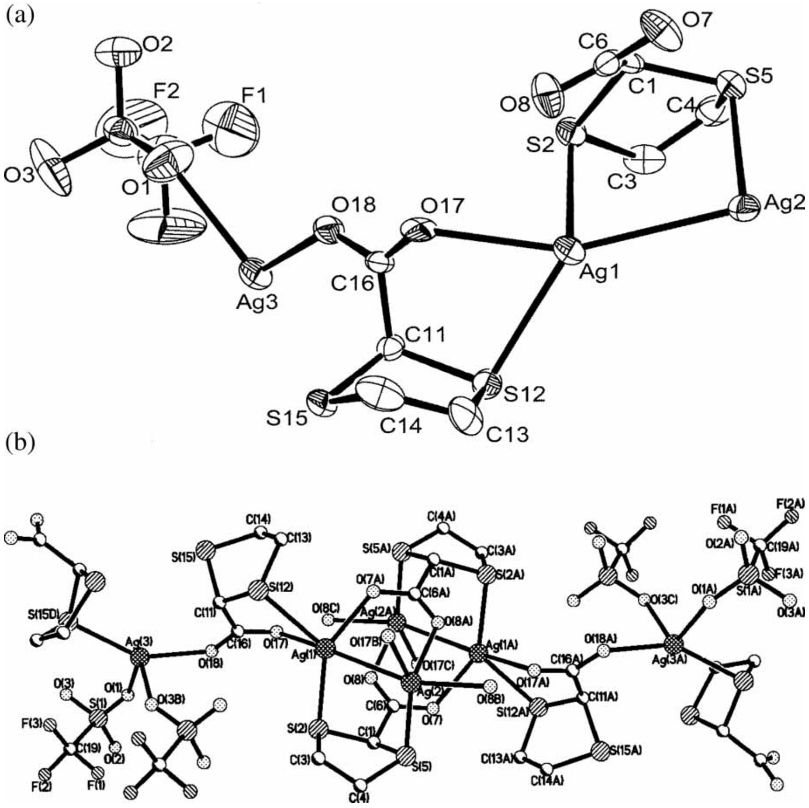


Figure 1. (a) Asymmetric unit of **1-OTf**. (b) Expanded view of **1-OTf**. Symmetry operations: $A = 2 - x, 1 - y, -z$; $B = x, 1 + y, z$; $C = 2 - x, -y, -z$; $D = 3/2 - x, -1/2 + y, 1/2 - z$.

Downloaded At: 13:00 30 January 2011

Table 1. Selected bond lengths (Å) and angles (°) for **1-OTf**.

| | | | |
|---|---|---|---|
| Ag(1)-S(2) | 2.557(3) | Ag(2)-S(5) | 2.423(3) |
| Ag(1)-O(17) | 2.592(9) | Ag(3)-O(18) | 2.272(7) |
| Ag(1)-S(12) | 2.737(3) | Ag(3)-O(1) | 2.567(10) |
| Ag(1)-Ag(2) | 3.0679(13) | | |
| S(2)-Ag(1)-O(17) | 88.17(19) | C(3)-S(2)-Ag(1) | 101.6(4) |
| S(2)-Ag(1)-S(12) | 127.72(9) | C(1)-S(2)-Ag(1) | 102.3(4) |
| O(17)-Ag(1)-S(12) | 67.83(16) | C(1)-S(5)-Ag(2) | 100.8(4) |
| S(2)-Ag(1)-Ag(2) | 81.62(7) | C(4)-S(5)-Ag(2) | 105.4(4) |
| O(17)-Ag(1)-Ag(2) | 155.34(15) | C(13)-S(12)-Ag(1) | 101.2(4) |
| S(12)-Ag(1)-Ag(2) | 135.33(7) | C(11)-S(12)-Ag(1) | 102.4(3) |
| S(5)-Ag(2)-Ag(1) | 95.02(7) | C(16)-O(17)-Ag(1) | 115.6(7) |
| O(18)-Ag(3)-O(1) | 100.4(3) | C(16)-O(18)-Ag(3) | 131.2(7) |
| | | S(1)-O(1)-Ag(3) | 141.8(7) |

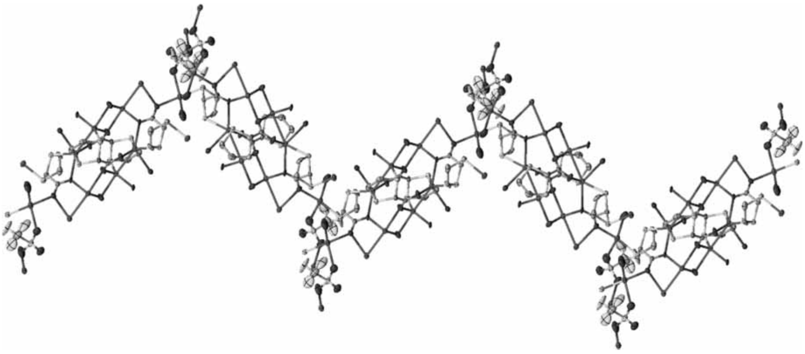


Figure 2. View of an isolated strand of **1-OTf** from the packing diagram.

structure, Ag(1) is pentacoordinate with bonds to carboxyl oxygen atoms from two different ligand molecules (2.294 and 2.607 Å) and bonds to sulfur atoms from two different ligand molecules (2.557 and 2.737 Å). The fifth interaction is with Ag(2), with the Ag(1)-Ag(2) distance of 3.068 Å suggestive of a ligand-supported argentophilic interaction (*14, 15*). The distance between Ag(1) and the adjacent symmetry generated Ag(2) (Ag(2A) in Figure 1(b)) is 3.823 Å, only moderately higher than the sum of the van der Waals radii (3.42 Å) (*16*). Ag(2) is pentacoordinate, with bonds to carboxyl oxygen atoms from three different ligand molecules (2.251–2.557 Å), one bond to a sulfur atom (2.423 Å), and the aforementioned interaction with Ag(1). Ag(3) is tetracoordinate, with bonds to oxygen atoms from two different triflate anions (2.418 and 2.567 Å), one bond to a carboxyl oxygen atom (2.272 Å), and one bond to a sulfur atom (2.484 Å). The packing diagram of **1-OTf** reveals a sheet-like structure in which each sheet consists of twisted strands. An isolated strand in the packing diagram is shown in Figure 2.

Other work in our laboratory has demonstrated that the identity of the counteranion is important in determining the final structure of these complexes. For example, the reaction of hydrolyzed dithiolane esters with silver nitrate does not give the same structure. This system, however, appears to be more complex, as we have determined the existence of more than one structure in crystals of this complex. Full details will be reported in due course.

## 3. Conclusion

In conclusion, we have demonstrated the ligating ability of 1,3-dithiolane-2-carboxylic acid, which can be conveniently generated by *in situ* hydrolysis of the phenyl ester. The formed

1,3-dithiolane-2-carboxylic acid interacts with silver triflate to give a sheet-like polymeric structure. While the dithiolane moiety has been little studied as a complexing group, our studies demonstrate it is effective as a ligating agent.

## 4. Experimental

Silver triflate and all solvents were obtained commercially and used as received. Phenyl 1,3-dithiolane-2-carboxylate was prepared as previously described (*11*). Infrared spectra were obtained on a Nicolet Magna-IR 560 spectrometer E.S.P.

### 4.1. *Synthesis of 1-OTf*

A solution of phenyl 1,3-dithiolane-2-carboxylate (100 mg, 0.44 mmol) in THF (5 ml) was layered over a solution of silver triflate (114 mg, 0.44 mmol) in water (1 ml). After several days in the dark, colorless needles had formed. The crystals were isolated by filtration and washed with THF and water. Yield: 55% (117 mg). mp 174-178°C. Due to the insolubility of the crystals in common organic solvents, NMR spectra could not be obtained. IR (KBr, cm$^{-1}$): 1594, 1382, 1261 1038, 646 (strong), 3449, 2932, 714 cm$^{-1}$ (medium).

### 4.2. *X-ray crystallography*

Data for **1-OTf** were collected at room temperature on a Bruker APEX diffractometer equipped with a CCD detector. The structures were solved by direct methods and subsequent difference Fourier synthesis using SHELXTL program package (Sheldrick, G.M., *SHELXTL* (1990), Bruker Analytical X-Ray Systems, Inc.). CCDC 606988 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk,or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Selected crystal data for **1-OTf** are collected in Table 2. Figure 1(a) was generated using Ortep-3 for Windows (*17*), and Figure 2 was generated using Mercury CSD (*18*).

Table 2. Selected crystal data for **1-OTf**

| | **1-OTf** |
|---|---|
| Empirical formula | $C_9H_{10}Ag_3F_3O_7S_5$ |
| Formula weight | 771.08 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$ (Å) | 15.562(2) |
| $b$ (Å) | 6.0318(8) |
| $c$ (Å) | 20.382(3) |
| $\beta$ (°) | 99.194(2) |
| $V$ (Å$^3$) | 1888.7(4) |
| $Z$ | 4 |
| Density (Mg/m$^3$) | 2.712 |
| $\mu$ (mm$^{-1}$) | 3.692 |
| $R_1$ [$I > 2\sigma(I)$] | 0.081 |
| $wR_2$ (all data) | 0.205 |

Downloaded At: 13:00 30 January 2011

## Acknowledgements

The authors thank the National Science Foundation (Grant No. 0092495) and the Welch Foundation (Grant No. N-1375) for support of this work.

## References

(1) Brammer, L.; Rodger, C.S.; Blake, A.J.; Brooks, N.R.; Champness, N.R.; Cunningham, J.W.; Hubberstey, P.; Teat, S.J.; Wilson, C.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **2002,** 4134–4142.
(2) Knaust, J.M.; Keller, S.W. *CrystEngComm* **2003,** *5,* 459–465.
(3) Green, M.; Draganjac, M.; Jiang, Y.; Nave, P.M.; Cordes, A.W.; Bryan, C.D.; Dixon, J.K.; Folkert, S.L.; Yu, C.H. *J. Chem. Cryst.* **2003,** *33,* 473–479.
(4) Blake, A.J.; Brooks, N.R.; Champness, N.R.; Cunningham, J.W.; Hubberstey, P.; Schröder, M. *CrystEngComm* **2000,** 6–10.
(5) Brooks, N.R.; Blake, A.J.; Champness, N.R.; Cunningham, J.W.; Hubberstey, P.; Teat, S.J.; Wilson, C.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **2001,** 2530–2538.
(6) Edema, J.J.H.; Buter, J.; Van Bolhuis, F.; Meetsma, A.; Kellogg, R.M. *Inorg. Chim. Acta* **1993,** *207,* 263–265.
(7) Rasanen, T.M.; Jaaskelainen, S.; Pakkanen, T.A. *J. Organomet. Chem.* **1997,** *548,* 263–268.
(8) Abel, E.W.; Orrell, K.G.; Qureshi, K.B.; Sik, V. *Polyhedron* **1988,** *7,* 1321–1327.
(9) Abel, E.W.; Orrell, K.G.; Qureshi, K.B.; Sik, V. *Polyhedron* **1988,** *7,* 1329–1333.
(10) Zhang, H.; Gondi, S.R.; Son, D.Y. *Acta Cryst.* **2006,** *E62,* m3086–m3088.
(11) Gondi, S.R.; Son, D.Y. *J. Sulfur Chem.* **2005,** *26,* 13–19.
(12) Bender, M.L. *Chem. Rev.* **1960,** *60,* 53–113.
(13) Affrossman, S.; Murray, J.P. *J. Chem. Soc. (B)* **1966,** 1015–1017.
(14) Amoedo-Portela, A.; Carballo, R.; Casas, J.S.; Garcia-Martinez, E.; Gomez-Alonso, C.; Sanchez-Gonzalez, A.; Sordo, J.; Vazquez-Lopez, E.M. *Z. Anorg. Allg. Chem.* **2002,** *628,* 939–950.
(15) Xie, Y.-B.; Bu, X.-H. *J. Clust. Sci.* **2003,** *14,* 471–482.
(16) Bondi, A. *J. Phys. Chem.* **1964,** *68,* 441–451.
(17) Farrugia, L.J. *J. Appl. Cryst.* **1997,** *30,* 565.
(18) Macrae, C.F.; Edgington, P.R.; McCabe, E.; Pidcock, E.; Shields, G.P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Cryst.* **2006,** *39,* 453–457.

Downloaded At: 13:00 30 January 2011