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NOTE

Solvent Evaporation Synthesis and Crystal Structure of Tetra(thiophene-3,4-dicarboxylate)tetrahydrate

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One new thiophene compound from 3,4-dibromothiophene, butyl lithium and anhydrous ether has been successfully synthesized. The compound has been characterized by X-ray single-crystal diffraction and shows a one-dimensional framework. The 3D supramolecular structure is formed *via* hydrogen bonding formation.

Keywords: Solvent evaporation, Crystal structure, Tetra(thiophene-3,4-dicarboxylate)tetrahydrate.

Thiophenes and their derivatives have been of interest for use in next generation electronic materials owing to their ease of production, synthetic versatility and low cost compared to traditional inorganic materials[1]. Uuntill now, there are a few examples of thiophenes derivatives which have been synthesized and characterized[2,3]. As part of our work, we report the synthesis and crystal structure of the title compound.

All reagent and solvents employed were commercially available and used as received without further purification.

General procedure: To a stirred suspension of ethereal butyl lithium (0.4 mol) at 203 K was added 3,4-dibromo thiophene (30.5 g, 0.126 mol) over 5 min. The mixture was stirred at 203 K for 0.5 h and then poured slowly into a slurry of dry ice in anhydrous ether. After 3 h, water (200 mL) was added to the ethereal suspension. The aqueous layer was separated and the ethereal layer was extracted several times with water. The combined aqueous phase was washed with ether and then warmed to remove dissolved ether. After cooling to 298 K, a small amount of a solid was filtered off. The filtrate was acidified to pH 1 with concentrated HCl and immersed in an ice-water bath. After several hours, the solid was filtered off. Colourless crystals of the compound formed.

Diffraction intensity data of the single crystal of the compound was collected on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å) by using a ω-scan mode. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHEXL 97[4]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement (Fig. 1). The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table-1. Selected bond and angle parameters are listed in Table-2.

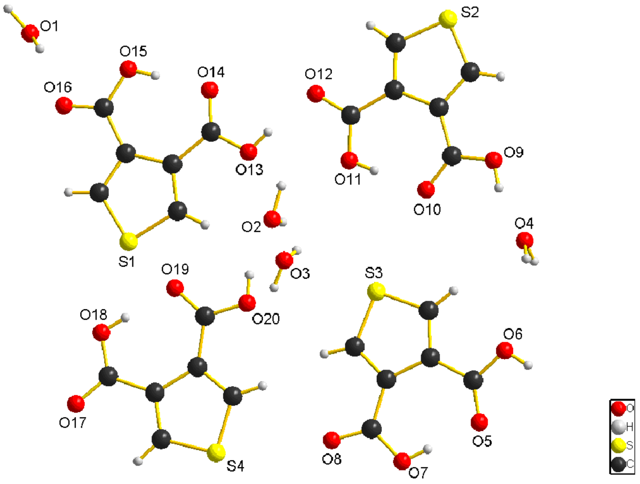

Fig. 1. Molecular structure of the title compound at 30 % probability displacement ellipsoids

X-ray diffraction analysis revealed that the fundamental building unit consists of tetrad (thiophene-3,4-dicarboxylate) and tetrahydrate as bridging ligands to construct a new coordination polymer. The C2-C5 and C3-C6 bond lengths are nearly

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY FOR THIOPHENE COMPOUND

Empirical formula	$C_{24}H_{24}O_{20}S_4$	Z, Calculated density (mg/m^3)	2, 1.641
Formula weight	760.67	Absorption coefficient (mm^{-1})	0.399
Crystal system space group	Triclinic, P-1	F(000)	784
Unit cell dimensions	a = 7.4394(10)Å	Limiting indices	$-9 \leq h \leq 8$
	b = 14.332(2)Å		$-17 \leq k \leq 17$
	c = 14.672(2)Å		$-17 \leq l \leq 17$
Volume (Å^3)	1539.8(4)	Largest diff. peak and hole (e/Å^3)	0.193 and-0.257
θ Range for data collection	2.78-25.50	Goodness-of-fit on F^2	1.016
Final R indices [I>2σ(I)]	R_1 = 0.0366; wR_2 = 0.0892	R indices (all data)	R_1 = 0.0530; wR_2 = 0.0996

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THIOPHENE COMPOUND

S(1)-C(13)	1.692(2)	S(3)-C(1)	1.700(2)
S(2)-C(7)	1.693(2)	S(4)-C(19)	1.696(2)
F(3)-C(1)	1.326(3)	O(1)-C(4)	1.222(2)
C(13)-S(1)-C(16)	91.76(10)	O(5)-C(6)-O(6)	122.20(19)
C(7)-S(2)-C(10)	91.69(10)	O(10)-C(11)-O(9)	122.4(2)
C(4)-S(3)-C(1)	91.67(10)	O(16)-C(18)-O(15)	119.3(2)
C(22)-S(4)-C(19)	91.61(10)	O(19)-C(24)-O(20)	122.31(19)

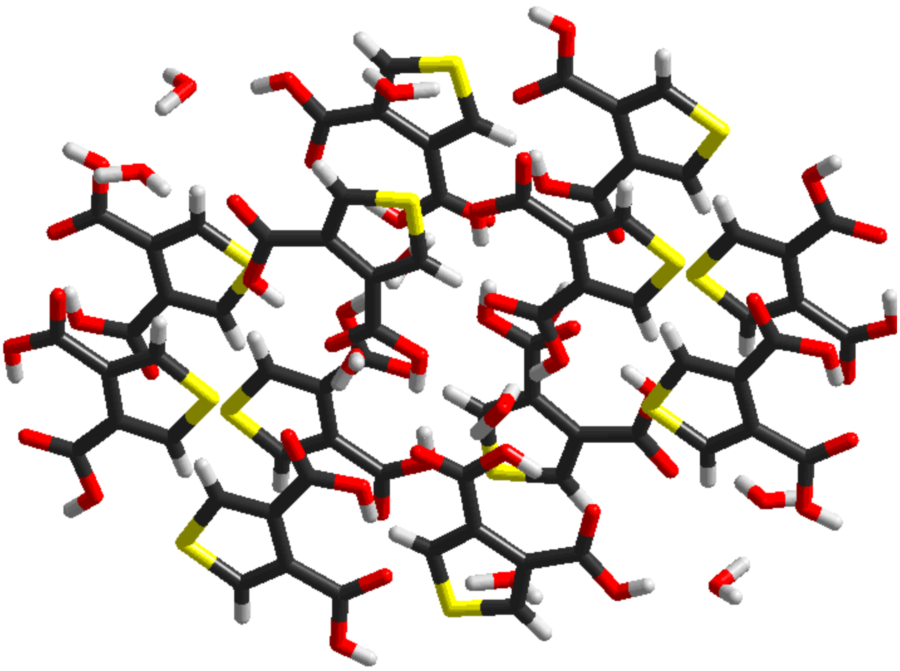

Fig. 2. 3D Structure formed *via* hydrogen bonding interactions

identical at 1.808(3) Å, 1.804(3) Å, respectively. The carboxylic and the carboxylate group as well as the water molecule. Some are listed as follows: O(18)-H(18)...O(19), [O...O = 2.527(2)\%A, O--H...O = 176.3\%]; O(15)-H(15)...O(14), [O...O = 2.531(2)\%A, O--H...O = 175.8\%]; O(13)-H(13)...O(11), [O...O = 3.116(2)\%A, O--H...O = 117.5\%];O(13)-H(13)...O(12), [O...O = 2.647(2)\%A, O--H...O = 172.1\%]; O(11)-H(11)...O(10), [O...O = 2.519(2) \%A, O--H...O = 178.4\%]; O(9)-H(9)...O(4), [O...O = 2.537(2)\%A, O--H...O = 164.9\%]; O(7)-H(7)...O(5), [O...O = 2.543(2)\%A, O--H...O = 176.3\%]; O(4)-H(8W)...O(1)#1, [O...O = 2.729(3)\%A, O--H...O = 146.6\%]; O(3)-H(5W)...O(8) #2, [O...O = 2.826(2)\%A, O--H...O = 169.9\%]; O(2)-H(4W)...O(3), [O...O = 2.892(3)\%A, O--H...O = 148.5\%]; O(1)-H(2W)...O(16), [O...O = 2.802(2)\%A, O--H...O = 154.5\%]. Symmetry codes: #1 -x + 1, -y + 1, -z + 1; #2 -x + 1, -y, -z + 1. The chains are further assembled by the intermolecular hydrogen bonding interaction leading to the formation of a 3D framework (Fig. 2).

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