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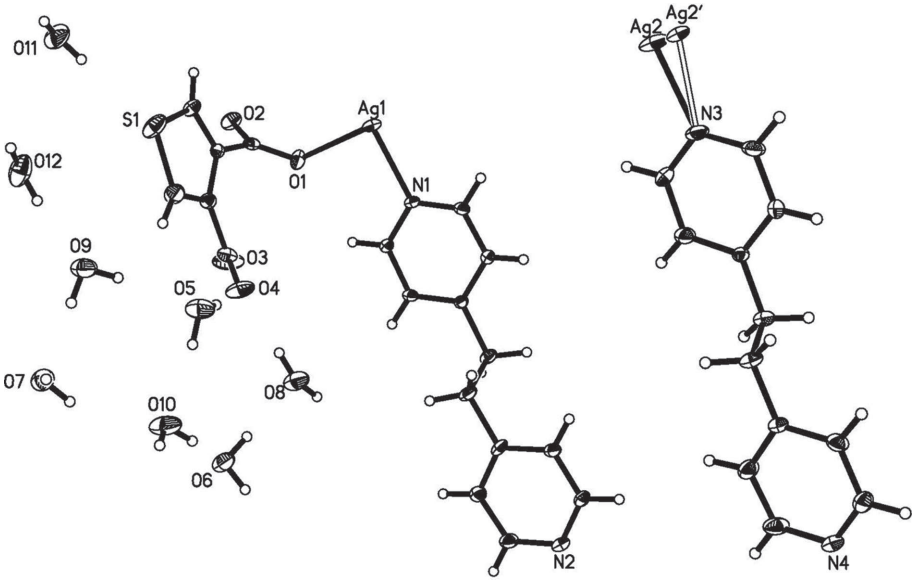
Crystal structure of poly[(thiophene-3, 4-dicarboxylato-κ^1*O*)bis[1,2-bis(4-pyridyl)ethane-κ^2*N*:*N*′]silver(I)] octahydrate, $C_{30}H_{42}Ag_2N_4O_{12}S$



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Abstract

$C_{30}H_{42}Ag_2N_4O_{12}S$, monoclinic, *Pc* (no. 7), $a = 11.4150(3)$ Å, $b = 17.3038(9)$ Å, $c = 9.3802(5)$ Å, $\beta = 104.701(4)°$, $V = 1792.15(14)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0320$, $wR_{ref}(F^2) = 0.0638$, $T = 293(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.20 × 0.18 × 0.16 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	12.2 cm^{-1}
Diffractometer, scan mode:	Xcalibur Eos, φ and ω
$2\theta_{max}$, completeness:	50°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6576, 4195, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3760
$N(param)_{refined}$:	453
Programs:	SHELX [1], CrysAlis^{PRO}

Source of materials

An excess of an aqueous NH_3 solution was slowly added to a suspension of $AgNO_3$ (0.0169 g, 0.1 mmol) in MeOH/H_2O (6 mL, 5:1 v/v), and the mixture was stirred for 30 min. Thiophene-3,4-dicarboxylic acid (0.0086 g, 0.05 mmol), 1,2-bis(4-pyridyl)ethane (bpa) (0.0184 g, 0.1 mmol) were then

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ag1	0.07394(3)	0.46122(2)	0.12248(6)	0.05222(13)
Ag2[a]	0.3113(2)	0.9996(8)	0.3502(4)	0.0695(15)
Ag2′[b]	0.3075(6)	1.0311(10)	0.3366(9)	0.0521(15)
C1	0.4893(5)	0.9323(4)	0.1988(7)	0.0590(17)
H1	0.4505	0.8879	0.2190	0.071*
C2	0.5828(7)	0.9246(3)	0.1327(9)	0.0545(14)
H2	0.6041	0.8757	0.1065	0.065*
C3	0.6456(5)	0.9882(3)	0.1045(6)	0.0330(13)
C4	0.6045(5)	1.0587(3)	0.1416(7)	0.0434(14)
H4	0.6423	1.1039	0.1234	0.052*
C5	0.5084(5)	1.0629(4)	0.2049(6)	0.0541(16)
H5	0.4822	1.1113	0.2271	0.065*
C6	0.7504(5)	0.9831(3)	0.0382(6)	0.0429(15)
H6A	0.7474	1.0258	−0.0297	0.051*
H6B	0.7456	0.9353	−0.0171	0.051*
C7	0.8713(5)	0.9856(4)	0.1579(7)	0.0510(16)
H7A	0.8736	1.0319	0.2169	0.061*
H7B	0.8759	0.9413	0.2224	0.061*
C8	0.9781(5)	0.9852(3)	0.0933(6)	0.0370(14)
C9	1.0230(5)	0.9196(3)	0.0469(7)	0.0606(17)
H9	0.9894	0.8720	0.0607	0.073*
C10	1.1170(5)	0.9224(4)	−0.0198(8)	0.0668(19)
H10	1.1441	0.8764	−0.0518	0.080*
C11	1.1291(5)	1.0511(4)	0.0066(7)	0.0546(17)
H11	1.1653	1.0978	−0.0066	0.066*
C12	1.0356(5)	1.0524(3)	0.0737(7)	0.0517(16)
H12	1.0111	1.0991	0.1060	0.062*
C13	0.2790(5)	0.4019(3)	−0.0059(6)	0.0393(14)
H13	0.2577	0.3549	0.0285	0.047*
C14	0.3761(5)	0.4045(3)	−0.0701(6)	0.0381(13)
H14	0.4188	0.3597	−0.0784	0.046*
C15	0.4088(5)	0.4731(3)	−0.1210(6)	0.0313(13)
C16	0.3427(6)	0.5379(3)	−0.1061(7)	0.0450(16)
H16	0.3625	0.5858	−0.1385	0.054*
C17	0.2481(6)	0.5308(3)	−0.0432(8)	0.0452(17)
H17	0.2037	0.5750	−0.0355	0.054*
C18	0.5164(5)	0.4782(3)	−0.1898(6)	0.0398(14)
H18A	0.5128	0.4358	−0.2585	0.048*
H18B	0.5120	0.5262	−0.2443	0.048*
C19	0.6349(5)	0.4748(3)	−0.0722(7)	0.0458(16)
H19A	0.6427	0.4246	−0.0247	0.055*
H19B	0.6346	0.5138	0.0020	0.055*
C20	0.7432(5)	0.4883(4)	−0.1372(6)	0.0401(16)
C21	0.8155(5)	0.4293(4)	−0.1607(7)	0.0472(14)
H21	0.8021	0.3792	−0.1326	0.057*
C22	0.9086(6)	0.4442(4)	−0.2262(8)	0.0502(17)
H22	0.9569	0.4032	−0.2408	0.060*
C23	0.8606(5)	0.5716(4)	−0.2476(7)	0.0452(15)
H23	0.8737	0.6211	−0.2793	0.054*
C24	0.7680(5)	0.5610(4)	−0.1804(7)	0.0431(15)
H24	0.7221	0.6030	−0.1643	0.052*
C25	0.1178(4)	0.2745(3)	0.3646(5)	0.0331(11)
C26	0.0715(5)	0.2916(3)	0.4814(6)	0.0454(13)
H26	−0.0103	0.3006	0.4731	0.054*
C27	0.2887(5)	0.2729(4)	0.5569(7)	0.0633(18)
H27	0.3700	0.2676	0.6061	0.076*
C28	0.2463(4)	0.2640(3)	0.4089(6)	0.0399(12)
C29	0.0407(4)	0.2720(3)	0.2100(6)	0.0369(12)
C30	0.3244(5)	0.2400(3)	0.3099(7)	0.0505(14)
N1	0.2151(5)	0.4654(3)	0.0077(6)	0.0388(14)
N2	0.9328(5)	0.5149(4)	−0.2699(6)	0.0428(13)
N3	0.4515(5)	1.0004(4)	0.2355(7)	0.0531(16)
N4	1.1705(5)	0.9875(3)	−0.0404(6)	0.0456(14)
O1	0.0686(4)	0.31415(18)	0.1169(5)	0.0548(8)
O2	−0.0501(3)	0.2281(2)	0.1861(4)	0.0556(10)
O3	0.2817(3)	0.1943(3)	0.2104(6)	0.0893(16)
O4	0.4285(3)	0.2673(3)	0.3376(5)	0.0811(14)
O5	0.5843(4)	0.3153(3)	0.6076(5)	0.0812(14)
H5A	0.5419	0.3046	0.5216	0.122*
H5B	0.6559	0.2984	0.6182	0.122*
O6	0.7931(3)	0.2026(3)	0.3612(5)	0.0710(13)
H6C	0.8417	0.2104	0.3075	0.107*
H6D	0.7316	0.2271	0.3071	0.107*
O7	0.7764(3)	0.1832(3)	0.9401(4)	0.0712(12)
H7C	0.7979	0.1849	0.8598	0.107*
H7D	0.8088	0.2204	0.9952	0.107*
O8	0.5950(3)	0.2794(3)	0.1875(5)	0.0823(14)
H8A	0.5430	0.2757	0.2330	0.123*
H8B	0.6026	0.2749	0.1001	0.123*
O9	0.5515(4)	0.2484(3)	0.8748(5)	0.0793(14)
H9A	0.6215	0.2280	0.8948	0.119*
H9B	0.5492	0.2623	0.7863	0.119*
O10	0.8111(4)	0.2424(3)	0.6438(5)	0.1015(18)
H10A	0.8194	0.2443	0.5564	0.152*
H10B	0.8759	0.2576	0.7038	0.152*
O11	0.0253(4)	0.2399(3)	0.8564(4)	0.0950(17)
H11A	0.0390	0.2624	0.9375	0.142*
H11B	0.0640	0.2532	0.8029	0.142*
O12	0.3242(4)	0.1822(3)	0.9342(5)	0.1005(19)
H12A	0.3887	0.1946	0.9103	0.151*
H12B	0.3172	0.2094	1.0069	0.151*
S1	0.17910(14)	0.29462(12)	0.64327(17)	0.0768(6)

[a]Occupancy: 0.72(3); [b]Occupancy: 0.28(3).

slowly added, and stirring was continued for another 30 min. The resultant colorless solution was allowed to stand in the dark at room temperature for a week. Colorless prism crystals of the title complex were obtained.

Experimental details

Absorption corrections were applied by using multi-scan program. Hydrogen atoms attached to C and O of the title complex and water molecules were located in difference electron density maps, and treated as riding atoms. The U_{iso} values of the hydrogen atoms of water molecules were set to $1.5U_{eq}$(O) and the U_{iso} values of all other hydrogen atoms were set to $1.2U_{eq}$(C). Silver atom Ag2 is disordered over two closely separated positions (Ag2, Ag2′) in the ratio of 0.28:0.72. Flack parameter: 0.00(10).

Comment

In the past decades, the syntheses of silver (I) complexes have attracted great interest because the silver(I) exhibits diverse coordination geometries such as linear, trigonal, square-planar and octahedral ones [2–6]. In recent years, many MOFs with more than two polymeric substructures in the crystalline state have been reported, which usually occur in an interpenetrating fashion [7, 8]. However, examples of metal-organic frameworks involving more than one coordination polymer with different structural motifs in a single crystal structures are rare [9, 10]. With the aim of constructing unusual coordination architectures, we have engaged in the synthesis of coordination polymers based on a new thiophene-3,4-dicarboxylic acid with silver center.

Single crystal structure analysis reveals that the title complex consists of two crystallographically independent Ag(I), one thiophene-3,4-dicarboxylato ligand, two bpa ligands and eight water molecules. As shown in the Figure, the central Ag1 cation adopts T-shaped coordination with two nitrogen atoms from two bpa ligands [Ag1—N1 = 2.141(2) and Ag1—N2′ = 2.157(7) Å, N2′—Ag1—N1 = 167.32(3)° (′ = −1+x, 1−y, z+1/2′)] in the horizontal direction. The coordination sphere is completed by one oxygen of one deprotonated L^{2-} [Ag1–O1 = 2.547(4) Å] in the axial direction. While the Ag2 adopts linear geometry [Ag2—N3 = 2.118(8) and Ag2—N4″ = 2.146(7) Å, N3—Ag2—N4″ = 177.71(3)° (″ = −1+x, 2−y, z+1/2′)] being coordinated by two nitrogen atoms from two different bpa ligands. In the title complex, each bpa ligand as a bidentate ligand links Ag(I) centers to form infinite 1D chains. There are two kinds of Ag-bpa chains (herein designated as A and B). Within chain A, bpa ligands bridge crystallographically unique Ag1 centers into an infinite Ag-bpa chain, with the thiophene-3,4-dicarboxylic acid ligand dangling on the side. Chain B is exclusively constructed with Ag2 ions and bpa ligands. Interestingly, water molecules are located in the gaps between the two types of chains. Adjacent chains are linked through hydrogen bonding interactions, resulting in three-dimensional frameworks.

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