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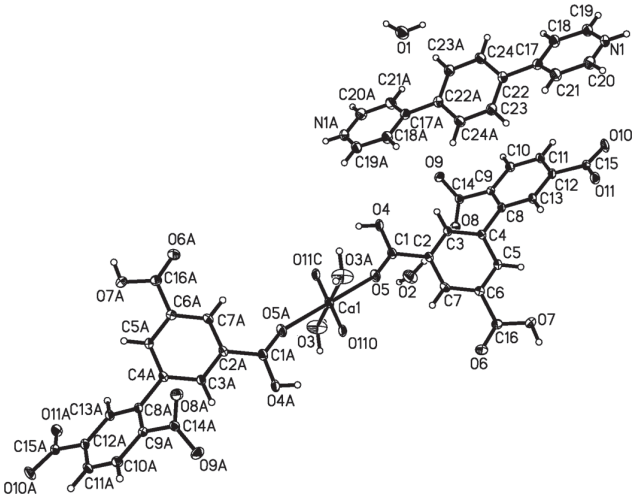
Crystal structure of 4,4′-(1,4-phenylene)bis(pyridin-1-ium) *catena*-poly[diaqua-bis(μ_2-3′,5′-dicarboxy-[1,1′-biphenyl]-2,5-dicarboxylato-κ^2O:O')] dihydrate, $C_{48}H_{42}O_{22}N_2Ca$



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Abstract

$C_{48}H_{42}O_{22}N_2Ca$, triclinic, $P\bar{1}$ (no. 2), $a = 7.2548(2)$ Å, $b = 11.7056(4)$ Å, $c = 14.6024(4)$ Å, $\alpha = 72.687(3)°$, $\beta = 82.667(2)°$, $\gamma = 73.303(3)°$, $V = 1132.76(6)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0403$, $wR_{ref}(F^2) = 0.0993$, $T = 293(2)$ K.

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

Source of material

A mixture of $Ca(OAc)_2 \cdot H_2O$ (0.1 mmol, 0.0176 g), biphenyl-2,5,3′,5′-tetracarboxylic acid (0.1 mmol, 0.033 g), 1,4-di(pyridin-4-yl)benzene (0.2 mmol, 0.015 g) and distilled water (10 mL) was heated in a 25 mL stainless steel reactor

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Table 1: Data collection and handling.

Crystal:	Block, colourless
Size:	0.41 × 0.32 × 0.28 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.23 mm^{-1}
Diffractometer, scan mode:	Bruker FRAMBO, φ and ω-scans
$2\theta_{max}$, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13169, 4209, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3588
$N(param)_{refined}$:	333
Programs:	Bruker programs [1], SHELX [2]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Ca1	1.0000	0.0000	0.0000	0.02588(15)
N1	0.2888(3)	1.01816(15)	0.45096(12)	0.0345(4)
H1	0.2532	1.0972	0.4424	0.041*
O1	0.4591(3)	0.18976(17)	0.83379(12)	0.0547(5)
H1W	0.4119	0.2740	0.8305	0.082*
H2W	0.5978	0.1585	0.8399	0.082*
O2	0.2174(3)	0.11264(16)	0.17397(13)	0.0566(5)
H3W	0.1683	0.0445	0.1937	0.085*
H4W	0.1453	0.1591	0.2146	0.085*
O3	0.8053(3)	−0.13190(19)	0.01694(13)	0.0672(6)
H5W	0.6933	−0.1436	0.0546	0.101*
H6W	0.7656	−0.1347	−0.0415	0.101*
O4	0.6941(2)	0.12995(13)	0.22316(9)	0.0355(4)
H4	0.7710	0.0613	0.2332	0.053*
O5	0.7544(2)	0.12476(14)	0.07079(10)	0.0426(4)
O6	0.3233(2)	0.44671(14)	−0.17993(10)	0.0420(4)
O7	0.1378(2)	0.61116(13)	−0.13538(10)	0.0333(3)
H7	0.0994	0.6317	−0.1899	0.050*
O8	0.0341(2)	0.27860(12)	0.29264(9)	0.0309(3)
O9	0.1961(2)	0.26086(13)	0.41699(10)	0.0406(4)
O10	−0.0899(2)	0.91697(13)	0.28802(10)	0.0425(4)
O11	0.1001(2)	0.90262(12)	0.15765(9)	0.0322(3)
C1	0.6625(3)	0.17342(17)	0.13190(14)	0.0265(4)
C2	0.5037(2)	0.28865(16)	0.10597(13)	0.0216(4)
C3	0.4078(2)	0.34745(16)	0.17488(13)	0.0216(4)
H3	0.4418	0.3134	0.2385	0.026*
C4	0.2618(2)	0.45656(16)	0.14985(12)	0.0206(4)
C5	0.2147(2)	0.50630(17)	0.05356(13)	0.0224(4)
H5	0.1187	0.5800	0.0355	0.027*
C6	0.3090(2)	0.44742(17)	−0.01549(13)	0.0227(4)
C7	0.4535(3)	0.33835(17)	0.01096(13)	0.0242(4)
H7A	0.5168	0.2984	−0.0350	0.029*
C8	0.1599(2)	0.52225(16)	0.22214(12)	0.0212(4)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C9	0.0900(3)	0.46126(16)	0.31216(12)	0.0218(4)
C10	−0.0050(3)	0.52967(17)	0.37542(13)	0.0273(4)
H10	−0.0523	0.4892	0.4347	0.033*
C11	−0.0309(3)	0.65637(17)	0.35245(13)	0.0278(4)
H11	−0.0953	0.7005	0.3957	0.033*
C12	0.0403(3)	0.71765(17)	0.26370(13)	0.0243(4)
C13	0.1340(3)	0.64953(16)	0.20039(13)	0.0233(4)
H13	0.1811	0.6905	0.1413	0.028*
C14	0.1083(3)	0.32310(17)	0.34219(13)	0.0236(4)
C15	0.0143(3)	0.85504(17)	0.23481(13)	0.0274(4)
C16	0.2583(3)	0.50040(18)	−0.11864(13)	0.0265(4)
C17	0.3978(3)	0.76490(18)	0.47631(14)	0.0291(4)
C18	0.2905(3)	0.81753(19)	0.54730(15)	0.0344(5)
H18	0.2548	0.7665	0.6049	0.041*
C19	0.2377(3)	0.94354(19)	0.53270(15)	0.0353(5)
H19	0.1655	0.9774	0.5803	0.042*
C20	0.3946(3)	0.9715(2)	0.38244(15)	0.0388(5)
H20	0.4306	1.0250	0.3263	0.047*
C21	0.4512(3)	0.84654(19)	0.39320(15)	0.0364(5)
H21	0.5258	0.8159	0.3447	0.044*
C22	0.4509(3)	0.62914(18)	0.48863(14)	0.0292(4)
C23	0.4801(3)	0.58160(19)	0.40948(15)	0.0357(5)
H23	0.4665	0.6360	0.3481	0.043*
C24	0.4716(3)	0.54417(19)	0.57991(15)	0.0355(5)
H24	0.4523	0.5732	0.6341	0.043*

with a Teflon liner at 413 K for 45 h, and then slowly cooled down to room temperature. Colourless block crystals of the title compound were obtained.

Experimental details

C-bound hydrogen atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2 U_{eq}(C). The hydrogen atom of the hydroxyl group was allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density, with U_{iso}(H) set to 1.5 U_{eq}(O).

Discussion

The synthetic development of coordination polymers (CPs) continues to attract much attention because of their intriguing structural topologies and potential applications in gas storage, separation, sensing and heterogeneous catalysis [3–6]. In the construction of CPs, multidentate organic ligands play a vital role since the structural integrity of these ligands in most cases remains unaltered throughout the mixed-ligands strategy incorporating *N*-donor colinkers with different lengths and rigidness/exibility has been proved successful to create various CPs. In particular, different conformations of the ligand often play an important role in the self-assembly processes to form metal-organic coordination polymers. The organic carboxylate ligands have been proven to be good candidates for the construction of CPs [7–10]. Thus, polycarboxylates have been widely utilized to construct coordination polymers [11, 12]. We chose 2,3′,5,5′-biphenyltetracarboxylic acid and 1,4-di(pyridin-4-yl) benzene to construct a new compound. In the course of this study the pure organic title compound was surprisingly obtained.

The asymmetric unit of the title structure contains one half of a Ca(II) ion, one 5,5′-dicarboxy-(1,10-biphenyl)-2,3′-dicarboxylate, one 4,4′-(1,4-phenylene)bis(pyridin-1-ium) cation and one water molecule. The calcium atom is six-coordinated by four oxygen atoms from two biphenyl-2,5,3′,5′-tetracarboxylate ligands, the Ca—O bond lengths range from 2.3040(13) to 2.3486(13) Å, and by two oxygen atoms from coordinated water molecules. The Ca—O3 bond length is 2.3186(18) Å. The O—Ca—O angles are in the range of 84.37(5)° to 180°. In addition, there are intermolecular hydrogen bonds between uncoordinated water molecules with adjacent biphenyl-2,5,3′,5′-tetracarboxylate anions: d(O(1)—H(1W)...O(6)B) = 2.837(2) Å, d(O(1)—H(2W)...O(11)A) = 3.073(2) Å, d(O(2)—H(4W)...O(8)) = 2.912(2) Å, d(O(2)—H(3W)...O(11)C) = 2.903(2) Å. Symmetry codes: A $-x+1, -y+1, -z+1$; B $x, y, z+1$; C $x, y-1, z$. These interactions result in an infinite three dimensional architecture. The bond lengths and angles are generally in the expected ranges [13, 14].

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