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Poly[bis(dimethylformamide- κ O)-(μ_8 -5,5''-dicarboxy-[1,1':4',1''-terphenyl]-2',3,3'',5'-tetracarboxylato- κ^8 O:O¹:O²:O³:O⁴:O⁵:O⁶:O⁷)dizinc(II)] – dimethylformamide (1/2), C₁₈H₁₉N₂O₈Zn

Abstract

C₁₈H₁₉N₂O₈Zn, orthorhombic, *Pbca* (no. 61), $a = 17.4714(12)$ Å, $b = 10.9180(7)$ Å, $c = 20.0697(14)$ Å, $V = 3828.4(4)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0449$, $wR_{\text{ref}}(F^2) = 0.1492$, $T = 100$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.33 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	18620, 3373, 0.059
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2334
$N(\text{param})_{\text{refined}}$:	264
Programs:	SHELX [1], Bruker Programs [2]

Source of material

Functional organic ligand [1,1':4',1''-terphenyl]-2',3,3'',5,5',5''-hexacarboxylic acid (H_6L) was purchased from Jinan Camolai Trading Company (China), and other reagents were of analytical grade and also commercially available and used as received. A mixture of H_6L (98.9 mg, 0.2 mmol), Zn(CH₃COO)₂ · 2H₂O (43.8 mg, 0.2 mmol) and 10 mL DMF were placed in a 15 mL Teflon-lined autoclave at 413 K for 3 days, then cooled to room temperature. Colorless block crystals were obtained in a yield of 52% (based on Zn).

Experimental details

The structure was solved by direct methods and refined using the SHELX software [1]. All hydrogen atoms were placed in the calculated positions.

Comment

Previously literature has confirmed that due to the degree of deprotonation, defines the number of metal centers each ligand is able to connect. The partially deprotonated H_6L

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	−0.1409(2)	0.0401(4)	0.0251(3)	0.0252(11)
C2	−0.2165(2)	0.0886(4)	0.0498(2)	0.0227(10)
C3	−0.2159(3)	0.1742(4)	0.1004(3)	0.0287(11)
H3	−0.1689	0.1963	0.1210	0.034*
C4	−0.2832(3)	0.2277(4)	0.1213(2)	0.0275(11)
C5	−0.2815(3)	0.3209(5)	0.1757(3)	0.0406(14)
C6	−0.3526(2)	0.1917(4)	0.0930(2)	0.0232(10)
H6	−0.3990	0.2286	0.1074	0.028*
C7	−0.3540(2)	0.1018(4)	0.0437(2)	0.0175(9)
C8	−0.2854(2)	0.0536(4)	0.0214(2)	0.0198(9)
H8	−0.2855	−0.0043	−0.0140	0.024*
C9	−0.4292(2)	0.0523(4)	0.0191(2)	0.0173(9)
C10	−0.4385(2)	−0.0732(4)	0.0139(2)	0.0188(9)
H10	−0.3962	−0.1249	0.0235	0.023*
C11	−0.4918(2)	0.1266(4)	0.0051(2)	0.0173(9)
C12	−0.4882(2)	0.2651(4)	0.0038(2)	0.0168(9)
C13	0.0025(5)	−0.1946(8)	0.3043(4)	0.093(3)
H13A	−0.0168	−0.2576	0.2738	0.140*
H13B	−0.0379	−0.1718	0.3358	0.140*
H13C	0.0467	−0.2266	0.3287	0.140*
C14	0.0573(5)	0.0123(6)	0.3039(3)	0.069(2)
H14A	0.0803	0.0720	0.2734	0.104*
H14B	0.0966	−0.0191	0.3343	0.104*
H14C	0.0167	0.0521	0.3298	0.104*
C15	0.0199(3)	−0.0824(5)	0.2022(3)	0.0365(12)
H15	−0.0025	−0.1505	0.1801	0.044*
C16	−0.1629(5)	0.2290(9)	0.3636(6)	0.126(4)
H16A	−0.1168	0.1833	0.3511	0.188*
H16B	−0.1640	0.2402	0.4120	0.188*
H16C	−0.1623	0.3093	0.3417	0.188*
C17	−0.3014(5)	0.2106(8)	0.3627(5)	0.101(3)
H17A	−0.3097	0.2903	0.3414	0.151*
H17B	−0.3031	0.2202	0.4112	0.151*
H17C	−0.3415	0.1535	0.3486	0.151*
C18	−0.2246(5)	0.0712(8)	0.3025(5)	0.091(3)
H18	−0.2700	0.0355	0.2850	0.109*
N1	0.0255(3)	−0.0873(4)	0.2663(2)	0.0440(12)
N2	−0.2281(3)	0.1636(4)	0.3434(3)	0.0486(13)
O1	−0.08762(18)	0.0348(3)	0.06653(18)	0.0356(9)
O2	−0.13633(17)	0.0137(3)	−0.03536(19)	0.0330(8)
O3	−0.2205(2)	0.3625(5)	0.1961(3)	0.0765(16)
O4	−0.3469(2)	0.3545(4)	0.1990(2)	0.0587(13)
H4	−0.3398	0.4085	0.2299	0.088*
O5	−0.51309(18)	0.3214(3)	0.05340(17)	0.0264(7)
O6	−0.46262(18)	0.3108(3)	−0.04835(17)	0.0282(8)
O7	0.04164(19)	0.0040(3)	0.16738(17)	0.0319(8)
O8	−0.1574(4)	0.0286(6)	0.2860(4)	0.115(2)
Zn1	0.02790(3)	0.00792(4)	0.06918(2)	0.01817(19)

exhibits nine different coordination modes [3] and plays an important role in the construction of functional MOFs. Up to now, there are more than ten cases of MOFs with distinctive structures and photoluminescence properties have been self-assembled by Zn(NO₃)₂ and *H₆L* through a systematic solvent-ratio-controlled or temperature-modulated solvothermal method [4–6]. In the present work, a novel 2D

zinc framework was synthesized by utilizing *H₆L* and zinc acetate dihydrate.

As shown in the upper view of the figure, the asymmetric unit of title compound consists of one Zn(II) atom, one half of an *H₆L* ligand, one coordinated *N,N*-dimethylformamide and one additional *N,N*-dimethylformamide molecule. In the structure, it can be seen that only four carboxyl groups of each ligand are deprotonized and connected with eight metal ions. Each Zn(II) centre is five coordinated by four oxygen atoms (O1, O2, O5 and O6) derived from four different *L*^{4−} ligands and one oxygen atom (O7) derived from coordinated *N,N*-dimethylformamide molecule, resulting in a slightly distorted trigonal-bipyramid [ZnO₅] coordination geometry. The bond angles around the Zn(II) atom vary from 86.29(13)° to 159.20(14)°, and the Zn–O bond distances range from 1.986(3) Å to 2.077(3) Å, which are consistent with the previously reported examples [7, 8]. Moreover, it is worth noting that the sum of three bond angles O5–Zn1–O7, O7–Zn1–O6, O6–Zn1–O5 is exactly 360°, demonstrating the O5, O6 and O7 atoms are highly coplanar.

As seen from the lower view of the figure (all solvent molecules and hydrogen atoms have been omitted), although the O3 and O4 atoms in each ligand are not involved in coordination, the Zn (II) center adopts the above coordination modes to connect with four adjacent ligands, forming a 2D network (perpendicular to the *c*-axis) with the DMF molecules in the gaps.

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