Crystal structure of *catena*-[pyridine-μ-biphenyl-3,3'-dicarboxylato -κ^4*O,O':O'',O'''*-zinc(II)], $C_{61}H_{37}NO_{16}Zn_4$

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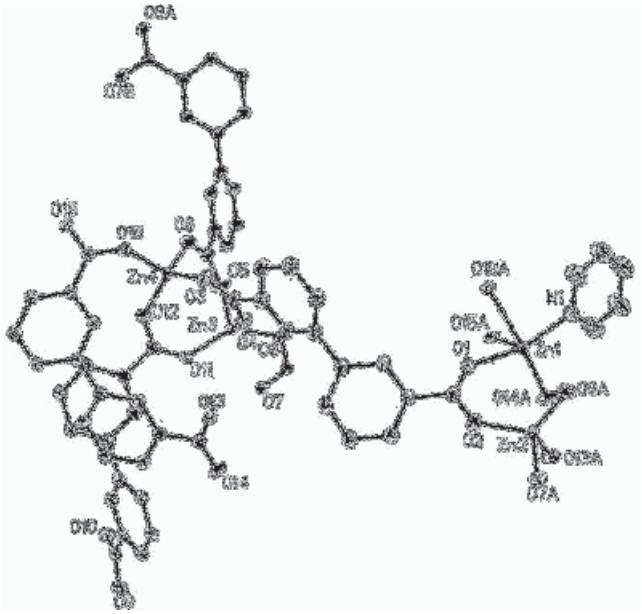

Abstract

$C_{61}H_{37}NO_{16}Zn_4$, monoclinic, $P2_1/c$ (no. 14), a = 12.585(6) Å, b = 19.704(8) Å, c = 23.047(5) Å, β = 108.43(1)°, V = 5422.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.0476, $wR_{ref}(F^2)$ = 0.1168, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless plates, size 0.12×0.13×0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	18.23 cm^{-1}
Diffractometer, scan mode:	Bruker APEX2 CCD, φ and ω
$2\theta_{max}$:	55.18°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	33280, 12371
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7852
$N(param)_{refined}$:	739
Programs:	SADABS [4] SAINT [5], SIR97 [6], SHELX [7], DIAMOND [8], WINGX [9]

Source of material

A mixture of 3,3'-*bpda* (3,3'-biphenyl dicarboxylic acid, 0.024 g, 0.1 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (0.030 g, 0.1 mmol), and NaOH (0.008 g, 0.2 mmol) in H_2O / pyridine (7.0 mL / 1mL) was placed in a 23 mL Teflon-lined stainless steel vessel and heated to 180 °C for 72 h to give rise to colourless block-shaped crystals, which were collected by filtration. The colourless crystals obtained were washed with water and dried in air.

Experimental details

All H atoms bonded to C atoms were added according to theoretical models, assigned isotropic displacement parameters and allowed to ride on their respective parent atoms [C–H = 0.93–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C)]. 379 restraints had to be used to refine the structural model.

Discussion

Recently, extensive investigation has focused on the construction of coordination polymers using multidentate N-donor or O-donor ligands [1-3]. Yet accurate structural control and deep understanding of the structure-property relationship remain the fundamental challenges, because different metal coordination environments and carboxylate group binding and bridging modes can provide a wide scope of coordination polymer topologies. Terefore, systematic investigation of an assembling system with the fixed metal centers and coordination organic molecules is crucial for gaining expected target products. The asymmetric unit of the title structure contains four Zn^{2+} ions, four biphenyl-3,3'-dicarboxylic anions and one pyridine molecule. Zn1 adopts a distorted trigonal bipyramid, coordinated by four oxygen atoms (Zn–O: 1.991(3) Å - 2.094(3) Å) from four different biphenyl-3,3'-dicarboxylic anions, and one nitrogen (Zn–N: 2.195(4) Å) atom from the pyridine molecule. Zn2, Zn3 and Zn4 all display distorted pyramidal coordination with four oxygen atoms (Zn–O: 1.919(3) Å - 2.015(3) Å) from different four biphenyl-3,3'-dicarboxylic anions. Zn1 and Zn2, Zn3 and Zn4 are connected by three carboxylate from three different biphenyl-3,3'-dicarboxylic anions to form pseudo-paddle wheel dimers, respectively. The two dimers are further connected by biphenyl-3,3'-dicarboxylic anions to form two dimensional (2D) layers along (001) plane. The adjacent 2D layers stack in a slightly off-set parallel fashion with the weak $\pi\cdots\pi$ interactions between neighboring pyridine molecules to form the 3D supermolecular structure.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(58)	4*e*	0.4431	0.662	0.8219	0.049
H(57)	4*e*	0.5295	0.5591	0.8582	0.051
H(60)	4*e*	0.7120	0.7169	0.7748	0.046
H(50)	4*e*	0.8129	0.5218	0.7693	0.043
H(54)	4*e*	1.1348	0.5779	0.8098	0.045
H(53)	4*e*	1.0947	0.6782	0.8515	0.046
H(26)	4*e*	0.0503	0.9157	0.6408	0.041
H(28)	4*e*	–0.1652	0.9934	0.4751	0.046
H(32)	4*e*	–0.1531	0.8855	0.6246	0.040
H(18)	4*e*	0.7131	1.0340	0.7943	0.052
H(8)	4*e*	0.8034	1.2332	0.7840	0.048

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Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(40)	4*e*	0.6854	0.8118	0.8821	0.042
H(44)	4*e*	0.3126	0.6985	0.9535	0.052
H(30)	4*e*	–0.4164	1.0064	0.5467	0.045
H(12)	4*e*	1.1285	1.1838	0.8252	0.050
H(24)	4*e*	–0.0756	0.8847	0.4606	0.047
H(38)	4*e*	0.7898	0.7455	1.0551	0.046
H(11)	4*e*	1.0947	1.0834	0.8683	0.053
H(36)	4*e*	1.0117	0.8162	0.9787	0.045
H(16)	4*e*	0.4522	1.0805	0.8511	0.057
H(56)	4*e*	0.7063	0.5366	0.8534	0.049
H(37)	4*e*	0.9720	0.7707	1.0614	0.047
H(4)	4*e*	0.6126	1.5578	0.5408	0.112
H(52)	4*e*	0.9158	0.6993	0.8525	0.046

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(42)	4*e*	0.6439	0.6684	1.0118	0.052
H(43)	4*e*	0.4656	0.6328	1.0041	0.055
H(10)	4*e*	0.9167	1.0585	0.8698	0.053
H(15)	4*e*	0.5307	1.1860	0.8826	0.060
H(5)	4*e*	0.7082	1.4892	0.6203	0.108
H(2)	4*e*	0.8114	1.4977	0.4491	0.114
H(23)	4*e*	0.0925	0.8380	0.4602	0.049
H(14)	4*e*	0.7012	1.2145	0.8718	0.058
H(1)	4*e*	0.9032	1.4280	0.5300	0.110
H(3)	4*e*	0.6575	1.5576	0.4528	0.114
H(29)	4*e*	–0.3362	1.0374	0.4729	0.047
H(46)	4*e*	0.5174	0.8324	0.9115	0.044
H(22)	4*e*	0.2419	0.8338	0.5495	0.046

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(3)	4*e*	0.51478(4)	0.88210(2)	0.69440(2)	0.0238(2)	0.0350(3)	0.0329(3)	0.0003(2)	0.0115(2)	0.0022(2)
Zn(4)	4*e*	0.36402(4)	0.87258(2)	0.78740(2)	0.0263(2)	0.0315(2)	0.0285(2)	0.0005(2)	0.0111(2)	0.0022(2)
Zn(2)	4*e*	1.15703(4)	1.37526(2)	0.75302(2)	0.0232(2)	0.0328(2)	0.0307(2)	–0.0011(2)	0.0083(2)	–0.0040(2)
Zn(1)	4*e*	0.88913(4)	1.37585(2)	0.65486(2)	0.0215(2)	0.0336(3)	0.0331(3)	–0.0014(2)	0.0094(2)	–0.0040(2)
O(4)	4*e*	0.5562(3)	0.9533(2)	0.7550(2)	0.056(2)	0.045(2)	0.064(2)	–0.018(2)	0.030(2)	–0.022(2)
O(5)	4*e*	0.3544(2)	0.8709(2)	0.6520(2)	0.021(2)	0.099(3)	0.048(2)	–0.003(2)	0.011(1)	–0.002(2)
O(6)	4*e*	0.2452(2)	0.8854(2)	0.7105(1)	0.032(2)	0.057(2)	0.033(2)	0.011(1)	0.008(1)	0.004(1)
O(8)	4*e*	0.5442(2)	0.9267(2)	0.6223(1)	0.022(2)	0.062(2)	0.039(2)	0.006(1)	0.013(1)	0.011(2)
O(16)	4*e*	0.3039(2)	0.8586(1)	0.8547(1)	0.035(2)	0.035(2)	0.035(2)	0.005(1)	0.018(1)	0.008(1)
O(7)	4*e*	0.6968(2)	0.8826(1)	0.6824(1)	0.025(2)	0.048(2)	0.035(2)	0.001(1)	0.008(1)	0.010(1)
O(13)	4*e*	0.8014(2)	0.8518(2)	0.8183(1)	0.032(2)	0.069(2)	0.031(2)	–0.009(2)	0.009(1)	0.011(2)
O(11)	4*e*	0.5563(2)	0.7948(2)	0.7325(2)	0.039(2)	0.035(2)	0.077(2)	0.010(1)	0.026(2)	0.018(2)
O(1)	4*e*	0.9125(3)	1.3022(1)	0.7226(1)	0.042(2)	0.038(2)	0.048(2)	–0.003(1)	0.011(2)	0.011(1)
O(15)	4*e*	0.2095(2)	0.8026(2)	0.9037(1)	0.023(2)	0.053(2)	0.046(2)	0.000(1)	0.013(1)	0.014(2)
O(10)	4*e*	0.9135(3)	0.4501(1)	0.7163(1)	0.048(2)	0.035(2)	0.048(2)	0.001(1)	0.019(2)	–0.013(1)
O(9)	4*e*	1.0985(3)	0.4643(2)	0.7579(2)	0.048(2)	0.038(2)	0.061(2)	0.010(2)	0.020(2)	–0.006(2)
O(12)	4*e*	0.4371(3)	0.7863(2)	0.7865(1)	0.054(2)	0.042(2)	0.055(2)	0.018(2)	0.028(2)	0.005(2)
O(3)	4*e*	0.4471(3)	0.9569(2)	0.8138(2)	0.060(2)	0.047(2)	0.059(2)	–0.027(2)	0.033(2)	–0.013(2)
O(2)	4*e*	1.0897(3)	1.3015(2)	0.7836(1)	0.038(2)	0.051(2)	0.053(2)	–0.018(2)	0.008(2)	0.006(2)
O(14)	4*e*	0.9784(2)	0.8630(2)	0.8745(1)	0.029(2)	0.086(2)	0.048(2)	–0.009(2)	0.020(2)	0.004(2)
N(1)	4*e*	0.8152(3)	1.4505(2)	0.5827(2)	0.047(2)	0.039(2)	0.056(2)	0.001(2)	0.008(2)	0.005(2)
C(58)	4*e*	0.5140(4)	0.6524(2)	0.8197(2)	0.044(1)	0.035(1)	0.044(1)	0.005(1)	0.015(1)	0.001(1)
C(57)	4*e*	0.5660(4)	0.5911(2)	0.8417(2)	0.046(1)	0.035(1)	0.045(1)	0.004(1)	0.014(1)	0.003(1)
C(60)	4*e*	0.6760(4)	0.6851(2)	0.7919(2)	0.042(1)	0.032(1)	0.041(1)	0.0047(9)	0.0141(9)	0.0000(9)
C(55)	4*e*	0.7301(4)	0.6249(2)	0.8148(2)	0.044(1)	0.0315(9)	0.040(1)	0.0055(8)	0.0129(8)	0.0005(8)
C(51)	4*e*	0.8451(4)	0.6118(2)	0.8129(2)	0.043(1)	0.0304(9)	0.0377(9)	0.0059(8)	0.0117(8)	0.0004(8)
C(50)	4*e*	0.8692(4)	0.5534(2)	0.7859(2)	0.042(1)	0.030(1)	0.037(1)	0.0052(9)	0.0112(9)	0.0012(9)
C(49)	4*e*	0.9766(4)	0.5414(2)	0.7833(2)	0.042(1)	0.029(1)	0.035(1)	0.0049(9)	0.0112(9)	0.0016(9)
C(54)	4*e*	1.0621(4)	0.5870(2)	0.8094(2)	0.043(1)	0.031(1)	0.036(1)	0.004(1)	0.010(1)	0.0017(9)
C(53)	4*e*	1.0384(4)	0.6466(2)	0.8350(2)	0.044(1)	0.031(1)	0.037(1)	0.004(1)	0.010(1)	0.0008(9)
C(61)	4*e*	0.5161(4)	0.7647(2)	0.7691(2)	0.041(1)	0.033(1)	0.042(1)	0.004(1)	0.014(1)	–0.000(1)
C(21)	4*e*	0.1620(3)	0.8759(2)	0.6038(2)	0.028(1)	0.048(1)	0.030(1)	0.0019(9)	0.0113(8)	0.0019(9)
C(26)	4*e*	0.0590(3)	0.9015(2)	0.6041(2)	0.028(1)	0.048(1)	0.030(1)	0.0018(9)	0.0120(9)	0.0026(9)
C(20)	4*e*	0.2609(3)	0.8772(2)	0.6598(2)	0.027(1)	0.045(1)	0.031(1)	0.002(1)	0.011(1)	0.002(1)
C(28)	4*e*	–0.1968(3)	0.9805(2)	0.5049(2)	0.030(1)	0.052(1)	0.035(1)	0.004(1)	0.0104(9)	0.009(1)
C(27)	4*e*	–0.1401(3)	0.9348(2)	0.5504(2)	0.0274(9)	0.048(1)	0.0313(9)	0.0033(8)	0.0110(8)	0.0053(8)
C(32)	4*e*	–0.1898(3)	0.9159(2)	0.5939(2)	0.026(1)	0.046(1)	0.030(1)	0.0032(9)	0.0104(9)	0.0049(9)
C(18)	4*e*	0.6774(4)	1.0646(2)	0.8127(2)	0.049(1)	0.037(1)	0.047(1)	–0.011(1)	0.021(1)	–0.004(1)
C(13)	4*e*	0.7281(4)	1.1266(2)	0.8331(2)	0.049(1)	0.0376(9)	0.048(1)	–0.0103(9)	0.0190(9)	–0.0043(9)
C(9)	4*e*	0.8407(4)	1.1436(2)	0.8285(2)	0.047(1)	0.0356(9)	0.045(1)	–0.0087(9)	0.0159(9)	–0.0030(8)
C(8)	4*e*	0.8617(4)	1.2030(2)	0.8011(2)	0.045(1)	0.034(1)	0.042(1)	–0.008(1)	0.015(1)	–0.0031(9)
C(6)	4*e*	0.9903(4)	1.2789(2)	0.7655(2)	0.042(1)	0.033(1)	0.039(1)	–0.006(1)	0.016(1)	–0.004(1)
C(34)	4*e*	0.8795(3)	0.8467(2)	0.8681(2)	0.026(1)	0.041(1)	0.034(1)	0.001(1)	0.010(1)	0.002(1)
C(40)	4*e*	0.7427(3)	0.8035(2)	0.9184(2)	0.026(1)	0.043(1)	0.035(1)	0.0010(9)	0.0083(9)	0.0052(9)
C(44)	4*e*	0.3843(4)	0.7122(2)	0.9552(2)	0.030(1)	0.048(1)	0.048(1)	–0.000(1)	0.008(1)	0.017(1)
C(48)	4*e*	0.9977(4)	0.4805(2)	0.7501(2)	0.042(1)	0.028(1)	0.034(1)	0.005(1)	0.012(1)	0.002(1)
C(47)	4*e*	0.2991(3)	0.8123(2)	0.8929(2)	0.027(1)	0.042(1)	0.039(1)	0.002(1)	0.011(1)	0.011(1)
C(39)	4*e*	0.7163(3)	0.7754(2)	0.9675(2)	0.0273(9)	0.044(1)	0.0367(9)	0.0008(8)	0.0083(8)	0.0083(8)
C(41)	4*e*	0.6002(4)	0.7547(2)	0.9629(2)	0.0282(9)	0.045(1)	0.041(1)	0.0007(8)	0.0089(8)	0.0127(8)
C(7)	4*e*	0.9684(4)	1.2177(2)	0.7987(2)	0.043(1)	0.034(1)	0.040(1)	–0.0067(9)	0.0143(9)	–0.0032(9)
C(31)	4*e*	–0.2931(3)	0.9415(2)	0.5924(2)	0.026(1)	0.046(1)	0.031(1)	0.003(1)	0.0105(9)	0.005(1)

Table 3. continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(19)	4*e*	0.5218(4)	0.9808(2)	0.7943(2)	0.046(1)	0.037(1)	0.047(1)	–0.011(1)	0.020(1)	–0.004(1)
C(35)	4*e*	0.8521(3)	0.8195(2)	0.9218(2)	0.026(1)	0.042(1)	0.035(1)	0.0008(9)	0.0087(8)	0.0034(9)
C(45)	4*e*	0.3998(3)	0.7722(2)	0.9265(2)	0.028(1)	0.044(1)	0.041(1)	0.0010(9)	0.0102(9)	0.0133(9)
C(30)	4*e*	–0.3479(3)	0.9881(2)	0.5473(2)	0.028(1)	0.049(1)	0.035(1)	0.005(1)	0.0100(9)	0.007(1)
C(12)	4*e*	1.0565(4)	1.1733(2)	0.8252(2)	0.046(1)	0.036(1)	0.043(1)	–0.006(1)	0.013(1)	–0.002(1)
C(24)	4*e*	–0.0164(4)	0.8822(2)	0.4970(2)	0.031(1)	0.055(1)	0.032(1)	0.004(1)	0.0104(9)	0.000(1)
C(38)	4*e*	0.8048(3)	0.7638(2)	1.0213(2)	0.029(1)	0.047(1)	0.036(1)	–0.000(1)	0.0068(9)	0.008(1)
C(11)	4*e*	1.0365(4)	1.1137(2)	0.8514(2)	0.048(1)	0.037(1)	0.045(1)	–0.005(1)	0.012(1)	–0.001(1)
C(36)	4*e*	0.9380(3)	0.8064(2)	0.9760(2)	0.028(1)	0.046(1)	0.037(1)	0.000(1)	0.0067(9)	0.004(1)
C(16)	4*e*	0.5203(4)	1.0923(2)	0.8460(2)	0.051(1)	0.041(1)	0.053(1)	–0.011(1)	0.021(1)	–0.007(1)
C(56)	4*e*	0.6724(4)	0.5779(2)	0.8389(2)	0.046(1)	0.033(1)	0.043(1)	0.005(1)	0.013(1)	0.0020(9)
C(37)	4*e*	0.9143(4)	0.7790(2)	1.0253(2)	0.029(1)	0.047(1)	0.037(1)	–0.000(1)	0.0051(9)	0.006(1)
C(4)	4*e*	0.6710(6)	1.5309(3)	0.5374(3)	0.114(3)	0.088(2)	0.080(2)	0.039(2)	0.035(2)	0.029(2)
C(52)	4*e*	0.9312(4)	0.6588(2)	0.8360(2)	0.045(1)	0.031(1)	0.038(1)	0.006(1)	0.010(1)	0.0000(9)
C(42)	4*e*	0.5827(4)	0.6947(2)	0.9903(2)	0.031(1)	0.049(1)	0.047(1)	0.000(1)	0.007(1)	0.017(1)
C(43)	4*e*	0.4758(4)	0.6735(2)	0.9860(2)	0.033(1)	0.050(1)	0.051(1)	–0.001(1)	0.006(1)	0.018(1)
C(10)	4*e*	0.9294(4)	1.0991(2)	0.8525(2)	0.049(1)	0.037(1)	0.046(1)	–0.008(1)	0.013(1)	–0.000(1)
C(15)	4*e*	0.5677(4)	1.1552(2)	0.8653(2)	0.054(1)	0.043(1)	0.056(1)	–0.010(1)	0.021(1)	–0.007(1)
C(5)	4*e*	0.7291(6)	1.4898(3)	0.5851(3)	0.111(3)	0.086(2)	0.078(2)	0.038(2)	0.037(2)	0.029(2)
C(2)	4*e*	0.7877(6)	1.4954(3)	0.4834(3)	0.120(3)	0.092(2)	0.076(2)	0.041(2)	0.038(2)	0.028(2)
C(23)	4*e*	0.0849(4)	0.8546(2)	0.4965(2)	0.032(1)	0.057(1)	0.033(1)	0.004(1)	0.0109(9)	–0.001(1)
C(14)	4*e*	0.6703(4)	1.1721(2)	0.8588(2)	0.053(1)	0.041(1)	0.054(1)	–0.011(1)	0.020(1)	–0.006(1)
C(1)	4*e*	0.8434(6)	1.4541(3)	0.5327(3)	0.120(3)	0.092(2)	0.073(2)	0.041(2)	0.042(2)	0.027(2)
C(3)	4*e*	0.6989(6)	1.5319(3)	0.4862(3)	0.118(3)	0.091(2)	0.079(2)	0.040(2)	0.035(2)	0.028(2)
C(29)	4*e*	–0.2995(3)	1.0069(2)	0.5034(2)	0.030(1)	0.052(1)	0.036(1)	0.005(1)	0.0095(9)	0.010(1)
C(46)	4*e*	0.5073(3)	0.7925(2)	0.9307(2)	0.028(1)	0.043(1)	0.040(1)	0.0010(9)	0.0102(9)	0.0128(9)
C(59)	4*e*	0.5693(4)	0.6990(2)	0.7942(2)	0.042(1)	0.033(1)	0.042(1)	0.0046(9)	0.0142(9)	0.0000(9)
C(22)	4*e*	0.1738(4)	0.8518(2)	0.5498(2)	0.030(1)	0.053(1)	0.032(1)	0.003(1)	0.0114(9)	–0.000(1)
C(17)	4*e*	0.5749(4)	1.0471(2)	0.8192(2)	0.048(1)	0.038(1)	0.049(1)	–0.011(1)	0.021(1)	–0.005(1)
C(25)	4*e*	–0.0308(3)	0.9062(2)	0.5505(2)	0.0284(9)	0.050(1)	0.0306(9)	0.0026(8)	0.0116(8)	0.0027(8)
C(33)	4*e*	0.6474(3)	0.9166(2)	0.6348(2)	0.022(2)	0.034(2)	0.031(2)	0.003(2)	0.010(2)	0.000(2)

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