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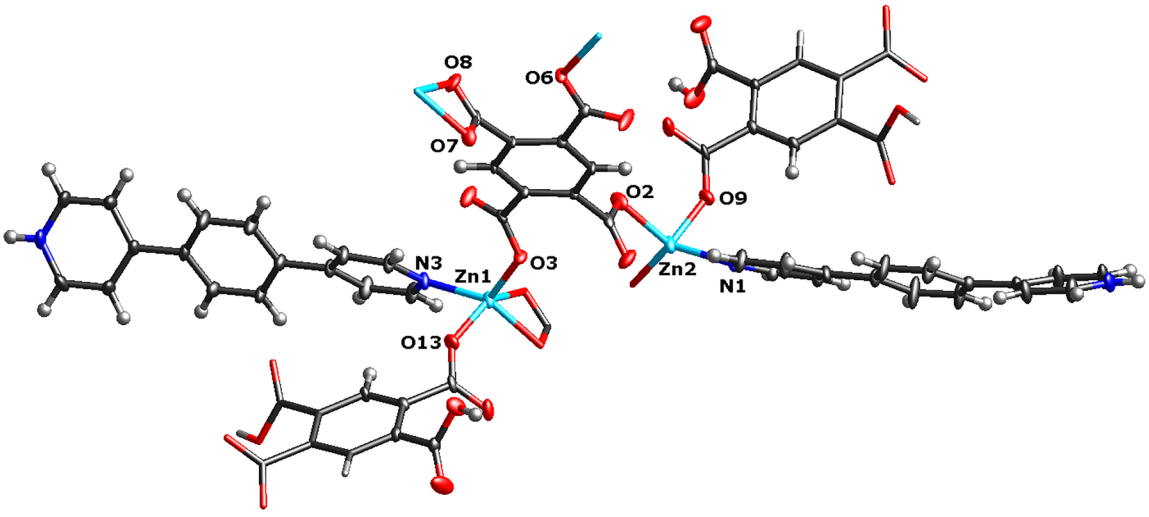
Crystal structure of poly[bis(4-(4-(pyridin-4-yl)phenyl)pyridin-1-ium-κ^1N)-(μ_4-benzene-1,2,4,5-tetracarboxylato-$\kappa^5O:O'$: $O'':O''':O''''$)-(μ_2-2,5-dicarboxyterephthalato-$\kappa^2O:O'$)dizinc(II)], $C_{52}H_{32}N_4O_{16}Zn_2$



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Abstract

$C_{52}H_{32}N_4O_{16}Zn_2$, monoclinic, $P2_1/c$ (no. 14), a = 27.6424(8) Å, b = 9.6359(3) Å, c = 16.8129(7) Å, β = 95.408(3)°, V = 4,458.3(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0654, $wR_{ref}(F^2)$ = 0.1966, T = 296(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.15 × 0.13 × 0.12 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	2.05 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max}, completeness:	71.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17,942, 8,444, 0.064
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5,189
$N(param)_{refined}$:	669
Programs:	Bruker,[1] Olex2,[2] SHELX[3]

1 Source of material

The mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (1 mmol, 297.5 mg), 1,4-di(pyridin-4-yl)benzene (dpb) (1 mmol, 232.3 mg), pyromellitic dianhydride (pmda) (1 mmol, 218.1 mg), dimethylformamide (2 mL) and H_2O (1 mL) were placed in a 25 mL Teflon-lined autoclave at 358 K for 48 h. After cooling to room temperature, colorless prismatic crystals were obtained.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4145 (2)	0.9251 (6)	0.1579 (4)	0.0450 (16)
H1	0.391195	0.856184	0.147300	0.054*
C2	0.4584 (2)	0.9124 (6)	0.1252 (4)	0.0494 (18)
H2	0.464027	0.836097	0.093537	0.059*
C3	0.49418 (18)	1.0134 (5)	0.1395 (4)	0.0321 (12)
C4	0.48219 (19)	1.1249 (6)	0.1863 (4)	0.0373 (13)
H4	0.504198	1.197159	0.196701	0.045*
C5	0.43800 (19)	1.1289 (5)	0.2172 (4)	0.0365 (13)
H5	0.431391	1.203987	0.249260	0.044*
C6	0.54230 (19)	1.0019 (6)	0.1064 (4)	0.0343 (13)
C7	0.5559 (2)	0.8848 (6)	0.0702 (5)	0.055 (2)
H7	0.534469	0.810231	0.064709	0.066*
C8	0.6008 (2)	0.8732 (6)	0.0413 (5)	0.056 (2)
H8	0.608919	0.791184	0.016669	0.067*
C9	0.6336 (2)	0.9800 (6)	0.0482 (3)	0.0340 (12)
C10	0.6196 (2)	1.0990 (7)	0.0839 (5)	0.063 (2)
H10	0.641062	1.173373	0.089607	0.075*
C11	0.5745 (2)	1.1117 (7)	0.1118 (5)	0.073 (3)
H11	0.565644	1.194931	0.134321	0.088*
C12	0.68247 (18)	0.9629 (6)	0.0206 (3)	0.0331 (12)
C13	0.6919 (2)	0.8714 (7)	−0.0399 (4)	0.0513 (17)
H13	0.666568	0.820605	−0.066042	0.062*
C14	0.7384 (2)	0.8551 (8)	−0.0617 (4)	0.0555 (19)
H14	0.744371	0.791893	−0.101414	0.067*
C15	0.7675 (2)	1.0206 (9)	0.0309 (4)	0.063 (2)
H15	0.793513	1.070980	0.055156	0.075*
C16	0.7221 (2)	1.0411 (8)	0.0541 (4)	0.060 (2)
H16	0.717314	1.107766	0.092594	0.072*
C17	0.06630 (19)	0.9385 (5)	0.2942 (4)	0.0359 (13)
H17	0.077719	0.859122	0.270711	0.043*
C18	0.0220 (2)	0.9316 (6)	0.3249 (4)	0.0402 (14)
H18	0.004592	0.848822	0.323514	0.048*
C19	0.00331 (19)	1.0515 (5)	0.3584 (4)	0.0335 (12)
C20	0.0317 (2)	1.1691 (6)	0.3583 (4)	0.0460 (16)
H20	0.020750	1.251674	0.378881	0.055*
C21	0.0765 (2)	1.1650 (6)	0.3280 (4)	0.0432 (15)
H21	0.095251	1.245203	0.330000	0.052*
C22	−0.0450 (2)	1.0500 (6)	0.3888 (4)	0.0355 (13)
C23	−0.0626 (2)	0.9325 (6)	0.4237 (5)	0.0514 (18)
H23	−0.043323	0.853300	0.428821	0.062*
C24	−0.1086 (2)	0.9305 (6)	0.4512 (4)	0.0500 (17)
H24	−0.120099	0.849558	0.472940	0.060*
C25	−0.13733 (19)	1.0490 (6)	0.4463 (3)	0.0327 (12)
C26	−0.1196 (2)	1.1672 (6)	0.4126 (3)	0.0367 (13)
H26	−0.138581	1.246954	0.408213	0.044*
C27	−0.07395 (19)	1.1685 (6)	0.3852 (4)	0.0366 (13)
H27	−0.062394	1.249949	0.364094	0.044*
C28	−0.18643 (19)	1.0492 (6)	0.4751 (3)	0.0353 (13)
C29	−0.1980 (2)	0.9601 (7)	0.5367 (4)	0.0454 (16)
H29	−0.174610	0.899685	0.560178	0.055*
C30	−0.2432 (2)	0.9619 (7)	0.5623 (4)	0.0489 (17)
H30	−0.250562	0.903500	0.603534	0.059*
C31	−0.2675 (2)	1.1340 (8)	0.4694 (4)	0.0519 (18)
H31	−0.291821	1.191695	0.446226	0.062*
C32	−0.2221 (2)	1.1385 (7)	0.4431 (4)	0.0450 (15)
H32	−0.215421	1.201638	0.403728	0.054*
C33	0.29555 (17)	0.8106 (5)	0.2394 (4)	0.0302 (12)
C34	0.27059 (16)	0.6732 (4)	0.2454 (3)	0.0203 (9)
C35	0.29695 (16)	0.5538 (4)	0.2368 (3)	0.0232 (10)
H35	0.329268	0.560790	0.226116	0.028*
C36	0.27645 (17)	0.4227 (5)	0.2437 (3)	0.0219 (10)
C37	0.22697 (15)	0.4120 (4)	0.2563 (3)	0.0196 (9)
C38	0.20067 (15)	0.5320 (4)	0.2669 (3)	0.0212 (10)
H38	0.168251	0.524955	0.276926	0.025*
C39	0.22166 (16)	0.6625 (5)	0.2628 (3)	0.0219 (10)
C40	0.30891 (17)	0.2979 (5)	0.2412 (3)	0.0226 (10)
C41	0.20048 (16)	0.2763 (4)	0.2572 (3)	0.0273 (11)
C42	0.19126 (16)	0.7877 (5)	0.2783 (3)	0.0230 (10)
C43	0.39936 (16)	1.0002 (6)	0.4311 (3)	0.0295 (11)
C44	0.45141 (17)	1.0039 (5)	0.4683 (3)	0.0256 (10)
C45	0.48863 (18)	1.0081 (5)	0.4183 (3)	0.0298 (11)
H45	0.481071	1.013878	0.363366	0.036*
C46	0.46273 (17)	0.9964 (5)	0.5504 (3)	0.0257 (10)
C47	0.42510 (18)	0.9997 (6)	0.6091 (3)	0.0304 (12)
C48	0.10104 (17)	1.0362 (5)	0.0634 (3)	0.0291 (12)
C49	0.04910 (17)	1.0128 (5)	0.0295 (3)	0.0253 (10)
C50	0.01234 (16)	1.0411 (5)	0.0776 (3)	0.0253 (10)
H50	0.020574	1.068855	0.130146	0.030*
C51	0.03680 (17)	0.9709 (5)	−0.0498 (3)	0.0258 (11)
C52	0.07373 (18)	0.9312 (6)	−0.1054 (3)	0.0306 (11)
N1	0.40408 (14)	1.0315 (4)	0.2040 (3)	0.0278 (10)
N2	0.77501 (17)	0.9300 (6)	−0.0258 (3)	0.0491 (14)
H2A	0.803890	0.918922	−0.039773	0.059*
N3	0.09379 (15)	1.0516 (4)	0.2961 (3)	0.0304 (10)
N4	−0.27718 (17)	1.0478 (6)	0.5280 (3)	0.0497 (14)
H4A	−0.305813	1.047357	0.544038	0.060*
O1	0.30478 (16)	0.8546 (4)	0.1725 (3)	0.0499 (12)
O2	0.30834 (14)	0.8722 (4)	0.3040 (3)	0.0452 (10)
O3	0.19834 (13)	0.8932 (3)	0.2355 (2)	0.0315 (8)
O4	0.16249 (16)	0.7814 (4)	0.3295 (3)	0.0501 (12)
O5	0.34754 (16)	0.3083 (4)	0.2109 (3)	0.0616 (16)
O6	0.29589 (12)	0.1877 (3)	0.2724 (2)	0.0308 (8)
O7	0.19119 (13)	0.2133 (4)	0.1921 (3)	0.0398 (9)
O8	0.18617 (15)	0.2340 (4)	0.3205 (3)	0.0477 (11)
O9	0.39015 (14)	1.0660 (4)	0.3684 (3)	0.0485 (11)
O10	0.37068 (15)	0.9273 (6)	0.4655 (3)	0.0638 (15)
O11	0.39712 (19)	1.1082 (5)	0.5999 (3)	0.0652 (16)
H11A	0.381152	1.115519	0.638396	0.098*
O12	0.42398 (19)	0.9185 (5)	0.6627 (3)	0.0739 (18)
O13	0.10989 (14)	1.0024 (4)	0.1351 (3)	0.0447 (10)
O14	0.12938 (13)	1.0894 (5)	0.0201 (3)	0.0481 (11)
O15	0.10559 (16)	0.8401 (5)	−0.0757 (2)	0.0487 (11)
H15A	0.123543	0.818483	−0.109796	0.073*
O16	0.07195 (19)	0.9719 (6)	−0.1730 (3)	0.0783 (19)
Zn1	0.15385 (2)	1.05080 (6)	0.23185 (4)	0.02071 (18)
Zn2	0.34487 (2)	1.03799 (6)	0.27064 (4)	0.02226 (18)

2 Experimental details

The C-bound H atoms were placed in calculated positions with C–H = 0.93 Å, N–H = 0.86 Å and O–H = 0.82 Å and refined by the riding model with U_{iso}(H) = 1.5U_{eq}(O) and 1.2U_{eq} for the remaining H atoms.

3 Comment

Coordination polymers (CPs) with different topologies and properties can be obtained by self-assembly reaction of different metal ions and organic ligands.[4,5] Using the ideas and methods of crystal engineering.[6,7] The main factors affecting the synthesis of coordination polymers are organic ligand, metal ion, solvent, pH value, temperature and synthesis methods (solvothermal method, solution method, ultrasonic method, diffusion method).[8–10] The differences in coordination configuration and coordination ability of different metal ions ultimately affect the structure and properties of coordination polymers.[11–13] The common coordination configurations of transition metal zinc ions are tetrahedral and octahedral configurations, while the trigonal bipyramidal configurations are relatively rare. Herein, rigid 1,4-di(pyridin-4-yl)benzene (dpb)[14,15] and pyromellitic dianhydride (pmda)[16,17] as ligands together with zinc nitrate were used to synthesise new coordination polymers.

The asymmetric unit consists of two Zn(II) cations, two 4-(4-(pyridin-4-yl)phenyl)pyridin-1-ium ($Hdpb^+$) ligands (derived from the protonated dpb), one partial deprotonated H_4pta ligand (derived from the decomposition of pmda; distributed over two halfs located around inversion centers), and one completely deprotonated H_4pta ligand (see the figure). The Zn1 cation has a triangular bipyramidal structure, which is linked by four oxygen atoms from two symmetry related pta^{4-} ligands and one H_2pta^{2-} ligand, as well as one nitrogen atom from $Hdpb^+$ ligand. The Zn2 cation has a tetrahedral structure, which is linked by three oxygen atoms from two symmetry related pta^{4-} ligands and one H_2pta^{2-} ligand, and one nitrogen atom from $Hdpb^+$ ligand. The Zn–O bond lengths range from 1.951(3) to 2.426(4) Å. The Zn–N bond lengths are 2.065(4) and 2.070(4) Å. The bond lengths and bond angles are all in normal ranges.[20] The mixed ligands connected the Zn cations to form a two-dimensional structure. In the crystal packing, the molecules are linked into three-dimensional supermolecular frameworks by N–H···O hydrogen bonds. In addition, intramolecular O–H···O hydrogen bonds further consolidate the crystal structure. In addition, the Zn-based fluorescent coordination polymers can be used for fluorescence detection or detection of crime scenes by fluorescence.[18,19]

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