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Crystal structure of poly[[tris(μ_2 -*cis*-1,2-cyclohexanedicarboxylato)- κ^2O , O']-bis[μ_3 -1,3,5-tris[(1*H*-imidazol-1-yl)methyl]benzene- κ^3N, N', N'']-trizinc(II)] – water (1/20), $C_{60}H_{106}N_{12}O_{32}Zn_3$

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Abstract

$C_{60}H_{106}N_{12}O_{32}Zn_3$, monoclinic, $P2_1/c$ (no. 14), $a = 18.9877(14)$ Å, $b = 19.7813(15)$ Å, $c = 21.0699(14)$ Å, $\beta = 103.345(2)^\circ$, $V = 7700.2(10)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0626$, $wR_{ref}(F^2) = 0.1752$, $T = 193$ K.

CCDC no.: 1982978

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.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.32 × 0.20 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.98 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	27.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	47361, 17545, 0.097
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 8283
$N(param)_{refined}$:	857
Programs:	PLATON [1, 2]

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Source of material

The ligand, 1,3,5-tris[(1*H*-imidazol-1-yl)methyl]benzene (timb), was synthesized according to the method reported previously [3]. All other reagents used were of commercially

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	−0.2046(3)	0.6754(2)	0.5746(2)	0.0388(11)
H1A	−0.2190	0.6466	0.6041	0.047*
C2	−0.1396(3)	0.7338(3)	0.5256(2)	0.0459(13)
H2A	−0.0998	0.7535	0.5142	0.055*
C3	−0.2095(3)	0.7441(3)	0.4948(2)	0.0457(13)
H3A	−0.2262	0.7720	0.4589	0.055*
C4	−0.3295(3)	0.7018(3)	0.5101(2)	0.0465(13)
H4A	−0.3493	0.7406	0.5283	0.056*
H4B	−0.3441	0.6614	0.5297	0.056*
C5	−0.3590(2)	0.6998(3)	0.4379(2)	0.0418(12)
C6	−0.3683(2)	0.6393(3)	0.4042(2)	0.0428(12)
H6A	−0.3583	0.5988	0.4269	0.051*
C7	−0.3927(2)	0.6382(3)	0.3359(2)	0.0440(12)
C8	−0.4070(3)	0.6990(3)	0.3030(3)	0.0511(14)
H8A	−0.4233	0.6992	0.2578	0.061*
C9	−0.3974(2)	0.7596(3)	0.3368(3)	0.0462(13)
C10	−0.3746(2)	0.7605(3)	0.4041(2)	0.0475(13)
H10A	−0.3698	0.8014	0.4266	0.057*
C11	−0.4150(3)	0.8262(3)	0.3004(3)	0.0660(17)
H11A	−0.3828	0.8611	0.3227	0.079*
H11B	−0.4070	0.8215	0.2568	0.079*
C12	0.4569(3)	0.6586(3)	0.7443(2)	0.0476(13)
H12A	0.4623	0.6753	0.7045	0.057*
C13 ^a	0.4209(9)	0.6037(8)	0.8128(8)	0.061(4)
H13A ^a	0.3919	0.5774	0.8330	0.074*
C13 ^{tb}	0.3993(7)	0.6360(7)	0.8216(6)	0.057(3)
H13 ^{tb}	0.3617	0.6307	0.8427	0.068*
C14 ^a	0.4921(9)	0.6130(8)	0.8367(9)	0.070(5)
H14A ^a	0.5213	0.5942	0.8742	0.084*
C14 ^{tb}	0.4709(8)	0.6435(7)	0.8487(7)	0.064(4)
H14 ^{tb}	0.4918	0.6425	0.8932	0.077*
C15	0.1826(3)	0.6978(3)	0.7433(2)	0.0471(13)
H15A	0.1583	0.6568	0.7419	0.057*
C16	0.2598(4)	0.7719(3)	0.7342(3)	0.0706(19)
H16A	0.3002	0.7930	0.7252	0.085*
C17	0.2098(4)	0.8023(3)	0.7595(3)	0.0741(19)
H17A	0.2089	0.8476	0.7709	0.089*
C18	0.0773(2)	0.7153(2)	0.5924(2)	0.0357(11)
H18A	0.0940	0.6710	0.5931	0.043*
C19	0.0167(3)	0.8027(2)	0.6066(2)	0.0429(13)
H19A	−0.0170	0.8306	0.6193	0.052*
C20	0.0670(3)	0.8232(2)	0.5747(2)	0.0468(13)
H20A	0.0740	0.8670	0.5613	0.056*
C21	0.1666(3)	0.7645(2)	0.5338(2)	0.0404(12)
H21A	0.2091	0.7469	0.5641	0.049*
H21B	0.1777	0.8099	0.5216	0.049*
C22	0.1490(2)	0.7198(2)	0.4731(2)	0.0317(10)
C23	0.1529(2)	0.6502(2)	0.4803(2)	0.0314(11)
H23A	0.1683	0.6316	0.5217	0.038*
C24	0.1344(2)	0.6079(2)	0.4268(2)	0.0329(10)
C25	0.1133(2)	0.6367(3)	0.3651(2)	0.0411(12)
H25A	0.0995	0.6090	0.3286	0.049*
C26	0.1127(2)	0.7061(3)	0.3575(2)	0.0406(12)
C27	0.1295(2)	0.7469(2)	0.4115(2)	0.0382(11)
H27A	0.1276	0.7936	0.4063	0.046*
C28	0.1415(3)	0.5324(2)	0.4351(2)	0.0401(12)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H28A	0.1309	0.5195	0.4763	0.048*
H28B	0.1066	0.5103	0.4004	0.048*
C29	0.2351(3)	0.4882(2)	0.3807(2)	0.0379(11)
H29A	0.2047	0.4842	0.3394	0.046*
C30	0.3288(3)	0.4869(2)	0.4604(2)	0.0415(12)
H30A	0.3762	0.4815	0.4844	0.050*
C31	0.2740(3)	0.5095(2)	0.4845(2)	0.0408(12)
H31A	0.2759	0.5223	0.5274	0.049*
C32	0.0946(3)	0.7351(3)	0.2890(2)	0.0564(15)
H32A	0.0697	0.7779	0.2890	0.068*
H32B	0.0625	0.7044	0.2600	0.068*
C33	0.4954(3)	0.4975(2)	0.3213(2)	0.0408(12)
H33A	0.5242	0.4711	0.3536	0.049*
C34	0.4028(3)	0.5387(3)	0.2537(3)	0.0760(19)
H34A	0.3554	0.5461	0.2307	0.091*
C35	0.4617(3)	0.5740(3)	0.2468(3)	0.078(2)
H35A	0.4623	0.6093	0.2179	0.094*
C36	0.5951(3)	0.5710(3)	0.2997(3)	0.0547(14)
H36A	0.6068	0.5759	0.2575	0.066*
H36B	0.6273	0.5372	0.3242	0.066*
C37	0.0397(2)	0.5552(2)	0.6696(2)	0.0342(11)
C38	0.0731(2)	0.4894(2)	0.65478(18)	0.0272(10)
H38A	0.0485	0.4536	0.6735	0.033*
C39	0.0585(2)	0.4751(2)	0.58145(19)	0.0340(11)
H39A	0.0779	0.5118	0.5601	0.041*
H39B	0.0067	0.4732	0.5635	0.041*
C40	0.0926(3)	0.4088(2)	0.5673(2)	0.0436(12)
H40A	0.0863	0.4037	0.5205	0.052*
H40B	0.0680	0.3714	0.5828	0.052*
C41	0.1729(3)	0.4061(2)	0.5999(2)	0.0460(13)
H41A	0.1925	0.3625	0.5916	0.055*
H41B	0.1984	0.4409	0.5817	0.055*
C42	0.1841(3)	0.4167(2)	0.6726(2)	0.0400(12)
H42A	0.1612	0.3801	0.6911	0.048*
H42B	0.2355	0.4157	0.6927	0.048*
C43	0.1524(2)	0.4842(2)	0.6881(2)	0.0331(11)
H43A	0.1556	0.4849	0.7352	0.040*
C44	0.1993(3)	0.5417(2)	0.6737(2)	0.0387(11)
C45	−0.1171(2)	0.6728(3)	0.7378(2)	0.0375(11)
C46	−0.1585(3)	0.6990(2)	0.7864(2)	0.0384(11)
H46A	−0.1946	0.7315	0.7637	0.046*
C47	−0.1992(3)	0.6415(3)	0.8132(2)	0.0453(13)
H47A	−0.2283	0.6637	0.8400	0.054*
C48	−0.1465(3)	0.5953(3)	0.8594(2)	0.0555(15)
H48A	−0.1737	0.5621	0.8779	0.067*
H48B	−0.1170	0.5712	0.8350	0.067*
C49	−0.0978(3)	0.6342(3)	0.9141(2)	0.0524(14)
H49A	−0.0632	0.6036	0.9405	0.063*
H49B	−0.1267	0.6540	0.9418	0.063*
C50	−0.0576(3)	0.6898(3)	0.8876(2)	0.0497(14)
H50A	−0.0289	0.7155	0.9236	0.060*
H50B	−0.0250	0.6698	0.8637	0.060*
C51	−0.1087(3)	0.7360(2)	0.8438(2)	0.0422(12)
H51A	−0.0811	0.7700	0.8268	0.051*
H51B	−0.1382	0.7591	0.8690	0.051*
C52	0.2526(3)	0.3958(3)	0.2398(3)	0.0568(15)
C53	0.3630(4)	0.6563(4)	0.5850(3)	0.0650(17)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C54 ^{rb}	0.4072(5)	0.7088(5)	0.5420(4)	0.039(2)
H54A ^b	0.4220	0.7486	0.5695	0.047*
C54 ^a	0.3726(6)	0.6631(7)	0.5247(5)	0.046(3)
H54B ^a	0.3344	0.6345	0.4989	0.055*
C55	0.3607(4)	0.7307(3)	0.4885(4)	0.084(2)
H55A	0.3814	0.7657	0.5194	0.101*
H55B	0.3089	0.7387	0.4763	0.101*
C56 ^{rb}	0.3403(5)	0.6718(6)	0.4283(5)	0.064(3)
H56A ^b	0.3140	0.6345	0.4418	0.076*
H56B ^b	0.3105	0.6916	0.3891	0.076*
C56 ^a	0.3859(7)	0.7401(8)	0.4356(6)	0.078(5)
H56C ^a	0.3495	0.7247	0.3982	0.093*
H56D ^a	0.3921	0.7883	0.4303	0.093*
C57 ^{rb}	0.4106(6)	0.6471(5)	0.4154(4)	0.050(3)
H57A ^b	0.4002	0.6089	0.3858	0.060*
H57E ^b	0.4304	0.6827	0.3931	0.060*
C57 ^a	0.4572(7)	0.7052(6)	0.4342(6)	0.064(4)
H57B ^a	0.4972	0.7325	0.4578	0.077*
H57C ^a	0.4616	0.7014	0.3894	0.077*
C58	0.4620(3)	0.6281(3)	0.4678(3)	0.0727(19)
H58A	0.4324	0.5975	0.4368	0.087*
H58B	0.5117	0.6124	0.4753	0.087*
C59 [′]	0.4759(4)	0.6795(4)	0.5276(4)	0.032(2)
H59A	0.5016	0.7179	0.5143	0.038*
C59	0.4416(5)	0.6246(6)	0.5221(5)	0.041(3)
H59B	0.4340	0.5769	0.5310	0.050*
C104	0.5209(4)	0.6547(4)	0.5838(3)	0.077(2)
N1	−0.1366(2)	0.69008(17)	0.57610(16)	0.0320(9)
N2	−0.2505(2)	0.70636(18)	0.52570(17)	0.0353(9)
N3	0.3050(2)	0.47298(18)	0.39505(17)	0.0378(9)
N4	0.2145(2)	0.50990(17)	0.43359(17)	0.0320(9)
N5	0.4254(2)	0.4899(2)	0.30058(19)	0.0446(10)
N6	0.5203(2)	0.5480(2)	0.29043(19)	0.0470(10)
N7	0.02274(19)	0.73479(18)	0.61726(16)	0.0317(9)
N8	0.1056(2)	0.76719(18)	0.56619(16)	0.0341(9)
N9	0.2430(2)	0.7063(2)	0.72367(17)	0.0439(10)
N10	0.1607(2)	0.7548(2)	0.76532(17)	0.0450(10)
N11	0.3952(2)	0.6381(2)	0.75412(19)	0.0484(11)
N12	0.5108(2)	0.6537(2)	0.7961(2)	0.0564(12)
O1	−0.07099(17)	0.71374(15)	0.72234(13)	0.0385(8)
O2	−0.12977(17)	0.61678(16)	0.71211(15)	0.0447(8)
O3	−0.00975(18)	0.58108(15)	0.62506(15)	0.0416(8)
O4	0.05900(19)	0.58174(19)	0.72451(17)	0.0647(11)
O5	0.26248(18)	0.54719(17)	0.71045(17)	0.0524(9)
O6	0.17671(18)	0.58255(15)	0.62889(15)	0.0440(8)
O7	0.32399(19)	0.6921(2)	0.61224(16)	0.0609(11)
O8	0.3900(4)	0.6010(4)	0.5941(4)	0.0326(19)
O8 [′]	0.3555(6)	0.5933(5)	0.6110(4)	0.075(3)
O9	0.43496(18)	0.39237(18)	0.41265(17)	0.0532(9)
O10 [′]	0.5069(6)	0.6899(6)	0.6146(6)	0.070(3)
O10	0.5411(5)	0.7042(5)	0.6369(5)	0.061(3)
O11	0.29557(19)	0.3616(2)	0.28403(18)	0.0594(10)
O12	0.2570(2)	0.4592(2)	0.23806(17)	0.0693(12)
Zn1	−0.04634(3)	0.66849(3)	0.64543(2)	0.03150(14)
Zn2	0.30049(3)	0.63607(3)	0.68745(3)	0.04090(16)
Zn3	0.36221(3)	0.42863(3)	0.33805(3)	0.04353(17)

^aOccupancy: 0.472(6), ^bOccupancy: 0.528(6).

available quality and were used as received without further purification. 0.1 mmol timb, 0.15 mmol 1,2-cyclohexanedicarboxylic acid, 0.15 mmol $ZnSO_4 \cdot 7H_2O$, 0.3 mmol tetrabutylammonium hydroxide and 15.0 mL water were mixed and placed in a thick Pyrex tube, which was sealed and heated to 413 K for 48 h. The tube was cooled to ambient temperature spontaneously and colourless block-shaped crystals of the title compound were obtained.

Elemental analysis

Calcd. for $C_{60}H_{106}N_{12}O_{32}Zn_3$: C, 42.26%; H, 6.22%; N, 9.86%; Found: C, 42.19%; H, 6.25%; N, 9.90%.

Experimental details

H atoms bound to C atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H = 0.93 (phenyl & imidazolyl), 0.97 (methylene) or 0.96 methyl Å and $U_{iso}(H) = 1.2U_{eq}(C)$. One imidazolyl ring of the timb ligand (atoms C13 and C14) and one cyclohexanedicarboxylate group (atoms O8, C54, C56, C57, C59 and O10) are disordered over two positions and were refined as having two orientations with site occupancies of 0.528(5) and 0.471(5). The guest water molecules were disordered and could not be modelled acceptably. The SQUEEZE routine [1] in PLATON [2] was used to remove the unassigned electron density. The residual electron density was assigned to twenty molecules present in the crystal [207e per asymmetric unit; one water molecule give 10e]. This suggestion was verified by a TGA (ThermoGravimetric Analysis) experiment.

Comment

It is well known that the self-assembly of metal-organic frameworks (MOFs) can be influenced by organic ligands, metal centers, temperature, solvent, counter ions, pH value, molar ratio of ligand-to-metal and so on [4]. Thus, it is still challenging to predict and control the structures and compositions of MOFs. Employing multidentate organic ligands and suitable metal ions *via* metal–ligand coordination, hydrogen-bonding and $\pi - \pi$ interactions, which is a major approach for the construction of novel MOFs with fascinating structures and interesting properties. Recently imidazole-containing tripodal ligands, such as 1,3-bis(1-imidazolyl)-5-(imidazol-1-yl-methyl)benzene [5], 1-(1-imidazolyl)3,5-bis(imidazol-1-ylmethyl)benzene [6], 2,4,6-tris[4-(imidazol-1-ylmethyl)phenyl]-1,3,5-triazine [7], 1,3,5-tris(imidazol-1-yl)-2,4,6-trimethyl-benzene [8], 1,3,5-tris(1-imidazolyl)benzene [9] and 1,3,5-tris[(1H-imidazol-1-yl)methyl]benzene [4], *etc.*, have been applied in constructing MOFs due to the presence of three possible coordinating arms. On the other hand, polycarboxylic acids have also been widely employed as an ligand in coordination reactions and in the assembly of metal-organic

frameworks because of its variable coordination modes after being deprotonated.

We focus our attention on the construction of novel MOFs with imidazole-containing and carboxylate-containing mixed ligands. In the present work, we successfully obtained a new Zn^{II} three-dimensional coordination polymer with 1,3,5-tris[(1*H*-imidazol-1-yl)methyl]benzene (timb) and 1,2-cyclohexanedicarboxylate *via* a solvothermal reaction.

Single-crystal X-ray diffraction structural analysis shows that the title complex crystallizes in the monoclinic space group *P*2₁/*c* and the asymmetric unit consists of three crystallographically independent Zn^{II} centres (Zn1, Zn2 and Zn3), two timb ligands and three 1,2-cyclohexanedicarboxylate dianions and twenty uncoordinated water molecules. Zn1 is coordinated by N3 and N7 from two individual tripodal timb ligands and by O1 and O3 from two different bridging 1,2-cyclohexanedicarboxylate anions, forming a distorted tetrahedral ZnN₂O₂ coordination geometry. The coordination environment of each Zn2 and Zn3 centre is very similar to that of Zn1. The Zn–N bond lengths range from 1.992(4) to 2.038(4) Å and the Zn–O bond length range from 1.948(3) to 2.065(3) Å, respectively. The timb ligand adopts *cis*, *trans* and *trans* substituent conformations and coordinates to three Zn^{II} centres (Zn1, Zn2 and Zn3), generating a Zn–timb–Zn chain (chain A) along the [1 0 0] direction. The 1,2-cyclohexanedicarboxylate anion acts as a bridging link between two Zn^{II} cations, giving rise to the formation of linear Zn–1,2-cyclohexanedicarboxylate–Zn chains (chain B) running parallel to the *a* axis. The adjacent A and B chains interlacing connect to each other *via* Zn^{II} centres, leading to a three-dimensional structure. There are disordered solvent water molecules in the crystal.

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References

1. Spek, A. L.: PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallogr.* **C71** (2015) 9–18.
2. Spek, A. L.: Structure validation in chemical crystallography. *Acta Crystallogr.* **D65** (2009) 148–155.
3. Liu, H.-K.; Sun, W.-Y.; Ma, D.-J.; Yu, K.-B.; Tang, W.-X.: The first X-ray structurally characterized M₃L₂ cage-like complex with tetrahedral metal centres and its encapsulation of a neutral guest molecule. *Chem. Commun.* **7** (2000) 591–592.
4. Luo, L.; Chen, K.; Liu, Q.; Lu, Y.; Okamura, T.; Lv, G. C.; Zhao, Y.; Sun, W.-Y.: Zinc(II) and cadmium(II) complexes with 1,3,5-benzenetricarboxylate and imidazole-containing ligands: structural variation *via* reaction temperature and solvent. *Cryst. Growth Des.* **13** (2013) 2312–2321.
5. Deng, Y.; Zhao, Y.; Wang, P.; Yao, Z.-Y.; Zhang, X.-D.; Sun, W.-Y.: Coordination polymers with 1,3-bis(1-imidazolyl)-5-(imidazol-1-ylmethyl)benzene and biphenyl-4,4'-dicarboxylate ligands: selective adsorption of gas and dye molecules. *Microporous Mesoporous Mater.* **241** (2017) 192–201.
6. Zhao, W.; Fan, J.; Okamura, T.; Sun, W. Y.; Ueyama, N.: Syntheses, crystal structures and anion-exchange properties of novel coordination polymers with imidazole-containing tripodal ligands. *Microporous Mesoporous Mater.* **78** (2005) 265–279.
7. Wan, S. Y.; Fan, J.; Okamura, T.; Zhu, H. F.; Ouyang, X. M.; Sun, W. Y.; Ueyama, N.: 2D 4.8² Network with threefold parallel interpenetration from nanometer-sized tripodal ligand and lead(II) nitrate. *Chem. Commun.* **21** (2002) 2520–2521.
8. Yan, W.-Y.; He, R.-T.; Dai, M.; Ren, Z.-G.; Li, H.-X.; Lang, J.-P.: Assembly of 1D and 2D zinc(II) coordination polymers from flexible polyimidazolyl-based ligands. *Inorg. Chem. Commun.* **36** (2013) 51–55.
9. Su, Z.; Fan, J.; Okamura, T.; Chen, M.-S.; Chen, S.-S.; Sun, W.-Y.; Ueyama, N.: Interpenetrating and self-penetrating zinc(II) complexes with rigid tripodal imidazole-containing ligand and benzenedicarboxylate. *Cryst. Growth Des.* **10** (2010) 1911–1922.