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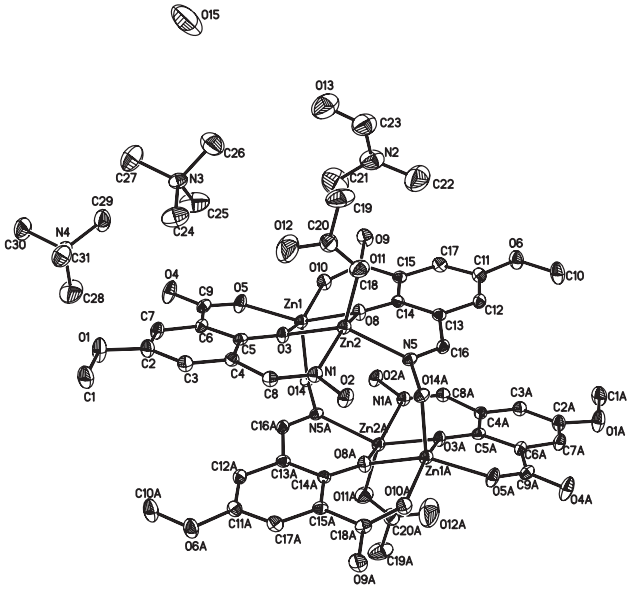
Crystal structure of tetramethylammonium bis(acetato-κ^1*O*)-tetrakis(μ$_3$-3-((hydroxyimino)methyl)-5-methoxy-2-oxidobenzoate-κ^5*O*,*O′*:*O′*,*N*:*O″*) tetrazinc(II) — *N*,*N′*-dimethylformamide — water (1/2/2), $C_{62}H_{96}Zn_4N_{10}O_{28}$



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Abstract

$C_{62}H_{96}Zn_4N_{10}O_{28}$, monoclinic, $P2_1/c$, $a = 12.1072(11)$ Å, $b = 27.878(3)$ Å, $c = 11.4494(9)$ Å, $\beta = 102.011(2)°$, $V = 3779.8(6)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0448$, $wR_{ref}(F^2) = 0.1092$, $T = 298(2)$ K.

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

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.42 × 0.31 × 0.30 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.34 mm^{-1}
Diffractometer, scan mode:	APEX2, φ and ω
θ_{max}, completeness:	25.0°>, 97%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18855, 6630, 0.045
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4732
$N(param)_{refined}$:	482
Programs:	Bruker programs [1], SHELX [2]

Source of material

H_3L (H_3L = 3-hydroxy-3-carboxyl-5-methoxybenzaldehyde oxime); systematic name: (E)-2-hydroxy-3-((hydroxyimino) methyl)-5-methoxybenzoic acid (0.0421 g, 0.2 mmol) in 10 mL DMF and $Zn(OAc)_2 \cdot H_2O$ (0.0663 g, 0.3 mmol) in 10 mL DMF were mixed and stirred for 30 min at room temperature, eight drops of methanol solution of the tetramethylammonium hydroxide were added. The solution was kept stirring for 5 h, then filtered. The filtrate was evenly divided into 6 test tubes to diffuse with the help of the ethanol and ether. After 1 week, the light yellow crystals suitable for single crystal X-ray measurements were obtained with the yield of 0.028 g, 22.0% based on Zn. Infrared spectrum (KBr, cm^{-1}): 3441 (s), 1652 (s), 1560 (s), 1488 (m), 1449 (w), 1420 (m), 1349 (s), 1265 (w), 1244 (w), 1152 (w), 1057 (m), 983 (m), 950 (m), 795 (s), 714 (w), 670 (w), 556 (w). Anal. calc. for $C_{62}H_{96}Zn_4N_{10}O_{28}$: C 44.00, H 5.67, N 8.28; found: C 42.23, H 5.14, N 7.89%.

Experimental details

The H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$, respectively [19]. The highest peak is located 0.361 Å from Cu1 and the deepest hole is situated −0.233 Å^3.

Comment

The Zn coordination polymers have drawn intense attention in recent decades owing to their special structures [3] and unique properties [4], which have potential applications in luminescence [5–10], gas absorption [11–13], photoluminescence [14, 15] and heterogeneous catalysis [16]. Especially, the

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.47791(4)	0.10806(2)	0.01684(4)	0.03022(14)
Zn2	0.60193(4)	0.02527(2)	0.18594(4)	0.02994(14)
O1	0.1971(3)	0.10619(11)	0.4927(3)	0.0593(9)
O2	0.5393(2)	−0.06752(9)	0.2949(3)	0.0420(7)
O3	0.4660(2)	0.06958(9)	0.1671(2)	0.0306(6)
O4	0.2989(3)	0.20140(10)	0.1820(3)	0.0574(9)
O5	0.3961(2)	0.16050(9)	0.0768(3)	0.0427(7)
O6	0.9488(3)	0.05748(11)	−0.2225(3)	0.0521(8)
N5	0.6568(3)	−0.03093(10)	0.0917(3)	0.0290(7)
O8	0.6141(2)	0.06527(9)	0.0394(2)	0.0343(6)
O9	0.6971(3)	0.18552(10)	−0.1420(3)	0.0530(9)
O10	0.5605(2)	0.15338(9)	−0.0700(3)	0.0426(7)
O11	0.7417(3)	0.03780(12)	0.3044(3)	0.0590(9)
O12	0.6606(4)	0.0849(2)	0.4003(5)	0.163(3)
O13	0.9380(5)	0.18877(19)	0.4226(5)	0.1163(17)
O14	0.3650(2)	0.07828(9)	−0.1178(2)	0.0331(6)
O15	0.9155(4)	0.21518(19)	0.9170(7)	0.167(3)
H15C	0.8464	0.2071	0.8984	0.200*
H15D	0.9195	0.2456	0.9180	0.200*
C1	0.1674(4)	0.06936(18)	0.5643(4)	0.0575(13)
H1A	0.1337	0.0434	0.5144	0.086*
H1B	0.1145	0.0815	0.6089	0.086*
H1C	0.2338	0.0581	0.6185	0.086*
C2	0.2634(3)	0.09390(15)	0.4124(4)	0.0398(10)
C3	0.3180(3)	0.05087(14)	0.4109(4)	0.0365(10)
H3	0.3101	0.0272	0.4658	0.044*
C4	0.3850(3)	0.04217(13)	0.3281(3)	0.0300(9)
C5	0.4006(3)	0.07779(13)	0.2443(3)	0.0283(9)
C6	0.3410(3)	0.12155(13)	0.2453(3)	0.0289(9)
C7	0.2745(3)	0.12796(14)	0.3294(4)	0.0371(10)
H7	0.2356	0.1567	0.3293	0.044*
C8	0.4346(3)	−0.00567(14)	0.3329(4)	0.0339(10)
H8	0.4115	−0.0279	0.3835	0.041*
C9	0.3450(3)	0.16362(14)	0.1627(4)	0.0335(9)
C10	1.0052(4)	0.01379(18)	−0.2309(5)	0.0607(14)
H10A	0.9531	−0.0090	−0.2747	0.091*
H10B	1.0349	0.0016	−0.1522	0.091*
H10C	1.0660	0.0190	−0.2716	0.091*
C11	0.8624(3)	0.05670(15)	−0.1603(4)	0.0362(10)
C12	0.8331(3)	0.01717(14)	−0.1020(4)	0.0352(10)
H12	0.8707	−0.0117	−0.1064	0.042*
C13	0.7480(3)	0.01934(13)	−0.0361(3)	0.0297(9)
C14	0.6900(3)	0.06275(13)	−0.0290(3)	0.0281(9)
C15	0.7155(3)	0.10262(13)	−0.0953(3)	0.0312(9)
C16	0.7197(3)	−0.02576(14)	0.0149(3)	0.0314(9)
H16	0.7501	−0.0535	−0.0106	0.038*
C17	0.8017(3)	0.09860(14)	−0.1583(4)	0.0363(10)
H17	0.8192	0.1251	−0.2005	0.044*
C18	0.6539(3)	0.15006(14)	−0.1025(4)	0.0339(10)
C19	0.8459(5)	0.0693(2)	0.4819(5)	0.088(2)
H19A	0.8398	0.0504	0.5503	0.132*
H19B	0.8545	0.1025	0.5043	0.132*
H19C	0.9105	0.0590	0.4520	0.132*
C20	0.7412(4)	0.06311(19)	0.3865(5)	0.0546(13)
C21	0.7993(6)	0.1718(3)	0.2006(7)	0.127(3)
H21A	0.7938	0.1862	0.1235	0.191*
H21B	0.7856	0.1956	0.2563	0.191*
H21C	0.7441	0.1467	0.1953	0.191*
C22	0.9523(7)	0.1192(3)	0.1621(7)	0.129(3)
H22A	0.9035	0.0918	0.1470	0.193*
H22B	1.0271	0.1090	0.1992	0.193*
H22C	0.9542	0.1350	0.0880	0.193*
C23	0.9681(6)	0.1615(2)	0.3485(7)	0.094(2)
H23	1.0379	0.1466	0.3718	0.112*
C24	0.5394(5)	0.15428(18)	0.5636(5)	0.0779(18)
H24A	0.4583	0.1540	0.5435	0.117*
H24B	0.5644	0.1505	0.6483	0.117*
H24C	0.5681	0.1284	0.5233	0.117*
C25	0.5443(6)	0.2073(2)	0.3962(5)	0.094(2)
H25A	0.5692	0.1807	0.3551	0.141*
H25B	0.5761	0.2365	0.3731	0.141*
H25C	0.4634	0.2093	0.3759	0.141*
C26	0.7055(5)	0.1995(2)	0.5570(6)	0.089(2)
H26A	0.7304	0.1980	0.6421	0.134*
H26B	0.7346	0.2281	0.5276	0.134*
H26C	0.7325	0.1719	0.5213	0.134*
C27	0.5420(6)	0.2406(2)	0.5897(6)	0.095(2)
H27A	0.4613	0.2429	0.5668	0.142*
H27B	0.5755	0.2698	0.5698	0.142*
H27C	0.5635	0.2352	0.6743	0.142*
C28	0.0904(6)	0.2847(3)	0.1926(6)	0.108(3)
H28A	0.0823	0.3063	0.1261	0.162*
H28B	0.0190	0.2811	0.2155	0.162*
H28C	0.1156	0.2540	0.1702	0.162*
C29	0.2822(5)	0.3149(2)	0.2555(6)	0.092(2)
H29A	0.3058	0.2872	0.2170	0.138*
H29B	0.3390	0.3229	0.3245	0.138*
H29C	0.2713	0.3414	0.2010	0.138*
C30	0.1301(5)	0.3479(2)	0.3432(6)	0.087(2)
H30A	0.1063	0.3708	0.2805	0.131*
H30B	0.1890	0.3615	0.4032	0.131*
H30C	0.0673	0.3395	0.3783	0.131*
C31	0.1963(5)	0.26706(19)	0.3883(5)	0.0712(16)
H31A	0.1281	0.2602	0.4153	0.107*
H31B	0.2526	0.2787	0.4539	0.107*
H31C	0.2232	0.2383	0.3572	0.107*
N1	0.5070(3)	−0.01959(11)	0.2736(3)	0.0325(8)
N2	0.9103(4)	0.15205(19)	0.2405(5)	0.0834(15)
N3	0.5814(3)	0.20043(13)	0.5262(3)	0.0445(9)
N4	0.1734(3)	0.30400(13)	0.2931(4)	0.0512(10)

tetranuclear Zn complexes are often used as catalysts. Copolymerization of CO_2 [17] and cyclohexene oxide and electrode posited precursor for ZnO nanosheets [18]. The 2-hydroxy-3-carboxyl-5-methoxybenzaldehyde oxime (L) acts as a N/O bridging ligand and has proven to be an excellent ligand in the synthesis of metal-organic complexes [19, 20] in the past. Therefore, we herein report the construction of a novel tetranuclear Zn compound with L as ligand. The syntheses and structures of the compound are described in this paper.

The asymmetric unit consists of two Zn^{II} ions, two HL ligands, one acetate, two tetramethyl ammonium cations, one DMF molecule and one water molecule. Each Zn^{II} ion exhibits a five-coordinated tetragonal pyramid configuration. For Zn1, the coordination atoms are from five oxygen atoms of three HL ligands to form a O5 coordination environment. The coordination atoms of Zn2 are supplied by three oxygen atoms and two nitrogen atoms to display a N_2O_3 coordination environment. The bond length range of Zn—O bonds and Zn—N bonds are 1.967–2.091 Å and 2.091–2.088 Å, respectively. Four Zn atoms are connected by O atoms to form the core of the complex. The bond angles of Zn(2)—O(3)—Zn(1), Zn(1)—O(8)—Zn(2) are 102.1° and 103.45°, respectively. Bond lengths and angles are all in the expected ranges.

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References

1. BRUKER. SAINT, APEX2 and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Ma, L. F.; Qin, J. H.; Han, M. L.; Wang, L. Y.; Du, M.: A unique 3-D Zn(II) coordination framework with 1,2,3-benzenetricarboxyl and 4,4′-bipyridyl tectons showing 4-connected self-penetrating network and helical character. Inorg. Chem. Commun. **14** (2011) 1584–1587.
4. Li, M. Y.; Wang, F.; Zhang, J.: Synthesis, structure and proton conductivity of a metal-organic framework with rich hydrogen-bonds between the layers. Inorg. Chem. Commun. **79** (2017) 37–40.
5. Chen, X. L.; Zhang, X. G.; Gao, L. J.; Ma, H. Y.: New examples of d^{10} metal-organic frameworks based on 4,4′-(hexafluoroisopropylidene)diphthalic acid: Synthesis crystal structure and luminesence. J. Mol. Struct. **1085** (2015) 45–51.
6. Zhang, S. Q.; Jiang, F. L.; Wu, M. Y.; Feng, R.; Ma, J.; Xu, W. T.; Hong, M. C.: The Zn(II)-organic coordination polymers based on 2-(pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylate ligands: crystal structure and luminescent properties. Inorg. Chem. Commun. **14** (2011) 1400–1405.
7. Bu, X. Z.; Wei, Z. W.; Zhang, C. H.; Ren, S. F.: Employing tetrahedral $\{Zn_4O\}$ clusters as building subunits to construct a new acentric metal-organic framework. Inorg. Chem. Commun. **48** (2014) 158–160.
8. Liu, B.; Yang, G. P.; Wang, Y. Y.; Liu, R. T.; Hou, L.; Shi, Q. Z.: Two new pH-controlled metal-organic frameworks based on polynuclear secondary building units with conformation-flexible cyclohexane-1,2,4,5-tetracarboxylate ligand. Inorg. Chim. Acta **367** (2011) 127–134.
9. Lv, C. W.; Li, J.; Hou, Z.; Li, M. K.: Synthesis, structure and luminescent property of a new Zn(II) coordination polymer with isolated tetrahedral $\{Zn_4O\}$ clusters as building subunits. Inorg. Chem. Commun. **36** (2013) 1–3.
10. Wang, D. Z.: Zinc(II) and cadmium(II) coordination polymers with bis(tetrazole) ligands: synthesis, structures and luminescent properties. Polyhedron **35** (2012) 142–148.
11. He, W. W.; Li, N.; Wang, X.; Hu, T. L.; Bu, X. H.: A cationic metal-organic framework based on {Zn4} cluster for rapid and selective adsorption of dyes. Chin. Chem. Lett. **29** (2018) 857–860.
12. Du, J.; Zou, G. L.: A novel microporous zinc(II) metal-organic framework with highly selectivity adsorption of CO_2 over CH_4. Inorg. Chem. Commun. **69** (2016) 20–23.
13. Moradpour, T.; Abbasi, A.; Hecke, K. V.: A nanoporous 3D zinc(II) metal-organic framework for selective adsorption of benzaldehyde and formaldehyde. J. Solid State Chem. **228** (2015) 36–41.
14. Liu, B.; Guo, K.; Feng, H. J.; Miao, W. N.; He, T. T.; Xu, L.: Mixed sulfoisophthalate and 1,2,4-triazole directed d^{10} metal coordination polymers: synthesis, property and structural diversity. J. Solid State Chem. **254** (2017) 47–54.
15. Guo, Y. Y.; Ma, P. T.; Wang, J. P.; Niu, J. Y.: Two multi-dimensional frameworks constructed from zinc coordination polymers with pyridine carboxylic acids. J. Solid State Chem. **184** (2011) 3121–3127.
16. Zhang, S. X.; He, H. M.; Sun, F. X.; Zhao, N.; Du, J. S.; Pan, Q. H.; Zhu, G. S.: A novel adenine-based zinc(II) metal-organic framework featuring the lewis basic sites for heterogeneous catalysis. Inorg. Chem. Commun. **79** (2017) 55–59.
17. Kröger, M.; Folli, C.; Walter, O.; Döring, M.: A new amidoimidomalonate zinc complex with a sedecameric solid state structure catalyzing the copolymerization of CO_2 and cyclohexene oxide. J. Organomet. Chem. **691** (2006) 3397–3402.
18. Liang, W. T.; Li, W. P.; Chen, H. N.; Liu, H. C.; Zhu, L. Q.: Exploiting electrodeposited flower-like $Zn_4(OH)_6SO_4{\cdot}4H_2O$ nanosheets as precursor for porous ZnO nanosheets. Electrochim. Acta **156** (2015) 171–178.
19. Pandey, J.; Mishra, M.; Bisht, S. S.; Sharma, A.; Tripathi, R. P.: An efficient chemoselective etherification of phenols in polyfunctional aromatic compounds. Tetrahedron Lett. **4** (2018) 695–698.
20. Cai, J.; Liu, L. G.; Hong, K. H.; Wang, P.; Li, L. S.; Cao, M.; Sun, C. L.; Wu, X. Q.; Zong, X.; Chen, J. Q.; Ji, M.: Discovery of phenoxybutanoic acid derivatives as potent endothelin antagonists with antithpentensive activity. Bioorg. Med. Chem. **23** (2015) 657–667.