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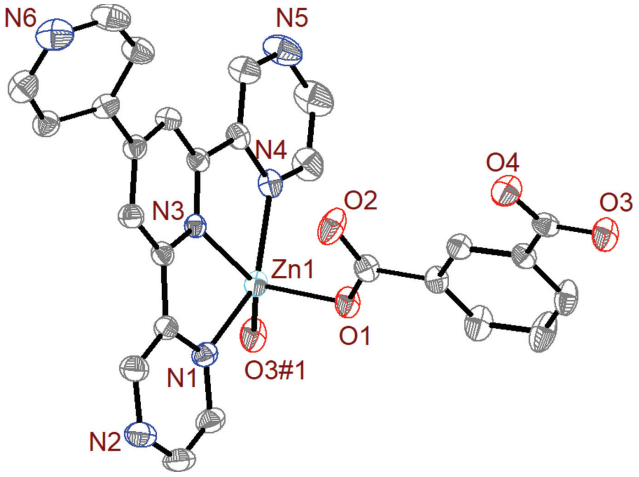
Crystal structure of *catena*-poly[(μ_2-isophthalato-κ^2*O*:*O*′)-(2,5-di(pyrazin-2-yl)-4,4′-bipyridine-κ^3*N*,*N*′,*N*″)zinc(II)] — water (2/5), $C_{26}H_{21}N_6O_{6.5}Zn$



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Abstract

$C_{26}H_{21}N_6O_{6.5}Zn$, monoclinic, *C*2/*c* (no. 15), $a = 18.3123(3)$ Å, $b = 8.97463(15)$ Å, $c = 30.1437(5)$ Å, $\beta = 99.5396(16)°$, $V = 4885.51(14)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0352$, $wR_{ref}(F^2) = 0.0746$, $T = 293(2)$ K.

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A part of the molecular structure is shown in the figure (The water molecules completing the asymmetric unit are not shown). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of py-pzpypz (28 mg, 0.1 mmol), H_2ip (16 mg, 0.1 mmol), $Zn(OAc)_2{\cdot}2\,H_2O$ (21 mg, 0.1 mmol) and H_2O (10 mL) was stirred for 30 min, and the pH value of the solution was adjusted to about 6 with 1 M KOH. Then the mixture was transferred to a 25 mL Teflon-lined stainless steel vessel and heated at 140 °C for 3 days, and then cooled to room temperature over 48 h. Colourless block crystals of the title compound were obtained.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.20 × 0.18 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.07 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	45759, 4533, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4224
$N(param)_{refined}$:	366
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3]

Experimental details

Using Olex2, the structure was solved with the SIR2004 structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

Comment

One of the currently active research areas to both chemists and physicists is design and construct of multifunctional materials [4–7]. Metal-organic coordination compounds provide an attracting approach in this area. The chemical and physical characteristics of ligands play an important role in regulating the properties of functional compounds [8–10]. Generally, the construction of the functional compounds is primarily dependent upon the advisable selection of the central metal and organic ligands. However, it is still difficult to control structures [11, 12].

Currently, a vast number of compounds with diverse structures and properties have been constructed over a decade. Then carboxylate ligands have been extensively employed due to their versatile coordination conformations

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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}
C1	0.39092(14)	0.0296(3)	0.39115(9)	0.0331(6)
H1	0.4059	0.0142	0.4218	0.040*
C2	0.35450(15)	−0.0828(3)	0.36537(9)	0.0368(6)
H2	0.3448	−0.1716	0.3792	0.044*
C3	0.34805(15)	0.0622(3)	0.30337(9)	0.0335(6)
H3	0.3339	0.0765	0.2726	0.040*
C4	0.38415(13)	0.1768(3)	0.32890(8)	0.0243(5)
C5	0.40075(12)	0.3254(3)	0.31115(8)	0.0235(5)
C6	0.37706(13)	0.3726(3)	0.26734(8)	0.0270(5)
H6	0.3515	0.3080	0.2461	0.032*
C7	0.39208(13)	0.5181(3)	0.25558(8)	0.0243(5)
C8	0.43245(13)	0.6099(3)	0.28784(8)	0.0251(5)
H8	0.4444	0.7067	0.2806	0.030*
C9	0.45456(12)	0.5548(3)	0.33091(8)	0.0218(5)
C10	0.36217(13)	0.5730(3)	0.20966(8)	0.0264(5)
C11	0.33255(15)	0.7148(3)	0.20257(9)	0.0356(6)
H11	0.3343	0.7814	0.2263	0.043*
C12	0.30034(17)	0.7553(3)	0.15958(10)	0.0447(7)
H12	0.2802	0.8503	0.1554	0.054*
C13	0.32754(15)	0.5342(3)	0.13091(9)	0.0374(6)
H13	0.3273	0.4719	0.1062	0.045*
C14	0.36044(14)	0.4819(3)	0.17251(8)	0.0294(6)
H14	0.3811	0.3871	0.1755	0.035*
C15	0.49467(12)	0.6432(3)	0.36902(8)	0.0245(5)
C16	0.52144(14)	0.7854(3)	0.36500(9)	0.0347(6)
H16	0.5163	0.8283	0.3366	0.042*
C17	0.53604(15)	0.6532(3)	0.44474(9)	0.0389(6)
H17	0.5424	0.6099	0.4732	0.047*
C18	0.56139(18)	0.7951(3)	0.43988(10)	0.0516(8)
H18	0.5844	0.8456	0.4653	0.062*
C19	0.32661(12)	0.4814(3)	0.42720(8)	0.0260(5)
C20	0.26596(12)	0.5188(3)	0.45334(8)	0.0247(5)
C21	0.20593(12)	0.6030(3)	0.43338(8)	0.0255(5)
H21	0.2034	0.6349	0.4038	0.031*
C22	0.14966(12)	0.6402(3)	0.45696(8)	0.0244(5)
C23	0.15469(14)	0.5952(3)	0.50135(8)	0.0346(6)
H23	0.1186	0.6241	0.5180	0.042*
C24	0.21324(15)	0.5074(4)	0.52098(9)	0.0440(8)
H24	0.2154	0.4743	0.5504	0.053*
C25	0.26845(14)	0.4688(3)	0.49710(9)	0.0364(6)
H25	0.3075	0.4090	0.5104	0.044*
C26	0.08247(13)	0.7206(3)	0.43355(8)	0.0267(5)
N1	0.40518(11)	0.1597(2)	0.37331(6)	0.0262(4)
N2	0.33277(13)	−0.0680(2)	0.32119(8)	0.0376(5)
N3	0.43827(10)	0.4159(2)	0.34187(6)	0.0214(4)
N4	0.50255(11)	0.5769(2)	0.40954(6)	0.0268(4)
N5	0.55438(14)	0.8635(3)	0.40024(8)	0.0483(6)
N6	0.29629(13)	0.6672(3)	0.12375(8)	0.0435(6)
O1	0.37827(9)	0.3969(2)	0.44632(6)	0.0313(4)
O2	0.32497(10)	0.5351(2)	0.38918(6)	0.0431(5)
O2AA	0.5000	0.9294(3)	0.2500	0.0572(8)
H2AA[a]	0.5237	0.9698	0.2736	0.086*
H2AB[a]	0.4721	0.9936	0.2350	0.086*
O3	0.03167(9)	0.7524(2)	0.45617(6)	0.0354(4)
O4	0.07727(10)	0.7540(2)	0.39328(6)	0.0379(5)
O5	0.09167(13)	0.5961(3)	0.31410(7)	0.0584(6)
H5A	0.1380	0.6023	0.3143	0.088*
H5B	0.0817	0.6268	0.3391	0.088*
O6	0.24536(12)	0.6419(3)	0.30920(7)	0.0514(5)
H6A	0.2664	0.5951	0.3324	0.077*
H6B	0.2691	0.7216	0.3062	0.077*
Zn1	0.45682(2)	0.35481(3)	0.40997(2)	0.02426(9)

[a]Occupancy: 0.5.

and strong coordination ability. The pyrazine analogues of these terpyridine-type ligands have received far less attention, with the replacement of one or more pyridine rings by pyrazine rings first reported [14].

The structure consists of [Zn(py-pzpypz)(ip)] moiety and two and a half isolated water molecules. The center Zn(II) ion resides in a distorted trigonal bipyramid and is coordinated by three nitrogen atoms from pyterpy ligand and two oxygen atoms from two different isophthalic acid ligands. The equatorial plane is composed of one nitrogen atom and two oxygen atoms (N3, O1, O3#1), while atoms N1 and N4 occupy the axial positions. The average Zn-N bond length is 2.1531(7) Å, and the Zn—O bond lengths are in a range of 2.0045(14)–2.0638(15) Å. The bond angles of N1—Zn1—N4 are 149.94(7)°, which are comparable to those found in other reported Zn(II) compounds [14, 15]. The same is true for the isophthalato ligand [16]. The two carboxyl groups of H_2ip ligand are completely deprotonated and link adjacent Zn(II) ions with coordination modes. The adjacent Zn(II) ions are bridged into one dimensional chain structure by oxygen atoms coming from ip^{2-} ligands (Figure). The terminal py-pzpypz ligands suspend on the chains.

The intermolecular hydrogen bonds occur between two oxygen atoms from uncoordinated water molecules. The intermolecular hydrogen bonds also occur between two oxygen atoms from uncoordinated water molecule and carboxylate group. Thereby, the title compound can be viewed as a one-dimensional supramolecular architecture further extended via these hydrogen bonds.

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References

1. Agilent Technologies: CrysAlis^{PRO} Software system, version 1.171.38.41r, Agilent Technologies UK Ltd, Oxford, UK (2011).
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Crystallogr. **42** (2009) 339–341.

3. Sheldrick, G. M.: SHELXT-integrated space-group and crystal-structure determination. Acta Crystallogr. **C71** (2015) 3–8.
4. Zhao, J. W.; Li, Y. Z.; Chen, L. J.; Yang, G. Y.: Research progress on polyoxometalate-based transition-metal-rare-earth heterometallic derived materials: synthetic strategie. Chem. Commun. **52** (2016) 4418–4445.
5. Xin, L. Y.; Liu, G. Z.; Li, X. L.; Wang, L. Y.: Structural diversity for a series of metal(II) complexes based on flexible 1,2-phenylenediacetate and dipyridyl-type coligand. Cryst. Growth Des. **12** (2012) 147–157.
6. Ling, S.; Slater, B.: Unusually large band gap changes in breathing metal-organic framework materials. J. Phys. Chem. C **119** (2015) 16667–16677.
7. Gong, L. L.; Yao, W. T.; Liu, Z. Q.; Zheng, A. M.; Li, J. Q.; Feng, X. F.; Ma, L. F.; Yan, C. S.; Luo, M. B.; Luo, F.: Photoswitching storage of guest molecules in metal–organic framework for photoswitchable catalysis: exceptional product, ultrahigh photocontrol, and photomodulated size selectivity. J. Mater. Chem. A **5** (2017) 7961–7967.
8. Halcrow, M. A.: Structure: function relationships in molecular spin-crossover complexes. Chem. Soc. Rev. **40** (2011) 4119–4142.
9. Wang, Y. F.; Li, S. H.; Ma, L. F.; Geng, J. L.; Wang, L. Y.: Syntheses, crystal structures, and magnetic studies of two cobalt(II) coordination polymers based on concurrent ligand extension. Inorg. Chem. Commun. **62** (2015) 42–46.
10. Mukherjee, S.; Desai, A. V.; Ghosh, S. K.: Potential of metal-organic frameworks for adsorptive separation of industrially and environmentally relevant liquid mixtures. Coord. Chem. Rev. **367** (2018) 82–126.
11. Zhang, W. Q.; Zhang, W. Y.; Wang, R. D.; Ren, C. Y.; Li, Q. Q.; Fan, Y. P.; Wang, Y. Y.: Effect of coordinated-solvent molecules on metal coordination sphere and solvent-induced transformations. Cryst. Growth Des. **17** (2017) 517–526.
12. Wang, Y. F.; Li, Z.; Sun, Y. C.; Zhao, J. S.; Wang, L. Y.: Structural modulation and properties of four cadmium(II) coordination architectures based on 3-(pyridin-4-yl)-5-(pyrazin-2-yl)-1*H*-1,2,4-triazole and aromatic polycarboxylate ligands. CrystEngComm **15** (2013) 9980–9987.
13. Miller, R. G.; Brooker, S.: Spin crossover, reversible redox, and supramolecular interactions in 3d complexes of 4-(4-pyridyl)-2,5-dipyrazyl-pyridine. Inorg. Chem. **54** (2015) 5398–5409.
14. Li, Y. P.; Ju, F. Y.; Li, G. L.; Xin, L. Y.; Liu, G. Z.: Syntheses, structures, and properties of two Zn(II)/Ag(I) complexes assembled from tetracarboxylic acids and *N*-donor ligands. Russ. J. Coord. Chem. **44** (2018) 214–219.
15. Ju, F. Y.; Li, Y. P.; Li, G. L.; Liu, G. Z.; Xin, L. Y.; Li, X. L.: Zinc(II) and cadmium(II) coordination polymers with various polynuclears spaced by semirigid 4-carboxybenzeneacetate and nitrogen-rich co-ligands: syntheses, structures and properties. Chin. J. Inorg. Chem. **32** (2016) 1876–1884.
16. Xu, C.; Liu, L.; Su, T.; Li, S.: Crystal structure of bis(μ_3-isophthalato-κ^3O:O':O'')(μ_2-1,4-bis((2-propyl-1*H*-benzo[*d*]imidazol-1-yl)methyl)benzene-κ^2N:N')dizinc(II), $C_{22}H_{19}N_2O_4Zn$. Z. Kristallogr. NCS **231** (2016) 913–915.