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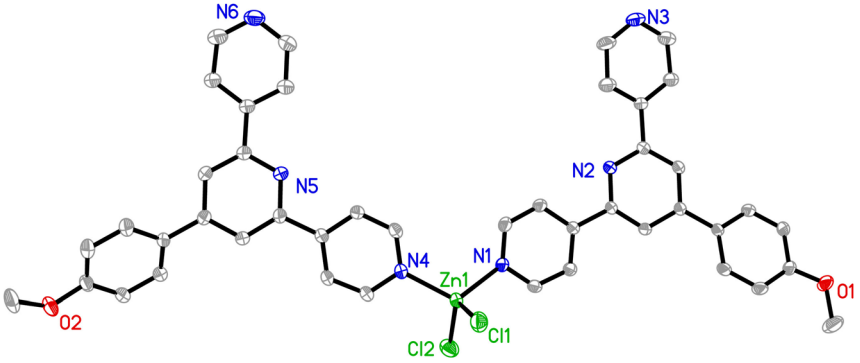
The crystal structure of dichloridobis[4′-(*p*-methoxylphenyl)-4,2′:6′,4″-terpyridine-*κN*] zinc(II), $C_{44}H_{34}Cl_2N_6O_2Zn$



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Abstract

$C_{44}H_{34}Cl_2N_6O_2Zn$, triclinic, $P\bar{1}$ (no. 2), a = 10.875(9) Å, b = 11.755(9) Å, c = 16.471(13) Å, α = 105.924(14)°, β = 97.552(13)°, γ = 104.507(13)°, V = 1,914(3) Å^3, Z = 2, $R_{gt}(F)$ = 0.0455, $wR_{ref}(F^2)$ = 0.1154, T = 296 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.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.27 × 0.23 × 0.19 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.83 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX2, φ and ω
θ_{max}, completeness:	25.0°, 98 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10,500, 6,597, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4,139
$N(param)_{refined}$:	498
Programs:	Bruker[1], SHELX[2,3], Olex2[4]

1 Source of materials

The reagents were purchased from standard commercial sources and used without further purification. A mixture of $ZnCl_2$ (0.014 g, 0.10 mmol), meophtpy (0.034 g, 0.10 mmol) was dispersed in C_2H_5OH (7 mL) solution and ammonia (25 %) was added dropwise until a clear colorless solution was obtained. The resultant solution was allowed slowly to evaporate under room temperature for two weeks to give light yellow crystals which were isolated by filtration and washed by deionized water and dried in air.

2 Experimental details

The structure was solved by Direct Methods with the SHELXT-2018 program. All H-atoms from C atoms were positioned with idealized geometry and refined isotropically (U_{iso}(H) = 1.2U_{eq}(C)) using a riding model with C–H = 0.93 and 0.97 Å.

3 Comment

In the past few years, metal-organic frameworks (MOFs) have been extensively studied for their diversity of

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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	0.79541(4)	0.32271(4)	0.29359(3)	0.04299(16)
Cl1	0.89579(10)	0.52398(10)	0.35097(7)	0.0619(3)
Cl2	0.91750(11)	0.20267(11)	0.24525(7)	0.0665(3)
O1	0.6831(3)	0.5574(3)	−0.42977(18)	0.0739(10)
O2	0.8372(3)	−0.0820(3)	0.95210(17)	0.0628(8)
N1	0.6693(3)	0.3011(3)	0.18164(18)	0.0426(8)
N2	0.3398(3)	0.3278(3)	−0.04697(18)	0.0389(8)
N3	−0.1240(3)	0.3359(4)	−0.0958(3)	0.0749(12)
N4	0.7115(3)	0.2641(3)	0.38399(19)	0.0442(8)
N5	0.4303(3)	0.1412(3)	0.58074(19)	0.0397(7)
N6	−0.0257(3)	0.1083(3)	0.6217(3)	0.0642(10)
C1	0.5410(3)	0.2845(4)	0.1672(2)	0.0475(10)
H1	0.496336	0.267950	0.209144	0.057*
C2	0.4723(3)	0.2910(3)	0.0929(2)	0.0429(10)
H2	0.382907	0.277492	0.085104	0.052*
C3	0.5361(3)	0.3174(3)	0.0300(2)	0.0344(8)
C4	0.6678(3)	0.3297(4)	0.0432(2)	0.0462(10)
H4	0.714029	0.343124	0.001304	0.055*
C5	0.7295(3)	0.3220(4)	0.1190(2)	0.0488(11)
H5	0.818321	0.331845	0.127225	0.059*
C6	0.4656(3)	0.3363(3)	−0.0471(2)	0.0344(8)
C7	0.5266(3)	0.3655(3)	−0.1103(2)	0.0364(9)
H7	0.612935	0.367429	−0.108476	0.044*
C8	0.4579(3)	0.3922(3)	−0.1770(2)	0.0343(8)
C9	0.3274(3)	0.3818(3)	−0.1773(2)	0.0368(9)
H9	0.277140	0.396649	−0.221169	0.044*
C10	0.2719(3)	0.3496(3)	−0.1127(2)	0.0365(9)
C11	0.1336(3)	0.3425(3)	−0.1085(2)	0.0405(9)
C12	0.0867(4)	0.3277(5)	−0.0376(3)	0.0739(15)
H12	0.139852	0.319265	0.008073	0.089*
C13	−0.0398(4)	0.3254(6)	−0.0345(3)	0.095(2)
H13	−0.068499	0.315802	0.014628	0.114*
C14	−0.0783(4)	0.3466(4)	−0.1644(3)	0.0650(13)
H14	−0.134522	0.352352	−0.209781	0.078*
C15	0.0470(4)	0.3499(4)	−0.1743(3)	0.0536(11)
H15	0.072316	0.357105	−0.224902	0.064*
C16	0.5206(3)	0.4328(3)	−0.2433(2)	0.0356(9)
C17	0.4471(3)	0.4314(3)	−0.3195(2)	0.0407(9)
H17	0.356870	0.401959	−0.329698	0.049*
C18	0.5038(3)	0.4721(4)	−0.3798(2)	0.0445(10)
H18	0.452002	0.468449	−0.430711	0.053*
C19	0.6377(4)	0.5188(4)	−0.3656(2)	0.0487(11)
C20	0.7130(4)	0.5229(4)	−0.2903(2)	0.0612(13)
H20	0.803090	0.554334	−0.279718	0.073*
C21	0.6540(3)	0.4800(4)	−0.2303(2)	0.0534(11)
H21	0.705846	0.483036	−0.179717	0.064*
C22	0.8188(4)	0.5960(6)	−0.4242(3)	0.104(2)
H22A	0.835559	0.612227	−0.476390	0.156*
H22B	0.854603	0.531886	−0.416643	0.156*
H22C	0.858409	0.670234	−0.375822	0.156*
C23	0.7809(4)	0.2293(5)	0.4396(3)	0.0725(15)
H23	0.865123	0.230599	0.433975	0.087*
C24	0.7364(4)	0.1914(4)	0.5050(3)	0.0646(14)
H24	0.790440	0.168712	0.542217	0.077*
C25	0.6117(3)	0.1870(3)	0.5157(2)	0.0377(9)
C26	0.5402(4)	0.2242(4)	0.4587(2)	0.0475(10)
H26	0.455754	0.223988	0.463075	0.057*
C27	0.5918(4)	0.2618(4)	0.3955(2)	0.0501(11)
H27	0.540543	0.287110	0.358438	0.060*
C28	0.5550(3)	0.1440(3)	0.5832(2)	0.0367(9)
C29	0.6243(3)	0.1082(3)	0.6439(2)	0.0402(9)
H29	0.710192	0.110242	0.643140	0.048*
C30	0.5655(3)	0.0696(3)	0.7054(2)	0.0388(9)
C31	0.4365(3)	0.0696(3)	0.7034(2)	0.0402(9)
H31	0.393718	0.045933	0.744158	0.048*
C32	0.3723(3)	0.1052(3)	0.6402(2)	0.0384(9)
C33	0.2347(3)	0.1056(3)	0.6348(2)	0.0424(10)
C34	0.1590(4)	0.0659(4)	0.6878(3)	0.0676(14)
H34	0.193089	0.036077	0.729632	0.081*
C35	0.0324(4)	0.0700(5)	0.6796(3)	0.0769(15)
H35	−0.015125	0.043852	0.717611	0.092*
C36	0.0483(4)	0.1473(4)	0.5711(3)	0.0665(13)
H36	0.011444	0.176680	0.529991	0.080*
C37	0.1757(4)	0.1478(4)	0.5748(3)	0.0571(12)
H37	0.221677	0.176454	0.536982	0.069*
C38	0.6346(3)	0.0281(3)	0.7705(2)	0.0404(9)
C39	0.7213(3)	−0.0379(4)	0.7511(3)	0.0493(10)
H39	0.736318	−0.058278	0.695373	0.059*
C40	0.7865(4)	−0.0745(4)	0.8124(2)	0.0526(11)
H40	0.842837	−0.120791	0.797483	0.063*
C41	0.7678(4)	−0.0421(4)	0.8956(3)	0.0472(10)
C42	0.6818(4)	0.0241(4)	0.9173(3)	0.0537(11)
H42	0.668181	0.045208	0.973355	0.064*
C43	0.6159(4)	0.0587(4)	0.8548(2)	0.0511(11)
H43	0.558054	0.103331	0.869526	0.061*
C44	0.8401(5)	−0.0316(5)	1.0421(3)	0.0764(15)
H44A	0.755147	−0.061289	1.052811	0.115*
H44B	0.865848	0.057328	1.058664	0.115*
H44C	0.901249	−0.056885	1.075231	0.115*

structures, topologies, properties and potential application in different fields like gas sorption, fluorescence sensing, magnetism and photodegradation, etc.[5–8] The successful synthesis of MOFs mainly relies on the careful selection of metal ions and organic links. In this text, Zn(II) ion is accepted for its success in the assembly of fluorescence complexes[9,10] and 4,2′:6′,4″-terpyridine ligand is accepted as it contains two terminal pyridine N atoms which would behave as bridges among metal ions.[11,12] A Zn(II) complex was obtained with 4′-(*p*-methoxylphenyl)-4,2′:6′,4″-terpyridine (meophtpy) as ligand and its structure has been determined. Just as it still possesses unsaturated coordination groups, the title complex may also behave as metalloligand, which are better alternative to direct the assembly of large molecular arrays and 1D, 2D, 3D coordination polymers and networks.[13,14]

As shown in the figure, the asymmetric unit contains one Zn(II) ion, two meophtpy ligands, and two Cl^- anions. Each Zn(II) ion is coordinated by two pyridyl N atoms from two meophtpy ligands, Zn1–N1 = 2.036(3) Å, Zn1–N4 = 2.062(3) Å and two chlorides, Zn1–Cl1 = 2.2340(18) Å, Zn1–Cl2 = 2.211(2) Å to furnish a distorted tetrahedral geometry. In this complex, the Cl–Zn–Cl bond angle is 116.55(7)°, the N–Zn–N bond angle is 115.56(14)° and the N–Zn–Cl bond angles range from 102.32(12)° to 108.65(11)°. All these bond lengths and angles are similar with other complexes with ZnN_2Cl_2 coordination environment.[12–17]

In the crystal structure, five C atoms, C4, C15, C18, C22 and C24 act as hydrogen donors, contributing hydrogen atoms H4, H15, H18, H22C and H12 to N3, Cl1, O1, Cl2, and N6 to form non-classic hydrogen bonds between molecules. In addition, there are two kinds of offset face to face π–π stacking interactions with center to center distances of 3.641(4) Å and 3.896(4) Å, between pyridine rings. The discrete complexes were further extended into 3D network mainly by the hydrogen bonding interaction and the π–π stacking interactions.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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