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The crystal structure of poly[(μ_3 -2,4,6-tris[4-(1*H*-imidazol-1-yl)phenyl]-1,3,5-triazine- $k^3N:N':N''$)-(nitrate- k^2O,O)-(nitrate- k^1O)zinc(II)] - *N,N*-dimethylacetamide (1/2), $C_{38}H_{39}N_{13}O_8Zn$

Abstract

$C_{38}H_{39}N_{13}O_8Zn$, monoclinic, $P2_1/c$ (no. 14), $a = 13.0155(7)$ Å, $b = 32.7011(14)$ Å, $c = 9.8464(4)$ Å, $\beta = 110.228(1)^\circ$, $V = 3932.4(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0476$, $wR_{ref}(F^2) = 0.1358$, $T = 150(2)$ K.

CCDC no.: 1922925

A part of the polymeric crystal 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:	Thin-block, colorless
Size:	$0.40 \times 0.32 \times 0.10$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.70 mm^{-1}
Diffractometer, scan mode:	Rigaku R-Axis, ω -scans
$\theta_{\max}$, completeness:	27.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	54345, 8932, 0.062
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6818
$N(\text{param})_{\text{refined}}$:	559
Programs:	Rigaku programs [1], SHELX [2, 3] DIAMOND [4]

Source of materials

Procedures for preparation of 2,4,6-tris[4-(1*H*-imidazol-1-yl)phenyl]-1,3,5-triazine (TIPT) was adapted from the reported paper [5, 6]. The characterization of TIPT was performed by comparison of its ¹H NMR and IR spectrum with those reported previously. ¹H-NMR (300 MHz, DMSO-*d*₆): 8.80 (d, $J = 8.7$ Hz, 6H), 8.46 (s, 3H), 7.96–7.87 (m, 9H), 7.18 (s, 3H); IR (cm^{−1}): 1604(s), 1522(vs), 1487(s), 1400(w), 1303(s), 1261(m), 1108(w), 1057(vs), 962(m), 904(w), 825(s), 730(m), 695(m), 638(w), 588(m). The crystal of $(C_{30}H_{21}N_{11}O_6Zn)_n \cdot 2(C_4H_9NO)$ was synthesized by the following procedure. TIPT (10.1 mg, 0.02 mmol, 1.0 eq), $Zn(NO_3)_2 \cdot 6H_2O$ (11.9 mg, 0.04 mmol, 2.0 eq) and in 8 mL *N,N*-dimethylacetamide were placed in a glass vial, which was then sealed and heated to 80°C in an oven for four days, then cooled down to room temperature by 6°C per

<https://doi.org/10.1515/ncrs-2019-0415>

Received June 16, 2019; accepted August 24, 2019; available online September 11, 2019

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

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Zn1	0.82139(2)	0.12744(2)	0.61964(3)	0.02862(10)
O1	0.97706(17)	0.10602(7)	0.7864(2)	0.0471(5)
O2	1.0899(2)	0.06018(8)	0.7639(3)	0.0714(8)
O3	0.96667(19)	0.08646(7)	0.5743(2)	0.0526(6)
O4	0.65668(15)	0.14707(5)	0.49301(19)	0.0351(4)
O5	0.70634(18)	0.11881(6)	0.3260(2)	0.0475(5)
O6	0.53324(18)	0.13053(7)	0.2884(2)	0.0482(5)
N1	0.39222(17)	0.31523(6)	1.0576(2)	0.0293(4)
N2	0.26043(17)	0.32561(6)	1.1719(2)	0.0293(4)
N3	0.32662(17)	0.25832(6)	1.1548(2)	0.0278(4)
N4	0.68812(17)	0.17632(6)	0.9252(2)	0.0279(4)
N5	0.78247(17)	0.15033(6)	0.7977(2)	0.0287(4)
N6	0.30007(17)	0.50598(6)	0.9288(2)	0.0306(5)
N7	0.24597(18)	0.57003(6)	0.8862(2)	0.0332(5)
N8	−0.02655(17)	0.22148(6)	1.4640(2)	0.0287(4)
N9	−0.11531(17)	0.17769(6)	1.5543(2)	0.0318(5)
N10	1.0127(2)	0.08341(7)	0.7086(3)	0.0415(6)
N11	0.6315(2)	0.13166(6)	0.3663(2)	0.0345(5)
C1	0.3895(2)	0.27528(7)	1.0870(3)	0.0267(5)
C2	0.4633(2)	0.24852(7)	1.0398(3)	0.0266(5)
C3	0.4785(2)	0.20748(7)	1.0810(3)	0.0306(5)
H3	0.4382(10)	0.195931	1.135680	0.037*
C4	0.5518(2)	0.18352(7)	1.0430(3)	0.0323(5)
H4	0.562605	0.155687	1.072053	0.039*
C5	0.6095(2)	0.20056(7)	0.9618(3)	0.0273(5)
C6	0.5937(2)	0.24121(7)	0.9169(3)	0.0288(5)
H6	0.632709	0.252444	0.859988	0.035*
C7	0.5205(2)	0.26508(7)	0.9563(3)	0.0281(5)
H7	0.509222	0.292837	0.926309	0.034*
C8	0.7731(2)	0.15397(8)	1.0206(3)	0.0345(6)
H8	0.788295	0.150281	1.121357	0.041*
C9	0.8299(2)	0.13848(8)	0.9403(3)	0.0340(6)
H9	0.893373	0.121830	0.976858	0.041*
C10	0.6970(2)	0.17307(7)	0.7923(3)	0.0301(5)
H10	0.648374	0.185427	0.706868	0.036*
C11	0.3251(2)	0.33885(7)	1.1003(3)	0.0273(5)
C12	0.3205(2)	0.38269(7)	1.0609(3)	0.0286(5)
C13	0.2428(2)	0.40850(7)	1.0837(3)	0.0328(5)
H13	0.193664	0.398065	1.127641	0.039*
C14	0.2365(2)	0.44935(7)	1.0429(3)	0.0340(6)
H14	0.183740	0.466879	1.059292	0.041*
C15	0.3084(2)	0.46440(7)	0.9776(3)	0.0289(5)
C16	0.3866(2)	0.43900(7)	0.9557(3)	0.0348(6)
H16	0.436173	0.449467	0.912704	0.042*
C17	0.3921(2)	0.39844(8)	0.9966(3)	0.0351(6)
H17	0.445347	0.381067	0.980807	0.042*
C18	0.3541(3)	0.52259(8)	0.8445(4)	0.0489(8)
H18	0.405181	0.509190	0.810406	0.059*
C19	0.3201(3)	0.56176(9)	0.8198(4)	0.0507(8)
H19	0.344165	0.580799	0.764297	0.061*
C20	0.2359(2)	0.53590(7)	0.9511(3)	0.0327(5)
H20	0.189516	0.532661	1.006585	0.039*
C21	0.2650(2)	0.28507(7)	1.1964(3)	0.0269(5)
C22	0.1927(2)	0.26862(7)	1.2712(3)	0.0278(5)
C23	0.1352(2)	0.29475(7)	1.3310(3)	0.0306(5)

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H23	0.144927	0.323471	1.327475	0.037*
C24	0.0636(2)	0.27938(8)	1.3956(3)	0.0321(5)
H24	0.025244	0.297457	1.436727	0.038*
C25	0.0488(2)	0.23722(7)	1.3997(3)	0.0278(5)
C26	0.1058(2)	0.21056(7)	1.3411(3)	0.0310(5)
H26	0.095704	0.181846	1.344298	0.037*
C27	0.1774(2)	0.22636(7)	1.2780(3)	0.0294(5)
H27	0.216898	0.208212	1.238791	0.035*
C28	−0.0934(2)	0.24419(8)	1.5173(3)	0.0370(6)
H28	−0.100216	0.273125	1.515926	0.044*
C29	−0.1475(2)	0.21716(8)	1.5719(3)	0.0363(6)
H29	−0.199612	0.224160	1.615756	0.044*
C30	−0.0426(2)	0.18129(8)	1.4897(3)	0.0315(5)
H30	−0.006121	0.158976	1.464330	0.038*
O7 ^a	1.0042(18)	0.1197(7)	0.275(2)	0.048(2)
N12 ^a	1.0880(4)	0.07909(13)	0.1608(4)	0.0490(9)
C31 ^a	0.9467(5)	0.0494(2)	0.2486(10)	0.067(2)
H31A ^a	0.967390	0.024609	0.208570	0.101*
H31B ^a	0.958397	0.045236	0.351425	0.101*
H31C ^a	0.869241	0.055490	0.196538	0.101*
C32 ^a	1.0169(4)	0.08529(14)	0.2318(5)	0.0459(10)
C33 ^a	1.0956(6)	0.0344(3)	0.1170(12)	0.071(2)
H33A ^a	1.148283	0.032336	0.066409	0.106*
H33B ^a	1.119806	0.017228	0.203896	0.106*
H33C ^a	1.023488	0.025194	0.052898	0.106*
C34 ^a	1.1545(8)	0.1128(3)	0.1472(8)	0.0487(17)
H34A ^a	1.201618	0.103986	0.093727	0.073*
H34B ^a	1.107195	0.135194	0.094815	0.073*
H34C ^a	1.199955	0.122281	0.243698	0.073*
O7 ^b	1.019(4)	0.1211(14)	0.258(5)	0.048(2)
N12 ^b	1.0463(7)	0.0571(2)	0.1929(8)	0.0490(9)
C31 ^b	1.1420(18)	0.1146(7)	0.121(2)	0.067(2)
H31D ^b	1.175967	0.091570	0.089143	0.101*
H31E ^b	1.096052	0.130068	0.037015	0.101*
H31F ^b	1.199221	0.132505	0.184046	0.101*
C32 ^b	1.0690(9)	0.0979(3)	0.2086(10)	0.0459(10)
C33 ^b	0.9778(12)	0.0414(5)	0.2658(19)	0.071(2)
H33D ^b	0.967069	0.011955	0.246937	0.106*
H33E ^b	1.012239	0.045976	0.370102	0.106*
H33F ^b	0.906692	0.055256	0.230604	0.106*
C34 ^b	1.1277(13)	0.0378(5)	0.1188(19)	0.0487(17)
H34D ^b	1.114284	0.008300	0.105312	0.073*
H34E ^b	1.114770	0.050739	0.024603	0.073*
H34F ^b	1.203757	0.042451	0.181360	0.073*
O8	0.5155(2)	0.02625(8)	1.2263(3)	0.0706(7)
N13	0.4789(2)	0.06326(9)	1.0203(3)	0.0532(7)
C35	0.6557(3)	0.02942(11)	1.1235(4)	0.0587(9)
H35A	0.665450	0.042259	1.038848	0.088*
H35B	0.711729	0.039619	1.211803	0.088*
H35C	0.662751	−0.000310	1.117724	0.088*
C36	0.5430(3)	0.03977(10)	1.1268(4)	0.0495(8)
C37	0.5095(3)	0.07749(11)	0.8991(4)	0.0588(9)
H37A	0.450261	0.094209	0.834406	0.088*
H37B	0.576467	0.093930	0.935804	0.088*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H37C	0.522515	0.053904	0.845821	0.088*
C38	0.3718(3)	0.07555(14)	1.0234(6)	0.0821(13)
H38A	0.334595	0.092578	0.938706	0.123*
H38B	0.327681	0.051150	1.021636	0.123*
H38C	0.381368	0.091175	1.111835	0.123*

^aOccupancies: ^a = 0.65, ^b = 0.35.

hour. Colorless crystals were obtained on the bottom of the vial, air dried. Yield: 5.4 mg, 31% (Based on TIPT). IR (cm^{-1}): 3235(br), 1644(w), 1604(w), 1522(m), 1487(s), 1400(w), 1303(vs), 1225(w), 1053(m), 962(w), 904(w), 817(s), 730(m), 695(m), 651(m), 617(m), 533(m), 467(m), 456(m), 439(w), 432(w), 416(w).

Experimental details

The positions of the hydrogen atoms were generated geometrically. Beamstop theta(min) was set too high resulting in one Alert level B, missing 12 of FCF reflections. One *N,N*-dimethylacetamide molecule was refined as disorder with two parts, which corresponds to a ratio of 0.65:0.35.

Comment

Metal-organic framework (MOF) is a porous inorganic-organic hybrid material, with many application such as in separation [7], heterogeneous catalysis [8], luminescent [9], biomedicine [10], carbon dioxide capture [11] and ferroelectricity [12]. Triangle ligands with terminal groups of carboxyl, tetrazole and imidazole, have been attracted attention for the construction of MOFs. 1,3,5-tris(pimidazol-ylphenyl)-benzene(TIPB) and 2,4,6-tris[4-(1*H*-imidazol-1-yl)phenyl]-1,3,5-triazine (TIPT) are triangle rigid ligands with terminal groups of imidazole. They were used for construction of more than 20 reported structures, concluding Co-based [13–16], Ni-based [16] and Cd-based [5, 6, 17, 18] MOFs. However, to the best of our knowledge, Zn-based metal-organic framework constructed from TIPT has not been reported so far.

The title compound crystallizes in space group $P2_1/c$ and an asymmetric unit contains one Zn ion, two coordinated nitrate ion, one TIPT and two *N,N*-dimethylacetamide molecules. The bond lengths and angles within these moieties are in the expected ranges. Zn^{2+} exhibits six-coordination with three N from TIPT and three O from two coordinated nitrate ion. The distance of Zn1–N5, Zn1–N7 and Zn1–N9 is 2.123(2) Å, 2.064(2) Å and 2.070(2) Å, respectively. The distance of Zn1–O1, Zn1–O3 and Zn1–O4 is 2.234(2) Å, 2.481(2) Å and 2.171(2) Å, respectively. Viewing imidazole ring closer for C=N bond, the distance of N5–C10, N7–C20 and N9–C30 is 1.324(3) Å, 1.315(3) Å and 1.315(3) Å, respectively.

For C–N bond, the distance of N5–C9, N7–C19 and N9–C20 is 1.379(3) Å, 1.367(3) Å and 1.386(3) Å, respectively. The angle of is C9–N5–C10, C19–N7–C20 and C29–N9–C30 is 105.9(2)°, 105.7(2)° and 106.0(2)°, respectively. In the perspective of topology analysis, Zn^{2+} ion serves as a three-connected node and TIPT acting as a trinodal building block resulting in a two-dimensional layer, which can be described as a uninodal three-connected **hcb** net with the point symbol (6^3) [19]. Between the 2D layers, there are many π – π interactions. 2D layers were connected by π – π interactions to extend the structure to a three dimensional framework. Void space in structure is occupied by *N,N*-dimethylacetamide solvent.

Acknowledgements: We gratefully acknowledge the financial support from Doctoral Scientific Research Foundation of Guangxi University of Chinese Medicine (XB017022), Cultivating High-level Talent Teams in the Qi Huang Project of Guangxi University of Chinese Medicine, China (2018002) and the National Science Foundation of Guangxi (2018GXNS-FAA281210).

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