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Poly[bis(μ-purin-9-ido-κ^2N^7:N^9)zinc]

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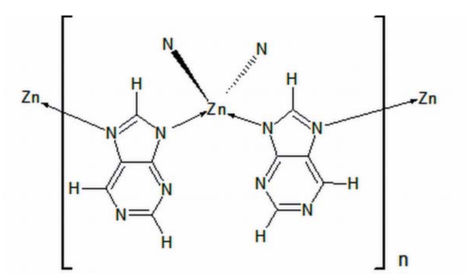
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.024; wR factor = 0.053; data-to-parameter ratio = 13.6.

In the title compound, $[Zn(C_5H_3N_4)_2]$, the Zn^{II} cation is in a nearly regular tetrahedral coordination by purinate ligands. Each purinate ligand chelates two Zn^{II} cations through two imidazole N atoms of the purinate anion ligand, leading to the formation of a three-dimensional network.

Related literature

For common applications of hybrid materials, see: Cui *et al.* (2012); Horcajada *et al.* (2012); Li *et al.* (2012); Stock & Biswas (2012); Suh *et al.* (2012); Sumida *et al.* (2012); Yoon *et al.* (2012). For characteristic zinc–nitrogen distances in metal-organic framework compounds, see: Cadiau *et al.* (2011).



Experimental

Crystal data

$[Zn(C_5H_3N_4)_2]$
M_r = 303.60
Orthorhombic, $P2_12_12_1$
a = 9.2332 (5) Å
b = 10.1337 (6) Å
c = 12.4186 (6) Å
V = 1161.96 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.11 mm^{-1}
T = 296 K
0.45 × 0.31 × 0.07 mm

Data collection

Bruker APEXII Quazar CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.580, T_{max} = 0.746
4522 measured reflections
2336 independent reflections
2129 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.053
S = 1.01
2336 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: 0.030 (13)

Table 1
Selected bond lengths (Å).

Zn1—N1	2.010 (2)	Zn1—N3	1.994 (2)
Zn1—N2	2.006 (2)	Zn1—N5	1.983 (2)

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *SHELXTL*.

The authors are grateful to Marc Leblanc for fruitful discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VN2034).

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Poly[bis(μ-purin-9-ido-$\kappa^2 N^7$:N^9)zinc]

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S1. Comment

The emerging class of hybrids materials known as Metal-Organic Frameworks (MOFs) has attracted much attention because of their enormous variety of interesting structural topologies (Stock & Biswas, 2012) and wide potential applications as functional materials, such as gas storage (Suh *et al.*, 2012; Sumida *et al.*, 2012), separation (Li *et al.*, 2012), catalysis (Yoon *et al.*, 2012) and luminescence (Cui *et al.*, 2012). Moreover, there is a growing interest in MOFs for biological application (Horcajada *et al.*, 2012) such as the drug controlled release or using MOFs based on endogenous linkers (nucleobases and amino acids). We report here on the synthesis and crystal structure of a new three-dimensional zinc MOFs material elaborated from purinate linkers.

The asymmetric unit of the title compound consists of one Zn^{II} cation and two non-equivalent purine molecules. Fig. 1 displays in a symmetry-expanded view the full coordination sphere of the Zn atom. Selected geometric parameters are given in Table 1. Zn^{II} are linked to four N atoms from two purinate anions to form quite regular tetrahedra. The coordination Zn—N bond lengths range from 1.983 (2) to 2.009 (3) Å which are in a good agreement with the literature (Cadiau *et al.*, 2011). The structure of $Zn(C_5H_3N_4)_2$ compound can be described as originating from deprotonated purinate anions ($C_5N_4H_3^-$) linked to Zn^{II} cations in order to generate a three-dimensional network as is shown in Fig.2.

S2. Experimental

Chemicals have been purchased from commercial sources and were used as received without further purification. The title compound was prepared under hydrothermal conditions at 393 K for 48 h using Teflon-lined autoclaves from a started mixture of zinc fluoride (Alfa Aesar), purine (Sigma-Aldrich) and deionized water under the following conditions: ZnF_2 (0.067 g, 0.65 mmol), $C_5H_4N_4$ (0.480 g, 4 mmol), H_2O (5 mL). The resulting crystalline product was washed with water and dried in air. Needle yellow crystals suitable for single-crystal X-ray diffraction were selected using an optical microscope.

S3. Refinement

Hydrogen atoms bonded to the ligands were positioned geometrically and refined using a riding model with C—H = 0.93 Å. These hydrogen atoms were assigned isotropic thermal parameters and $U_{iso}(H) = 1.2 \times U_{eq}(C)$.

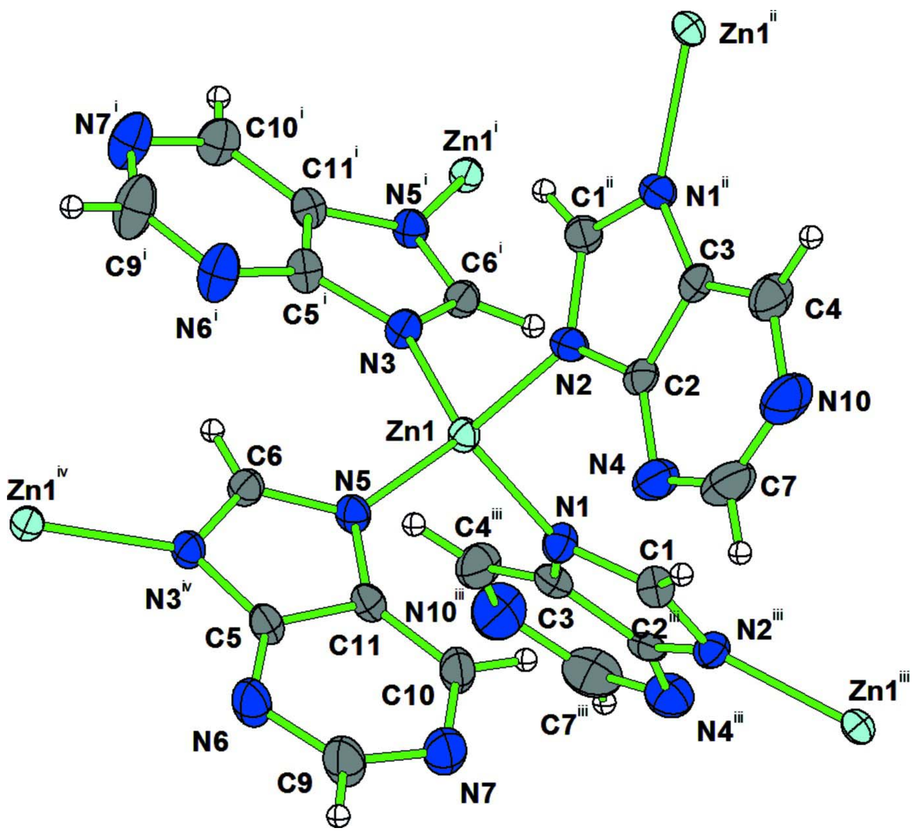

Figure 1

A view of the structure of the title compound showing the coordination environment of the Zn atom; displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) –*x*, –0.5+*y*, 1.5–*z*; (ii) –0.5+*x*, 1.5-*y*, 1–*z*; (iii) 0.5+*x*, 1.5–*y*, 1–*z*; (iv) –*x*, 0.5+*y*, 1.5–*z*

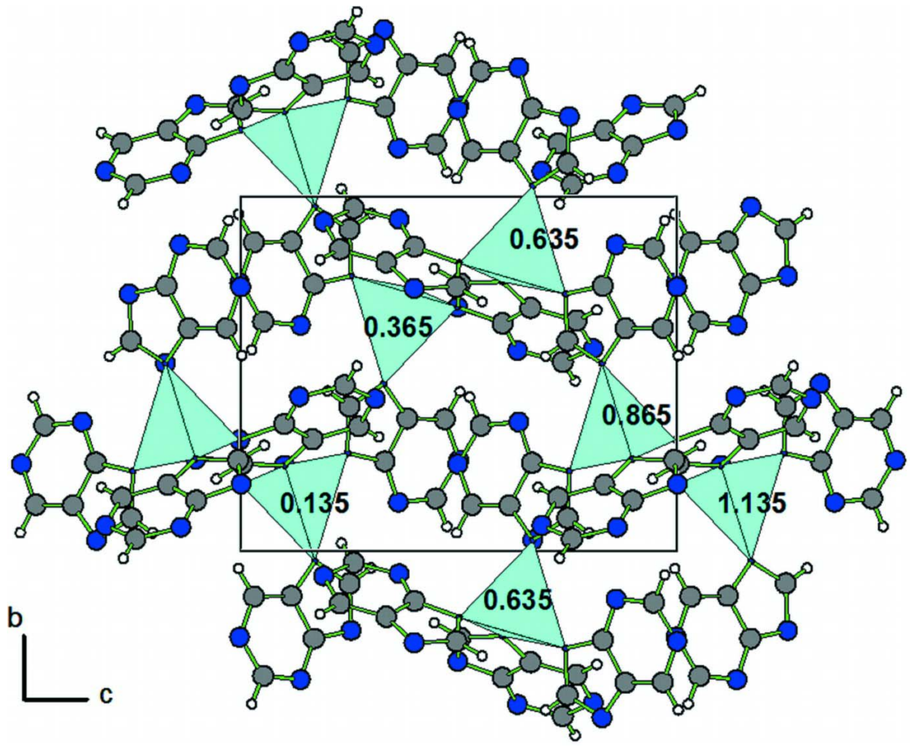

Figure 2

Projection of the structure along the *a* axis showing the three-dimensional network. The numbers refer to the *x*-coordinates of the Zn^{II} cations.

Poly[bis(μ-purin-9-ido-κ^2N^7:N^9)zinc]

Crystal data

$[Zn(C_5H_3N_4)_2]$
M_r = 303.60
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 9.2332 (5) Å
b = 10.1337 (6) Å
c = 12.4186 (6) Å
V = 1161.96 (11) Å^3
Z = 4
F(000) = 608
D_x = 1.735 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 896 reflections
θ = 2–11°
μ = 2.11 mm^{-1}
T = 296 K
Needle, yellow
0.45 × 0.31 × 0.07 mm

Data collection

Bruker APEXII Quazar CCD diffractometer
Radiation source: ImuS microsource
Mirror monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.580, T_{max} = 0.746
4522 measured reflections
2336 independent reflections
2129 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 29.0°, θ_{min} = 3.3°
h = −12→11
k = −10→13
l = −15→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.053$
$S = 1.01$
2336 reflections
172 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.014P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Absolute structure: Flack (1983)
Absolute structure parameter: 0.030 (13)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Zn1	0.05827 (3)	0.83956 (3)	0.63470 (2)	0.01682 (8)
N1	0.2523 (2)	0.7592 (2)	0.60162 (16)	0.0211 (5)
N2	−0.0615 (2)	0.81227 (19)	0.50179 (15)	0.0202 (5)
N3	−0.0333 (2)	0.7247 (2)	0.74592 (16)	0.0200 (5)
N4	0.0678 (3)	0.9343 (2)	0.3640 (2)	0.0310 (5)
N5	0.0775 (2)	1.0294 (2)	0.67090 (16)	0.0198 (5)
N6	0.1801 (3)	1.3634 (2)	0.63818 (19)	0.0335 (6)
N7	0.3055 (3)	1.2441 (3)	0.4986 (2)	0.0356 (6)
C1	0.3147 (3)	0.7551 (3)	0.5048 (2)	0.0216 (6)
H1	0.2743	0.7967	0.4452	0.026*
C2	−0.0407 (3)	0.8578 (2)	0.39896 (19)	0.0189 (5)
C3	0.3449 (3)	0.6859 (2)	0.66539 (19)	0.0214 (6)
C4	−0.1555 (3)	0.8505 (4)	0.2285 (2)	0.0337 (7)
H4	−0.2284	0.8209	0.1827	0.040*
C5	0.1262 (3)	1.2481 (3)	0.6690 (2)	0.0214 (6)
C6	0.0102 (3)	1.0927 (3)	0.7501 (2)	0.0201 (6)
H6	−0.0487	1.0494	0.7995	0.024*
C7	0.0542 (4)	0.9665 (3)	0.2603 (3)	0.0399 (8)
H7	0.1256	1.0216	0.2324	0.048*
N10	−0.0503 (4)	0.9289 (3)	0.19110 (19)	0.0436 (7)
C9	0.2668 (4)	1.3533 (3)	0.5524 (2)	0.0386 (8)
H9	0.3052	1.4321	0.5267	0.046*
C10	0.2476 (3)	1.1293 (3)	0.5314 (2)	0.0275 (7)

H10	0.2709	1.0512	0.4961	0.033*
C11	0.1542 (3)	1.1274 (2)	0.61731 (19)	0.0197 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01916 (15)	0.01367 (13)	0.01764 (14)	0.00023 (14)	0.00213 (13)	−0.00095 (13)
N1	0.0207 (12)	0.0231 (12)	0.0196 (12)	0.0036 (10)	0.0009 (10)	−0.0011 (10)
N2	0.0180 (11)	0.0203 (12)	0.0222 (11)	−0.0017 (11)	−0.0017 (10)	−0.0009 (9)
N3	0.0238 (14)	0.0147 (11)	0.0215 (11)	0.0011 (10)	0.0041 (11)	0.0020 (9)
N4	0.0270 (13)	0.0319 (13)	0.0342 (13)	−0.0027 (11)	0.0072 (15)	0.0007 (12)
N5	0.0242 (13)	0.0150 (11)	0.0203 (10)	−0.0006 (10)	0.0010 (10)	−0.0004 (9)
N6	0.0483 (15)	0.0243 (13)	0.0281 (12)	−0.0110 (11)	0.0090 (13)	−0.0048 (12)
N7	0.0438 (16)	0.0312 (14)	0.0316 (12)	−0.0104 (12)	0.0115 (12)	−0.0034 (11)
C1	0.0251 (15)	0.0198 (13)	0.0200 (12)	0.0025 (11)	−0.0016 (12)	0.0008 (11)
C2	0.0159 (14)	0.0167 (13)	0.0241 (12)	0.0052 (11)	0.0026 (11)	−0.0017 (11)
C3	0.0190 (14)	0.0233 (15)	0.0220 (14)	−0.0035 (12)	−0.0041 (12)	−0.0031 (11)
C4	0.0288 (17)	0.052 (2)	0.0204 (14)	0.0018 (17)	0.0006 (13)	0.0007 (16)
C5	0.0294 (16)	0.0172 (14)	0.0175 (13)	−0.0034 (12)	−0.0012 (12)	−0.0016 (11)
C6	0.0212 (14)	0.0187 (13)	0.0204 (13)	−0.0001 (11)	0.0027 (11)	0.0000 (10)
C7	0.0324 (18)	0.0397 (18)	0.0477 (19)	−0.0041 (18)	0.015 (2)	0.0052 (15)
N10	0.0399 (17)	0.0639 (19)	0.0270 (14)	−0.0063 (17)	0.0099 (15)	0.0064 (13)
C9	0.056 (2)	0.0285 (18)	0.0313 (16)	−0.0165 (17)	0.0122 (16)	−0.0052 (14)
C10	0.0344 (18)	0.0237 (17)	0.0244 (15)	−0.0009 (12)	0.0039 (14)	−0.0061 (12)
C11	0.0245 (15)	0.0180 (14)	0.0167 (13)	−0.0019 (10)	−0.0027 (12)	−0.0004 (10)

Geometric parameters (Å, º)

Zn1—N1	2.010 (2)	C1—N2^{iii}	1.333 (4)
Zn1—N2	2.006 (2)	C1—H1	0.9300
Zn1—N3	1.994 (2)	C2—C3^{i}	1.397 (4)
Zn1—N5	1.983 (2)	C3—C4^{iii}	1.368 (3)
N1—C1	1.335 (4)	C3—C2^{iii}	1.397 (4)
N1—C3	1.382 (3)	C4—N10	1.338 (4)
N2—C1^{i}	1.333 (4)	C4—C3^{i}	1.368 (3)
N2—C2	1.371 (3)	C4—H4	0.9300
N3—C6^{ii}	1.356 (3)	C5—N3^{iv}	1.381 (3)
N3—C5^{ii}	1.381 (3)	C5—C11	1.405 (3)
N4—C7	1.335 (4)	C6—N3^{iv}	1.356 (3)
N4—C2	1.339 (3)	C6—H6	0.9300
N5—C6	1.328 (3)	C7—N10	1.348 (4)
N5—C11	1.390 (3)	C7—H7	0.9300
N6—C5	1.327 (3)	C9—H9	0.9300
N6—C9	1.337 (4)	C10—C11	1.372 (4)
N7—C9	1.341 (4)	C10—H10	0.9300
N7—C10	1.343 (3)		
N5—Zn1—N3	116.54 (9)	N2—C2—C3^{i}	108.7 (2)

N5—Zn1—N2	111.68 (8)	C4^{iii}—C3—N1	134.0 (3)
N3—Zn1—N2	104.81 (8)	C4^{iii}—C3—C2^{iii}	117.9 (2)
N5—Zn1—N1	111.08 (9)	N1—C3—C2^{iii}	108.1 (2)
N3—Zn1—N1	106.44 (9)	N10—C4—C3^{i}	119.5 (3)
N2—Zn1—N1	105.50 (9)	N10—C4—H4	120.3
C1—N1—C3	103.4 (2)	C3^{i}—C4—H4	120.3
C1—N1—Zn1	125.61 (19)	N6—C5—N3^{iv}	127.2 (2)
C3—N1—Zn1	130.69 (17)	N6—C5—C11	124.4 (2)
C1^{i}—N2—C2	103.6 (2)	N3^{iv}—C5—C11	108.3 (2)
C1^{i}—N2—Zn1	126.39 (18)	N5—C6—N3^{iv}	115.5 (3)
C2—N2—Zn1	129.99 (18)	N5—C6—H6	122.3
C6^{ii}—N3—C5^{ii}	103.8 (2)	N3^{iv}—C6—H6	122.3
C6^{ii}—N3—Zn1	122.31 (19)	N4—C7—N10	127.8 (3)
C5^{ii}—N3—Zn1	133.86 (17)	N4—C7—H7	116.1
C7—N4—C2	112.6 (3)	N10—C7—H7	116.1
C6—N5—C11	104.3 (2)	C4—N10—C7	117.8 (2)
C6—N5—Zn1	126.50 (18)	N6—C9—N7	128.3 (3)
C11—N5—Zn1	129.08 (17)	N6—C9—H9	115.9
C5—N6—C9	112.8 (2)	N7—C9—H9	115.9
C9—N7—C10	117.2 (3)	N7—C10—C11	119.9 (2)
N2^{iii}—C1—N1	116.2 (3)	N7—C10—H10	120.1
N2^{iii}—C1—H1	121.9	C11—C10—H10	120.1
N1—C1—H1	121.9	C10—C11—N5	134.6 (2)
N4—C2—N2	127.0 (2)	C10—C11—C5	117.4 (2)
N4—C2—C3^{i}	124.4 (2)	N5—C11—C5	108.0 (2)

Symmetry codes: (i) $x-1/2, -y+3/2, -z+1$; (ii) $-x, y-1/2, -z+3/2$; (iii) $x+1/2, -y+3/2, -z+1$; (iv) $-x, y+1/2, -z+3/2$.