

catena-Poly[[*(diaquazinc)- μ -3-carboxypyrazine-2-carboxylato- $\kappa^4 N^1, O^2; N^4, O^3$]* nitrate]

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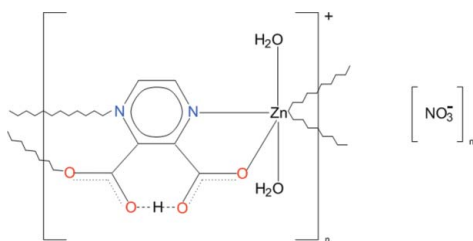
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.032; wR factor = 0.097; data-to-parameter ratio = 16.2.

The crystal structure of the title compound, $\{[Zn(C_6H_3N_2O_4)(H_2O)_2]NO_3\}_n$, is built of zigzag cationic chains propagating in [010] with nitrate anions located in the space between the chains. The Zn^{II} ion is coordinated by N and O atoms of two symmetry-related ligands in equatorial sites, and by two water O atoms at the axial sites of a distorted octahedron. One carboxylate group of the ligand remains protonated, serving as a donor in a short intramolecular O—H...O hydrogen bond. The coordinated water molecules are donors and the nitrate O atoms act as acceptors in a network of O—H...O hydrogen bonds.

Related literature

For the crystal structures of Zn^{II} complexes with pyrazine-2,3-dicarboxylato and aqua ligands, see: Richard *et al.* (1974); Ptasiwicz-Bąk & Leciejewicz (1999); Gryz *et al.* (2005).



Experimental

Crystal data

 $[Zn(C_6H_3N_2O_4)(H_2O)_2]NO_3$ $M_r = 330.52$ Monoclinic, $P2_1/n$ $a = 8.7431$ (17) Å $b = 10.867$ (2) Å $c = 11.412$ (2) Å $\beta = 100.48$ (3)° $V = 1066.2$ (4) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 2.36$ mm⁻¹
 $T = 293$ K

0.20 × 0.19 × 0.15 mm

Data collection

Kuma KM-4 four-circle diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)
 $T_{\min} = 0.636$, $T_{\max} = 0.747$
3232 measured reflections3101 independent reflections
2397 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
3 standard reflections every 200 reflections
intensity decay: 1.6%

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.097$
 $S = 1.03$
3101 reflections
192 parametersH atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.81$ e Å⁻³
 $\Delta\rho_{\min} = -0.48$ e Å⁻³

Table 1

Selected bond lengths (Å).

Zn1—O6	2.052 (2)	Zn1—O1	2.0816 (17)
Zn1—O5	2.069 (2)	Zn1—N1	2.1663 (18)
Zn1—O4 ⁱ	2.0769 (18)	Zn1—N2 ⁱ	2.1946 (19)

Symmetry code: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H61...O13 ⁱⁱ	0.84 (4)	1.90 (4)	2.732 (3)	176 (3)
O5—H52...O12 ⁱⁱⁱ	0.83 (4)	1.88 (4)	2.696 (3)	169 (4)
O6—H62...O11 ⁱⁱⁱ	0.72 (5)	2.04 (5)	2.758 (3)	175 (5)
O5—H51...O3 ⁱⁱⁱ	0.73 (6)	2.37 (5)	2.983 (3)	142 (5)
O5—H51...O11 ⁱ	0.73 (6)	2.63 (6)	3.094 (4)	123 (5)
O2—H3...O3	1.20 (5)	1.22 (5)	2.404 (2)	170 (4)

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x - 1, y, z$.

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2377).

References

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supplementary materials

Acta Cryst. (2012). E68, m75 [doi:10.1107/S1600536811054031]

***catena*-Poly[[*(diaquazinc)-μ*-3-carboxypyrazine-2-carboxylato-κ⁴N¹,O²;N⁴,O³] nitrate]**

W. Starosta and J. Leciejewicz

Comment

The structures of three Zn^{II} coordination compounds with pyrazine-2,3-dicarboxylate ligand (2,3-PZDC), each with a different molecular pattern were reported. In the triclinic structure of Zn(2,3-PZDC)(H₂O)₂.H₂O (Richard *et al.*, 1974) molecular ribbons are observed while the monoclinic Zn(2,3-PZDC)(H₂O)₃.H₂O (Ptasiewicz-Bąk & Leciejewicz, 1999) shows a zigzag catenated molecular pattern. The monoclinic structure of (H₃O)⁺₂ [Zn(2,3-PZDC)²⁻ is built of catenated doubly layered polyanions with hydronium cations in the interstitials (Gryz *et al.* 2005). The structure of the title compound is composed of zigzag molecular chains propagating along the crystal *b* axis in which Zn^{II} ions are coordinated by *N,O* chelating groups of two singly deprotonated ligand molecules; their planes make a dihedral angle of 82.1 (1)° each to the other (Fig. 1). Two water O atoms complete the coordination of the Zn^{II} ion to six, located at the apices of a distorted octahedron. O1, N1, O4ⁱ and O5 atoms form its basal plane with r.m.s. of 0.1408 (2) Å. Zn—O and Zn—N bond lengths are close to those observed in the structures of other Zn complexes with the title ligand (Richard, *et al.*, 1974; Ptasiewicz-Bąk & Leciejewicz, 1999; Gryz, *et al.*, 2005). A pyrazine ring is planar [r.m.s. 0.0146 (2) Å, the carboxylate groups C7/O1/O2 and C8/O3/O4 make with it dihedral angles of 4.8 (1)° and 171.9 (1)°, respectively. One of the carboxylate groups remains protonated and participates in a short, intra-molecular hydrogen bond of 2.404 (2) Å. Consequently, each building unit of the chain shows a singly positive charge which is compensated by a nitrate anion located in the space between chains (Fig. 2). Hydrogen bonds are observed between coordinated water molecules which act as donors and nitrate O atoms as acceptors (Table 2).

Experimental

Single crystals of the title compound were found incidently in the course of an attempt to obtain dinuclear magnesium-zinc complex with the pyrazine-2,3-dicarboxylate ligand. A solution containing 2 mmols of pyrazine-2,3-dicarboxylic acid dihydrate, 1 mmol of magnesium nitrate dihydrate and a small excess over 1 mmol of zinc nitrate hexahydrate in 100 mL of doubly distilled water was boiled under reflux with stirring for 10 h. After cooling to room temperature, two drops of 95% hydrazine were added to the solution which was left to crystallise. Colourless single-crystal blocks of the title compound and crystals of Zn(H₂O)₆(NO₃)₂ were found in an unidentified polycrystalline material after evaporation to dryness. The crystals of the title complex were extracted, washed with ethanol and dried in air.

Refinement

Water hydrogen atoms were located in a difference map and refined isotropically while H atoms attached to pyrazine-ring C atoms were located at calculated positions and treated as riding on the parent atoms with C—H=0.93 Å and $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$.

Figures

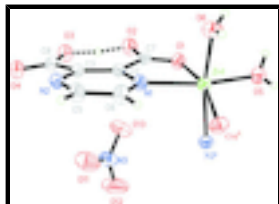


Fig. 1. A structural unit of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: (i) $-x + 1/2, y + 1/2, -z + 1/2$. An intramolecular hydrogen bond is shown by dashed lines.

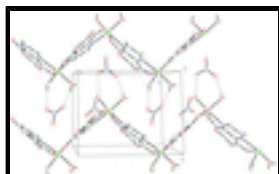


Fig. 2. Packing diagram of the structure viewed along the c axis.

catena-Poly[[*(diaquazinc)- μ -3-carboxypyrazine-2-carboxylato- $\kappa^4 N^1, O^2; N^4, O^3$*] nitrate]

Crystal data

$[\text{Zn}(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]\text{NO}_3$

$M_r = 330.52$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1/n$

$a = 8.7431$ (17) Å

$b = 10.867$ (2) Å

$c = 11.412$ (2) Å

$\beta = 100.48$ (3)°

$V = 1066.2$ (4) Å³

$Z = 4$

$F(000) = 664$

$D_x = 2.059$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 6\text{--}15^\circ$

$\mu = 2.36$ mm⁻¹

$T = 293$ K

Blocks, colourless

$0.20 \times 0.19 \times 0.15$ mm

Data collection

Kuma KM-4 four-circle diffractometer

Radiation source: fine-focus sealed tube graphite

profile data from $\omega/2\theta$ scans

Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)

$T_{\min} = 0.636, T_{\max} = 0.747$

3232 measured reflections

3101 independent reflections

2397 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.012$

$\theta_{\max} = 30.1^\circ, \theta_{\min} = 2.6^\circ$

$h = -10 \rightarrow 12$

$k = -15 \rightarrow 0$

$l = -16 \rightarrow 0$

3 standard reflections every 200 reflections

intensity decay: 1.6%

Refinement

Refinement on F^2

Least-squares matrix: full

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

$$R[F^2 > 2\sigma(F^2)] = 0.032$$

$$wR(F^2) = 0.097$$

$$S = 1.03$$

3101 reflections

192 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.8069P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.81 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	-0.00406 (3)	0.82559 (2)	0.26307 (2)	0.02503 (9)
C7	0.0503 (2)	0.68275 (19)	0.06020 (18)	0.0235 (4)
C2	0.1549 (2)	0.61605 (18)	0.16261 (17)	0.0212 (4)
N1	0.1442 (2)	0.66517 (17)	0.26888 (16)	0.0255 (4)
C3	0.2546 (2)	0.51569 (19)	0.15702 (18)	0.0214 (4)
C8	0.3008 (3)	0.45650 (19)	0.04721 (19)	0.0247 (4)
C6	0.2221 (3)	0.6151 (2)	0.36834 (19)	0.0303 (5)
H6	0.2153	0.6495	0.4418	0.036*
O5	-0.1653 (2)	0.96368 (18)	0.2120 (2)	0.0403 (4)
N2	0.3300 (2)	0.46525 (17)	0.25858 (16)	0.0246 (3)
O3	0.2334 (2)	0.48857 (16)	-0.05626 (14)	0.0314 (3)
O4	0.4046 (2)	0.37756 (16)	0.06479 (15)	0.0313 (3)
O2	0.0421 (2)	0.64513 (17)	-0.04597 (14)	0.0323 (4)
O1	-0.02615 (19)	0.77131 (15)	0.08585 (14)	0.0295 (3)
O6	-0.1700 (2)	0.71769 (19)	0.3183 (2)	0.0373 (4)
C5	0.3133 (3)	0.5120 (2)	0.36293 (19)	0.0294 (4)
H5	0.3634	0.4752	0.4330	0.035*
O11	0.5234 (3)	0.7166 (3)	0.2043 (2)	0.0568 (6)
O12	0.5562 (3)	0.8786 (3)	0.1012 (3)	0.0758 (9)
O13	0.3449 (2)	0.7771 (2)	0.05949 (19)	0.0463 (5)
N3	0.4762 (2)	0.7915 (2)	0.1237 (2)	0.0366 (5)
H61	-0.166 (4)	0.723 (3)	0.392 (3)	0.035 (8)*
H52	-0.256 (5)	0.946 (4)	0.181 (4)	0.056 (11)*

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H62	-0.251 (6)	0.722 (4)	0.289 (4)	0.081 (16)*
H51	-0.165 (6)	1.002 (5)	0.265 (5)	0.095 (19)*
H3	0.143 (5)	0.574 (4)	-0.056 (4)	0.088 (15)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02357 (14)	0.02086 (13)	0.02998 (14)	-0.00042 (9)	0.00303 (9)	-0.00081 (9)
C7	0.0212 (9)	0.0232 (9)	0.0241 (9)	-0.0025 (7)	-0.0014 (7)	0.0015 (7)
C2	0.0199 (8)	0.0202 (8)	0.0224 (9)	-0.0013 (7)	0.0010 (7)	0.0010 (7)
N1	0.0253 (8)	0.0249 (9)	0.0249 (8)	0.0031 (7)	0.0006 (7)	-0.0020 (6)
C3	0.0205 (9)	0.0197 (8)	0.0234 (8)	-0.0014 (7)	0.0022 (7)	-0.0003 (7)
C8	0.0260 (10)	0.0236 (9)	0.0246 (9)	-0.0015 (7)	0.0047 (7)	-0.0003 (7)
C6	0.0353 (11)	0.0328 (11)	0.0214 (9)	0.0080 (9)	0.0016 (8)	-0.0015 (8)
O5	0.0317 (10)	0.0276 (9)	0.0589 (13)	0.0062 (7)	0.0010 (9)	-0.0050 (8)
N2	0.0231 (8)	0.0236 (8)	0.0260 (8)	0.0020 (6)	0.0013 (6)	0.0012 (6)
O3	0.0360 (9)	0.0348 (9)	0.0231 (7)	0.0068 (7)	0.0041 (6)	0.0002 (6)
O4	0.0353 (9)	0.0296 (8)	0.0297 (8)	0.0079 (7)	0.0075 (7)	0.0003 (6)
O2	0.0345 (9)	0.0363 (9)	0.0233 (7)	0.0070 (7)	-0.0022 (6)	-0.0015 (6)
O1	0.0291 (8)	0.0264 (8)	0.0295 (8)	0.0060 (6)	-0.0035 (6)	-0.0009 (6)
O6	0.0315 (10)	0.0400 (10)	0.0393 (11)	-0.0078 (8)	0.0041 (8)	0.0034 (8)
C5	0.0318 (11)	0.0309 (11)	0.0236 (9)	0.0057 (9)	-0.0004 (8)	0.0014 (8)
O11	0.0473 (12)	0.0708 (16)	0.0467 (12)	-0.0080 (11)	-0.0060 (9)	0.0132 (11)
O12	0.0526 (15)	0.0659 (17)	0.100 (2)	-0.0293 (13)	-0.0098 (14)	0.0186 (16)
O13	0.0259 (9)	0.0682 (14)	0.0428 (10)	-0.0089 (9)	0.0006 (8)	0.0042 (10)
N3	0.0265 (10)	0.0452 (12)	0.0379 (11)	-0.0069 (9)	0.0052 (8)	-0.0012 (9)

Geometric parameters (\AA , $^\circ$)

Zn1—O6	2.052 (2)	C6—C5	1.382 (3)
Zn1—O5	2.069 (2)	C6—H6	0.9300
Zn1—O4 ⁱ	2.0769 (18)	O5—H52	0.83 (4)
Zn1—O1	2.0816 (17)	O5—H51	0.73 (6)
Zn1—N1	2.1663 (18)	N2—C5	1.327 (3)
Zn1—N2 ⁱ	2.1946 (19)	N2—Zn1 ⁱⁱ	2.1947 (19)
C7—O1	1.237 (3)	O3—H3	1.22 (5)
C7—O2	1.268 (3)	O4—Zn1 ⁱⁱ	2.0769 (18)
C7—C2	1.529 (3)	O2—H3	1.20 (5)
C2—N1	1.344 (3)	O6—H61	0.84 (4)
C2—C3	1.405 (3)	O6—H62	0.72 (5)
N1—C6	1.330 (3)	C5—H5	0.9300
C3—N2	1.342 (3)	O11—N3	1.241 (3)
C3—C8	1.527 (3)	O12—N3	1.230 (3)
C8—O4	1.238 (3)	O13—N3	1.254 (3)
C8—O3	1.269 (3)		
O6—Zn1—O5	90.99 (9)	C2—C3—C8	128.54 (18)
O6—Zn1—O4 ⁱ	93.59 (8)	O4—C8—O3	122.9 (2)
O5—Zn1—O4 ⁱ	102.46 (9)	O4—C8—C3	117.00 (19)

O6—Zn1—O1	101.00 (8)	O3—C8—C3	120.06 (19)
O5—Zn1—O1	89.65 (9)	N1—C6—C5	120.2 (2)
O4 ⁱ —Zn1—O1	160.90 (7)	N1—C6—H6	119.9
O6—Zn1—N1	89.06 (8)	C5—C6—H6	119.9
O5—Zn1—N1	164.96 (9)	Zn1—O5—H52	120 (3)
O4 ⁱ —Zn1—N1	92.55 (7)	Zn1—O5—H51	107 (4)
O1—Zn1—N1	75.58 (7)	H52—O5—H51	110 (5)
O6—Zn1—N2 ⁱ	166.71 (8)	C5—N2—C3	120.11 (19)
O5—Zn1—N2 ⁱ	85.27 (8)	C5—N2—Zn1 ⁱⁱ	123.90 (15)
O4 ⁱ —Zn1—N2 ⁱ	74.86 (7)	C3—N2—Zn1 ⁱⁱ	115.27 (14)
O1—Zn1—N2 ⁱ	91.74 (7)	C8—O3—H3	114 (2)
N1—Zn1—N2 ⁱ	97.85 (7)	C8—O4—Zn1 ⁱⁱ	120.67 (15)
O1—C7—O2	122.53 (19)	C7—O2—H3	113 (2)
O1—C7—C2	117.50 (19)	C7—O1—Zn1	119.46 (14)
O2—C7—C2	119.96 (19)	Zn1—O6—H61	112 (2)
N1—C2—C3	119.66 (18)	Zn1—O6—H62	121 (4)
N1—C2—C7	111.79 (18)	H61—O6—H62	108 (4)
C3—C2—C7	128.54 (18)	N2—C5—C6	120.6 (2)
C6—N1—C2	119.93 (19)	N2—C5—H5	119.7
C6—N1—Zn1	124.51 (15)	C6—C5—H5	119.7
C2—N1—Zn1	115.56 (14)	O12—N3—O11	122.2 (2)
N2—C3—C2	119.29 (18)	O12—N3—O13	118.0 (3)
N2—C3—C8	112.05 (18)	O11—N3—O13	119.8 (2)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O6—H61 \cdots O13 ⁱⁱⁱ	0.84 (4)	1.90 (4)	2.732 (3)	176 (3)
O5—H52 \cdots O12 ^{iv}	0.83 (4)	1.88 (4)	2.696 (3)	169 (4)
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O5—H51 \cdots O11 ⁱ	0.73 (6)	2.63 (6)	3.094 (4)	123 (5)
O2—H3 \cdots O3	1.20 (5)	1.22 (5)	2.404 (2)	170 (4)

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

Fig. 1

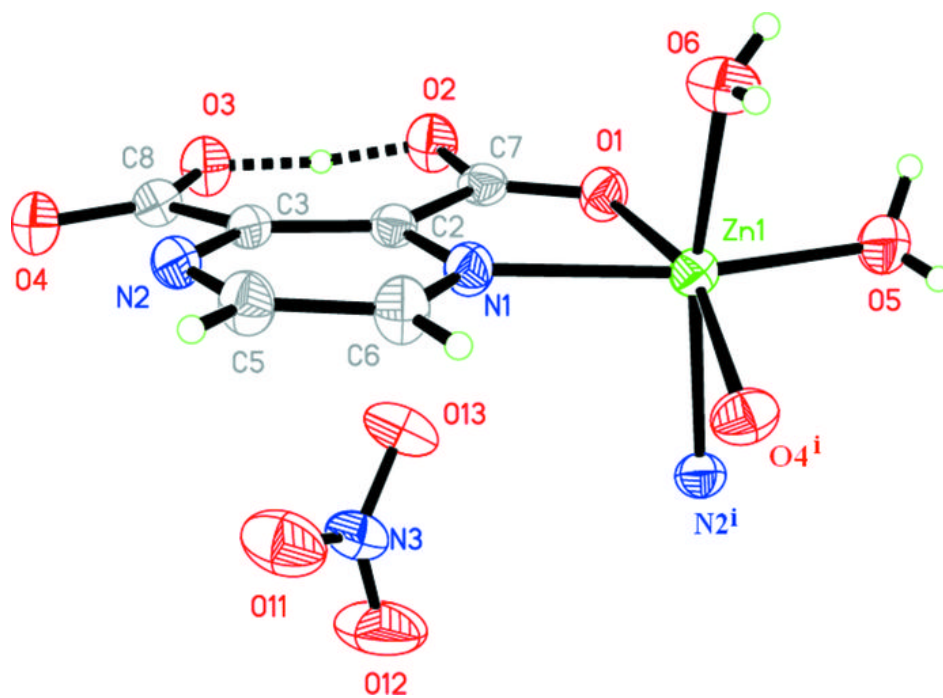


Fig. 2

