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cyclo-Tetrakis[μ-*N*-(2-hydroxybenzoyl)-*N*′-(2-hydroxy-3-methoxybenzylidene)-hydrazine(2–)]tetrazinc(II) *N*,*N*-dimethylformamide tetrasolvate

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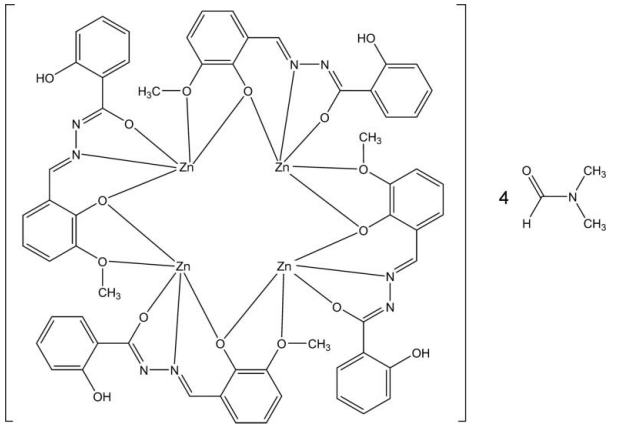
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.008 Å; R factor = 0.046; wR factor = 0.154; data-to-parameter ratio = 14.2.

The title compound, $[Zn_4(C_{15}H_{12}N_2O_4)_4]\cdot 4C_3H_7NO$, is isostructural with its Co^{II} analogue. The compound contains *N*-(2-hydroxybenzoyl)-*N*-(2-hydroxy-3-methoxybenzylidene)-hydrazine anions and Zn^{II} cations linked into tetrameric complexes about a position of $\overline{4}$ point symmetry. Each Zn^{II} cation is pentacoordinated with a distorted square-based pyramidal geometry. The ligand exhibits an intramolecular O—H···N hydrogen bond.

Related literature

One reason to study hydrazine and its analogues is to understand better the mechanism of enzymes containing vitamin B6. For related literature, see: Maghler *et al.* (1982); Rath *et al.* (1997, 1998). For the analogous Co^{II} complex, see: Gao *et al.* (2007).



Experimental

Crystal data

$[Zn_4(C_{15}H_{12}N_2O_4)_4]\cdot 4C_3H_7NO$
M_r = 1690.93
Tetragonal, $I4_1/a$
a = 24.1202 (10) Å
c = 13.093 (2) Å
V = 7617.2 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.32 mm^{-1}
T = 293 (2) K
0.15 × 0.15 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.826, T_{max} = 0.826
19270 measured reflections
3529 independent reflections
2249 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.154
S = 1.00
3529 reflections
248 parameters
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn1—N1	1.961 (4)	Zn1—O2^{i}	2.028 (3)
Zn1—O2	1.948 (3)	Zn1—O5^{i}	2.275 (3)
Zn1—O3	1.936 (3)		

Symmetry code: (i) $y+\frac{1}{4}, -x+\frac{3}{4}, -z+\frac{3}{4}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···N2	0.82	1.88	2.589 (5)	144

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2214).

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supplementary materials

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cyclo-Tetrakis[μ-*N*-(2-hydroxybenzoyl)-*N*'-(2-hydroxy-3-methoxybenzylidene)hydrazine(2-)]tetrazinc(II) *N*,*N*-dimethylformamide tetrasolvate

Y.-X. Gao, L.-B. Wang and Y.-L. Niu

Comment

The title compound, $[Zn_4(C_{15}H_{12}N_2O_4)_4]\cdot 4C_3H_7NO$, is isostructural with its Co^{II} analogue (Gao *et al.*, 2007). As shown in Figure 1, each Zn^{II} cation is penta-coordinated by four O atoms and one N atom, forming a distorted square-based pyramidal geometry. The Zn—O bond lengths are in the range 1.936 (3)–2.275 Å, and Zn—N = 1.961 (4) Å. The Zn^{II} cations are linked into tetrameric complexes about positions of $\bar{4}$ point symmetry by four *N*-(2-hydroxybenzoyl)-*N*-(2-hydroxy-3-methoxybenzylidene)-hydrazine anions (Figure 2). The ligand exhibits an intramolecular O—H···N hydrogen bond.

Experimental

All chemicals were used as purchased from Shanghai chemical Co. Ltd. A mixture of zinc(II) acetate (0.5 mmol) and *N*-(2-hydroxybenzoyl)-*N*-(2-hydroxy-3-methoxybenzylidene)-hydrazine (0.5 mmol) in DMF (30 ml) was refluxed for 1 h then filtered. Colourless crystals were obtained after a few days standing at room temperature with a yield of 15%. Elemental analysis calculated: C 51.09, H 4.49, N 9.93%; found: C 51.01, H 4.55, N 9.90%.

Refinement

H atoms were placed geometrically and refined as riding with C—H = 0.93 or 0.96 Å, O—H = 0.82 Å, and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(O).

Figures

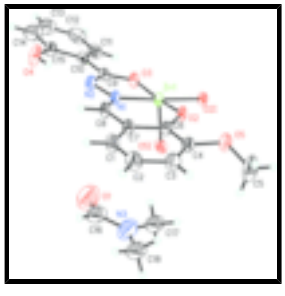

Fig. 1. The asymmetric unit of the title compound, showing displacement ellipsoids at 50% probability for non-H atoms. Atoms labeled with the subscript I are generated by the symmetry operator $-y + 3/4$, $x - 1/4$, $-z + 3/4$.

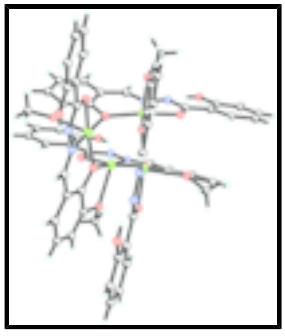

Fig. 2. Tetrameric complex formed about the position of $\bar{4}$ point symmetry.

cyclo-Tetrakis[μ-_N_-(2-hydroxybenzoyl)-_N_'-(2-hydroxy-3-\ methoxybenzylidene)hydrazine(2-)]tetrazinc(II)} _N_,_N_-dimethylformamide tetrasolvate

Crystal data

$[Zn_4(C_{15}H_{12}N_2O_4)_4]\cdot 4C_3H_7NO$	$Z = 4$
$M_r = 1690.93$	$F_{000} = 3488$
Tetragonal, $I4_1/a$	$D_x = 1.474$ Mg m^{-3}
Hall symbol: -I 4ad	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 24.1202$ (10) Å	Cell parameters from 3529 reflections
$b = 24.1202$ (10) Å	$\theta = 1.7$–25.5º
$c = 13.093$ (2) Å	$\mu = 1.32$ mm^{-1}
$\alpha = 90$º	$T = 293$ (2) K
$\beta = 90$º	Cube, colourless
$\gamma = 90$º	0.15 × 0.15 × 0.15 mm
$V = 7617.2$ (12) Å^3	

Data collection

Bruker APEXII CCD diffractometer	3529 independent reflections
Radiation source: fine-focus sealed tube	2249 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.052$
$T = 293(2)$ K	$\theta_{max} = 25.5$º
φ and ω scans	$\theta_{min} = 1.7$º
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$h = -29\rightarrow26$
$T_{min} = 0.826$, $T_{max} = 0.826$	$k = -26\rightarrow29$
19270 measured reflections	$l = -15\rightarrow15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.046$	H-atom parameters not refined

$wR(F^2) = 0.154$	$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 20.3206P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
3529 reflections	$\Delta\rho_{max} = 0.43$ e Å^{-3}
248 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3405 (2)	0.2402 (2)	0.6596 (4)	0.0602 (14)
H1	0.3377	0.2495	0.7284	0.072*
C2	0.3006 (2)	0.2089 (2)	0.6154 (4)	0.0642 (15)
H2	0.2703	0.1975	0.6538	0.077*
C3	0.3046 (2)	0.1934 (2)	0.5123 (4)	0.0579 (13)
H3	0.2767	0.1718	0.4833	0.069*
C4	0.34886 (19)	0.20960 (19)	0.4540 (3)	0.0460 (11)
C5	0.3122 (3)	0.1772 (4)	0.2909 (5)	0.116 (3)
H5A	0.2997	0.1411	0.3118	0.175*
H5B	0.3233	0.1759	0.2205	0.175*
H5C	0.2827	0.2035	0.2989	0.175*
C6	0.39010 (18)	0.24382 (18)	0.4953 (3)	0.0410 (10)
C7	0.38608 (19)	0.25887 (19)	0.6020 (3)	0.0449 (11)
C8	0.42652 (19)	0.29078 (19)	0.6552 (3)	0.0473 (11)
H8	0.4225	0.2952	0.7253	0.057*
C9	0.54307 (19)	0.36577 (18)	0.6185 (4)	0.0451 (11)
C10	0.5861 (2)	0.39546 (19)	0.6751 (4)	0.0496 (12)
C11	0.6263 (2)	0.4233 (2)	0.6198 (5)	0.0648 (15)
H11	0.6246	0.4240	0.5489	0.078*
C12	0.6693 (3)	0.4505 (3)	0.6705 (7)	0.089 (2)
H12	0.6964	0.4696	0.6341	0.107*
C13	0.6710 (3)	0.4484 (3)	0.7795 (7)	0.096 (2)
H13	0.7002	0.4656	0.8134	0.115*
C14	0.6319 (3)	0.4226 (3)	0.8351 (6)	0.088 (2)
H14	0.6339	0.4225	0.9060	0.105*

C15	0.5884 (2)	0.3959 (2)	0.7857 (4)	0.0642 (15)
C16	0.2793 (4)	0.3665 (4)	0.6165 (8)	0.108 (3)
H16	0.2618	0.3529	0.6746	0.129*
C17	0.2830 (5)	0.3663 (6)	0.4320 (9)	0.205 (6)
H17A	0.2659	0.3988	0.4038	0.307*
H17B	0.2782	0.3358	0.3857	0.307*
H17C	0.3218	0.3730	0.4421	0.307*
C18	0.2097 (4)	0.3197 (4)	0.5211 (8)	0.134 (3)
H18A	0.1976	0.3105	0.5888	0.201*
H18B	0.2182	0.2863	0.4843	0.201*
H18C	0.1809	0.3396	0.4862	0.201*
N1	0.46812 (16)	0.31377 (15)	0.6114 (3)	0.0445 (9)
N2	0.50458 (16)	0.34242 (17)	0.6749 (3)	0.0494 (10)
N3	0.2579 (3)	0.3533 (3)	0.5269 (6)	0.114 (2)
O1	0.3203 (3)	0.3951 (3)	0.6286 (6)	0.157 (3)
O2	0.43283 (12)	0.25892 (13)	0.4338 (2)	0.0425 (7)
O3	0.54506 (13)	0.36375 (13)	0.5177 (2)	0.0488 (8)
O4	0.5508 (2)	0.3710 (2)	0.8454 (3)	0.0883 (13)
H4	0.5281	0.3546	0.8097	0.133*
O5	0.35790 (13)	0.19336 (14)	0.3519 (2)	0.0552 (9)
Zn1	0.48656 (2)	0.31666 (2)	0.46560 (4)	0.0434 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.064 (3)	0.079 (4)	0.037 (3)	−0.005 (3)	0.016 (2)	−0.003 (3)
C2	0.056 (3)	0.079 (4)	0.057 (3)	−0.016 (3)	0.016 (3)	0.001 (3)
C3	0.053 (3)	0.067 (3)	0.054 (3)	−0.012 (2)	0.004 (2)	−0.003 (3)
C4	0.051 (3)	0.052 (3)	0.034 (3)	−0.001 (2)	0.001 (2)	0.000 (2)
C5	0.094 (5)	0.182 (8)	0.073 (5)	−0.058 (5)	0.002 (4)	−0.053 (5)
C6	0.046 (3)	0.046 (3)	0.031 (2)	0.000 (2)	0.0032 (19)	0.0023 (19)
C7	0.050 (3)	0.053 (3)	0.031 (2)	−0.003 (2)	0.007 (2)	−0.001 (2)
C8	0.058 (3)	0.060 (3)	0.024 (2)	−0.003 (2)	0.011 (2)	−0.006 (2)
C9	0.053 (3)	0.046 (3)	0.036 (3)	0.006 (2)	−0.002 (2)	−0.010 (2)
C10	0.053 (3)	0.045 (3)	0.051 (3)	0.007 (2)	−0.004 (2)	−0.014 (2)
C11	0.057 (3)	0.059 (3)	0.079 (4)	0.000 (3)	−0.001 (3)	−0.019 (3)
C12	0.060 (4)	0.072 (4)	0.134 (7)	−0.009 (3)	0.004 (4)	−0.032 (4)
C13	0.077 (5)	0.078 (5)	0.132 (7)	0.001 (4)	−0.036 (5)	−0.039 (5)
C14	0.094 (5)	0.087 (5)	0.082 (5)	0.010 (4)	−0.039 (4)	−0.030 (4)
C15	0.072 (4)	0.067 (3)	0.054 (3)	0.009 (3)	−0.017 (3)	−0.017 (3)
C16	0.097 (6)	0.123 (7)	0.102 (7)	0.008 (5)	−0.005 (5)	0.013 (5)
C17	0.198 (12)	0.305 (18)	0.111 (9)	−0.080 (12)	−0.029 (9)	0.033 (10)
C18	0.114 (7)	0.129 (7)	0.159 (10)	0.003 (6)	−0.016 (6)	−0.014 (7)
N1	0.055 (2)	0.055 (2)	0.0239 (19)	−0.0004 (18)	0.0017 (17)	−0.0064 (17)
N2	0.055 (2)	0.065 (3)	0.028 (2)	−0.004 (2)	−0.0002 (18)	−0.0077 (18)
N3	0.098 (5)	0.161 (7)	0.085 (5)	−0.007 (5)	−0.018 (4)	0.011 (5)
O1	0.139 (6)	0.199 (7)	0.131 (6)	−0.023 (5)	−0.025 (5)	−0.010 (5)
O2	0.0501 (18)	0.0563 (18)	0.0211 (14)	−0.0046 (14)	0.0036 (13)	−0.0038 (13)

O3	0.061 (2)	0.0550 (19)	0.0307 (18)	−0.0062 (15)	0.0049 (15)	−0.0041 (14)
O4	0.114 (4)	0.114 (4)	0.037 (2)	−0.025 (3)	−0.015 (2)	−0.010 (2)
O5	0.056 (2)	0.072 (2)	0.0377 (19)	−0.0142 (16)	0.0000 (15)	−0.0126 (16)
Zn1	0.0547 (4)	0.0517 (4)	0.0238 (3)	−0.0025 (2)	0.0031 (2)	−0.0027 (2)

Geometric parameters (Å, °)

C1—C2	1.352 (7)	C12—H12	0.930
C1—C7	1.408 (6)	C13—C14	1.343 (10)
C1—H1	0.930	C13—H13	0.930
C2—C3	1.404 (8)	C14—C15	1.390 (8)
C2—H2	0.930	C14—H14	0.930
C3—C4	1.370 (6)	C15—O4	1.342 (7)
C3—H3	0.930	C16—O1	1.214 (10)
C4—C6	1.401 (6)	C16—N3	1.321 (10)
C4—O5	1.411 (5)	C16—H16	0.930
C5—O5	1.416 (7)	C17—N3	1.418 (12)
C5—H5A	0.960	C17—H17A	0.960
C5—H5B	0.960	C17—H17B	0.960
C5—H5C	0.960	C17—H17C	0.960
C6—O2	1.358 (5)	C18—N3	1.418 (10)
C6—C7	1.446 (6)	C18—H18A	0.960
C7—C8	1.424 (6)	C18—H18B	0.960
C8—N1	1.282 (6)	C18—H18C	0.960
C8—H8	0.930	N1—N2	1.393 (5)
C9—N2	1.313 (6)	O2—Zn1^{i}	2.028 (3)
C9—O3	1.322 (5)	O4—H4	0.820
C9—C10	1.463 (6)	O5—Zn1^{i}	2.275 (3)
C10—C11	1.383 (7)	Zn1—N1	1.961 (4)
C10—C15	1.449 (7)	Zn1—O2	1.948 (3)
C11—C12	1.395 (8)	Zn1—O3	1.936 (3)
C11—H11	0.930	Zn1—O2^{ii}	2.028 (3)
C12—C13	1.429 (11)	Zn1—O5^{ii}	2.275 (3)
C2—C1—C7	120.3 (5)	C15—C14—H14	120.3
C2—C1—H1	119.9	O4—C15—C14	116.6 (6)
C7—C1—H1	119.9	O4—C15—C10	123.6 (5)
C1—C2—C3	120.8 (5)	C14—C15—C10	119.8 (6)
C1—C2—H2	119.6	O1—C16—N3	124.8 (9)
C3—C2—H2	119.6	O1—C16—H16	117.6
C4—C3—C2	120.8 (5)	N3—C16—H16	117.6
C4—C3—H3	119.6	N3—C17—H17A	109.4
C2—C3—H3	119.6	N3—C17—H17B	109.5
C3—C4—C6	120.5 (4)	H17A—C17—H17B	109.5
C3—C4—O5	124.7 (4)	N3—C17—H17C	109.5
C6—C4—O5	114.8 (4)	H17A—C17—H17C	109.5
O5—C5—H5A	109.5	H17B—C17—H17C	109.5
O5—C5—H5B	109.5	N3—C18—H18A	109.5
H5A—C5—H5B	109.5	N3—C18—H18B	109.5

O5—C5—H5C	109.5	H18A—C18—H18B	109.5
H5A—C5—H5C	109.5	N3—C18—H18C	109.5
H5B—C5—H5C	109.5	H18A—C18—H18C	109.5
O2—C6—C4	117.9 (4)	H18B—C18—H18C	109.5
O2—C6—C7	123.8 (4)	C8—N1—N2	116.3 (4)
C4—C6—C7	118.2 (4)	C8—N1—Zn1	128.9 (3)
C1—C7—C8	116.5 (4)	N2—N1—Zn1	114.8 (3)
C1—C7—C6	119.3 (4)	C9—N2—N1	108.9 (4)
C8—C7—C6	124.2 (4)	C16—N3—C17	123.9 (9)
N1—C8—C7	123.5 (4)	C16—N3—C18	120.4 (8)
N1—C8—H8	118.3	C17—N3—C18	115.4 (8)
C7—C8—H8	118.3	C6—O2—Zn1	124.7 (3)
N2—C9—O3	124.8 (4)	C6—O2—Zn1^{i}	120.3 (3)
N2—C9—C10	115.3 (4)	Zn1—O2—Zn1^{i}	113.10 (14)
O3—C9—C10	119.9 (4)	C9—O3—Zn1	110.3 (3)
C11—C10—C15	119.5 (5)	C15—O4—H4	109.5
C11—C10—C9	118.0 (5)	C4—O5—C5	119.4 (4)
C15—C10—C9	122.5 (5)	C4—O5—Zn1^{i}	111.4 (3)
C10—C11—C12	120.0 (6)	C5—O5—Zn1^{i}	122.0 (4)
C10—C11—H11	120.0	O3—Zn1—O2	168.57 (13)
C12—C11—H11	120.0	O3—Zn1—N1	80.97 (14)
C11—C12—C13	118.6 (7)	O2—Zn1—N1	91.83 (14)
C11—C12—H12	120.7	O3—Zn1—O2^{ii}	98.19 (13)
C13—C12—H12	120.7	O2—Zn1—O2^{ii}	88.56 (12)
C14—C13—C12	122.5 (6)	N1—Zn1—O2^{ii}	177.14 (14)
C14—C13—H13	118.7	O3—Zn1—O5^{ii}	90.08 (13)
C12—C13—H13	118.7	O2—Zn1—O5^{ii}	100.61 (13)
C13—C14—C15	119.5 (7)	N1—Zn1—O5^{ii}	107.61 (13)
C13—C14—H14	120.3	O2^{ii}—Zn1—O5^{ii}	75.09 (11)

Symmetry codes: (i) −*y*+3/4, *x*−1/4, −*z*+3/4; (ii) *y*+1/4, −*x*+3/4, −*z*+3/4.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···N2	0.82	1.88	2.589 (5)	144

Fig. 1

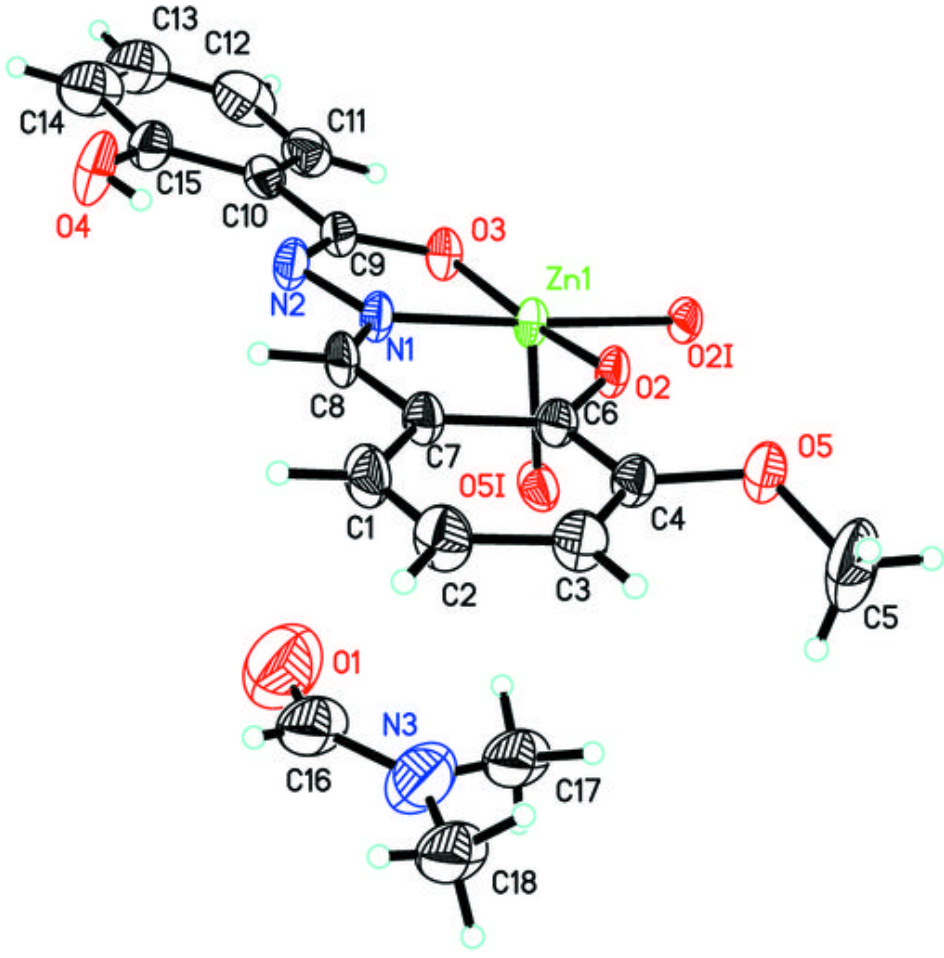
C13
C12
C14
C11
C15
O4
C10
O3
C9
N2
Zn1
N1
O2I
C8
O2
C6
C7
O5
O5I
C1
C4
C2
C3
C5
O1
N3
C16
C17
C18

Fig. 2