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Bis(pyridine-2-carbaldehyde thiosemicarbazone)zinc(II) dinitrate dihydrate

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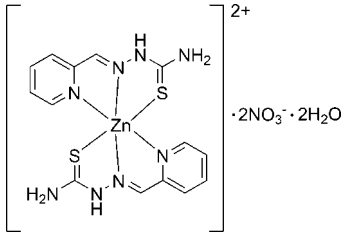
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.008 Å; R factor = 0.057; wR factor = 0.123; data-to-parameter ratio = 13.8.

The asymmetric unit of the title compound, $[Zn(C_7H_8N_4S)_2](NO_3)_2\cdot 2H_2O$, contains two $Zn(pht)_2$ cations (pht is pyridine-2-carbaldehyde thiosemicarbazone), four nitrate anions and four water molecules. In the cations, each Zn^{II} ion adopts a distorted octahedral coordination geometry, being chelated by two tridentate pht ligands. In the crystal, the cations, anions and water molecules are connected *via* O—H···O and N—H···O hydrogen bonds into a three-dimensional network.

Related literature

For related structures, see: Antholine *et al.* (1977); Ainscough *et al.* (1998).



Experimental

Crystal data

$[Zn(C_7H_8N_4S)_2](NO_3)_2\cdot 2H_2O$
M_r = 585.89
Monoclinic, $P2_1/c$
a = 21.4623 (14) Å
b = 16.6324 (12) Å
c = 13.2764 (10) Å
β = 102.876 (2)°
V = 4620.1 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.31 mm^{-1}
T = 120 K
0.25 × 0.22 × 0.20 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*a*)
T_{min} = 0.736, T_{max} = 0.780
22904 measured reflections
8732 independent reflections
5113 reflections with $I > 2\sigma(I)$
R_{int} = 0.077

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.123
S = 1.02
8732 reflections
631 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···O7	0.86	2.19	2.966 (6)	150
N4—H4B···O7	0.86	2.17	2.957 (6)	153
N4—H4C···O3W	0.86	2.03	2.840 (5)	157
N7—H7A···O1	0.86	1.96	2.813 (6)	172
N8—H8A···O2	0.86	2.08	2.906 (6)	160
N8—H8B···O6^{i}	0.86	2.04	2.870 (6)	163
N11—H11B···O10	0.86	1.87	2.710 (5)	167
N12—H12B···O11	0.86	2.02	2.876 (6)	173
N12—H12C···O8^{ii}	0.86	2.27	3.114 (6)	168
N15—H15A···O4W^{iii}	0.86	1.87	2.733 (5)	178
N16—H16A···O6^{iii}	0.86	2.11	2.909 (6)	155
N16—H16B···O4^{iv}	0.86	2.02	2.873 (5)	173
O1W—H1WA···O4^{v}	0.85	2.32	3.042 (5)	144
O1W—H1WB···O3	0.85	2.39	3.041 (6)	134
O2W—H2WA···O5^{iv}	0.85	2.33	2.927 (6)	128
O2W—H2WB···O3	0.85	2.47	3.141 (6)	136
O3W—H3WA···O10^{vi}	0.85	2.22	2.800 (5)	126
O3W—H3WB···O9^{vii}	0.85	2.24	2.978 (6)	145
O4W—H4WA···O2W	0.85	2.09	2.746 (6)	133
O4W—H4WB···O6	0.85	2.55	2.958 (5)	111

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008*b*); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5358).

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supplementary materials

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Bis(pyridine-2-carbaldehyde thiosemicarbazone)zinc(II) dinitrate dihydrate

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Comment

The examination of the antitumor properties of N-heterocyclic carboxaldehyde thiosemicarbazones has been extended to the consideration of some of their first-row transition metal complexes (Antholine *et al.* 1977, Ainscough *et al.* 1998). Meanwhile, zinc plays an important role in various biological systems and is a vital component an essential cofactor, critical for numerous cellular processes and may be a major regulatory ion in the metabolism of cells. Herein, we report a Zn^{II} complex, $Zn(pht)_2.2NO_3.2H_2O$ (pht= 2-(pyridine-2-carbaldehyde)hydrazinecarbothioamide).

The asymmetric unit of the title compound, contains two $Zn(pht)_2$ cations (pht = 2-(pyridine-2-carbaldehyde)hydrazinecarbothioamide), which have the similar structure, four nitrates and four free water molecules. In the $Zn(pht)_2$ cations, each Zn^{II} ions adopts a distorted octahedral coordination geometry, being chelated by two tridentate pht ligands. In a pht, all the atoms are approximatively coplanar, and the distances of the C=N bond are 1.269 (6)–1.283 (6) Å, which are shorter than those of C—N bond (1.303 (7)–1.369 (6) Å), being considered to have full double-bond character. In packing, All the $Zn(pht)_2$ cations, nitrates and water molecules are linked each other *via* O—H···O and N—H···O hydrogen bonds into a three-dimensional supramolecular network.

Experimental

A mixture of pht (0.036 g, 0.2 mmol), $Zn(NO_3)_2.6H_2O$ (0.029 g, 0.1 mmol), and water (8 ml) were heated ina 15 ml Teflon-lined vessel at 120 ° for 3 days, followed by slow cooling (5 ° h^{-1}) to room temperature. After filtration, colorless block crystals were collected and dried in air (0.018 g, yield *ca* 30.7% based on pht).

Refinement

All H atoms attached to C and N atoms were fixed geometrically and treated as riding with C—H = 0.93 Å and N—H = 0.86 Å with U_{iso}(H) = 1.2 U_{eq}(C or N). H atoms of water molecules were located in difference Fourier maps and included in the subsequent refinement with O—H= 0.85Å with U_{iso}(H) = 1.2 U_{eq}(O).

Figures

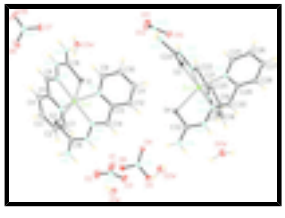


Fig. 1. View of the asymmetric unit of the title compoundcompound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

Bis(pyridine-2-carbaldehyde thiosemicarbazone)zinc(II) dinitrate dihydrate

Crystal data

$[Zn(C_7H_8N_4S)_2](NO_3)_2\cdot 2H_2O$	$F(000) = 2400$
$M_r = 585.89$	$D_x = 1.685$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 785 reflections
$a = 21.4623$ (14) Å	$\theta = 2.4$–$28.0°$
$b = 16.6324$ (12) Å	$\mu = 1.31$ mm^{-1}
$c = 13.2764$ (10) Å	$T = 120$ K
$\beta = 102.876$ (2)°	Block, colorless
$V = 4620.1$ (6) Å^3	0.25 × 0.22 × 0.20 mm
$Z = 8$	

Data collection

Bruker SMART APEX CCD diffractometer	8732 independent reflections
Radiation source: fine-focus sealed tube	5113 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.077$
φ and ω scan	$\theta_{max} = 26.0°$, $\theta_{min} = 1.6°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008a)	$h = -25\rightarrow21$
$T_{min} = 0.736$, $T_{max} = 0.780$	$k = -20\rightarrow12$
22904 measured reflections	$l = -16\rightarrow16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.057$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.123$	H-atom parameters constrained
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
8732 reflections	$(\Delta/\sigma)_{max} = 0.029$
631 parameters	$\Delta\rho_{max} = 0.81$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.43$ e Å^{-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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.25244 (3)	0.23919 (3)	0.57658 (4)	0.02381 (17)
Zn2	0.22452 (3)	0.75501 (3)	0.82766 (4)	0.02208 (17)
S1	0.18156 (7)	0.30117 (8)	0.42437 (10)	0.0301 (4)
S2	0.32904 (7)	0.17217 (8)	0.48824 (11)	0.0330 (4)
S3	0.14317 (7)	0.65650 (8)	0.85347 (10)	0.0280 (3)
S4	0.30520 (7)	0.65526 (8)	0.80976 (10)	0.0280 (4)
C1	0.3251 (3)	0.1529 (3)	0.7846 (4)	0.0339 (15)
H1A	0.3582	0.1887	0.7831	0.041*
C2	0.3318 (3)	0.0998 (3)	0.8668 (4)	0.0378 (16)
H2A	0.3684	0.1004	0.9195	0.045*
C3	0.2829 (3)	0.0460 (3)	0.8692 (4)	0.0386 (16)
H3A	0.2863	0.0094	0.9231	0.046*
C4	0.2294 (3)	0.0477 (3)	0.7902 (4)	0.0332 (15)
H4A	0.1959	0.0123	0.7900	0.040*
C5	0.2258 (3)	0.1028 (3)	0.7106 (4)	0.0266 (13)
C6	0.1702 (3)	0.1088 (3)	0.6264 (4)	0.0277 (13)
H6A	0.1362	0.0731	0.6202	0.033*
C8	0.1178 (2)	0.2397 (3)	0.4168 (4)	0.0223 (12)
C9	0.1696 (3)	0.3390 (3)	0.7026 (4)	0.0270 (13)
H9A	0.1368	0.3033	0.6752	0.032*
C10	0.1577 (3)	0.4020 (3)	0.7660 (4)	0.0285 (14)
H10A	0.1173	0.4086	0.7797	0.034*
C11	0.2065 (3)	0.4540 (3)	0.8076 (4)	0.0330 (15)
H11A	0.1996	0.4961	0.8499	0.040*
C12	0.2655 (3)	0.4431 (3)	0.7859 (4)	0.0298 (14)
H12A	0.2992	0.4773	0.8137	0.036*
C13	0.2735 (3)	0.3807 (3)	0.7222 (3)	0.0200 (12)
C14	0.3341 (3)	0.3668 (3)	0.6934 (4)	0.0256 (13)
H14A	0.3701	0.3973	0.7214	0.031*
C16	0.3920 (3)	0.2337 (3)	0.5309 (4)	0.0288 (13)
C17	0.3197 (3)	0.8776 (3)	0.7546 (4)	0.0286 (14)
H17A	0.3479	0.8639	0.8161	0.034*
C18	0.3399 (3)	0.9322 (3)	0.6897 (4)	0.0300 (14)
H18A	0.3812	0.9530	0.7059	0.036*
C19	0.2978 (3)	0.9545 (3)	0.6017 (4)	0.0334 (15)
H19A	0.3097	0.9922	0.5577	0.040*
C20	0.2369 (3)	0.9208 (3)	0.5776 (4)	0.0291 (14)
H20A	0.2073	0.9359	0.5182	0.035*

C21	0.2214 (2)	0.8643 (3)	0.6445 (4)	0.0207 (12)
C22	0.1609 (3)	0.8202 (3)	0.6203 (4)	0.0256 (13)
H22A	0.1292	0.8320	0.5621	0.031*
C24	0.0965 (3)	0.6578 (3)	0.7329 (4)	0.0232 (13)
C25	0.1337 (3)	0.8917 (3)	0.8776 (4)	0.0278 (13)
H25A	0.1075	0.8782	0.8141	0.033*
C26	0.1147 (3)	0.9538 (3)	0.9340 (4)	0.0285 (14)
H26A	0.0771	0.9819	0.9077	0.034*
C27	0.1520 (3)	0.9729 (3)	1.0289 (4)	0.0320 (14)
H27A	0.1398	1.0135	1.0686	0.038*
C28	0.2086 (3)	0.9305 (3)	1.0648 (4)	0.0320 (14)
H28A	0.2350	0.9427	1.1286	0.038*
C29	0.2246 (3)	0.8702 (3)	1.0038 (4)	0.0235 (13)
C30	0.2841 (3)	0.8244 (3)	1.0344 (4)	0.0258 (13)
H30A	0.3132	0.8343	1.0963	0.031*
C32	0.3575 (3)	0.6699 (3)	0.9239 (4)	0.0242 (13)
N1	0.2738 (2)	0.1546 (2)	0.7083 (3)	0.0270 (11)
N2	0.1698 (2)	0.1650 (2)	0.5611 (3)	0.0234 (10)
N3	0.1180 (2)	0.1775 (2)	0.4824 (3)	0.0273 (11)
H3B	0.0855	0.1460	0.4745	0.033*
N4	0.06559 (19)	0.2474 (2)	0.3439 (3)	0.0275 (11)
H4B	0.0346	0.2140	0.3405	0.033*
H4C	0.0624	0.2858	0.2997	0.033*
N5	0.2263 (2)	0.3291 (2)	0.6810 (3)	0.0225 (10)
N6	0.3358 (2)	0.3111 (2)	0.6284 (3)	0.0243 (11)
N7	0.3911 (2)	0.2952 (2)	0.5973 (3)	0.0287 (11)
H7A	0.4247	0.3239	0.6195	0.034*
N8	0.4457 (2)	0.2266 (3)	0.4975 (4)	0.0427 (13)
H8A	0.4766	0.2598	0.5183	0.051*
H8B	0.4495	0.1888	0.4552	0.051*
N9	0.2622 (2)	0.8438 (2)	0.7334 (3)	0.0231 (10)
N10	0.15389 (19)	0.7643 (2)	0.6836 (3)	0.0195 (10)
N11	0.1020 (2)	0.7152 (2)	0.6629 (3)	0.0244 (11)
H11B	0.0732	0.7204	0.6067	0.029*
N12	0.0521 (2)	0.6028 (2)	0.7020 (3)	0.0316 (12)
H12B	0.0286	0.6047	0.6404	0.038*
H12C	0.0466	0.5650	0.7433	0.038*
N13	0.1877 (2)	0.8507 (2)	0.9102 (3)	0.0229 (10)
N14	0.2938 (2)	0.7703 (2)	0.9722 (3)	0.0212 (10)
N15	0.3479 (2)	0.7262 (2)	0.9943 (3)	0.0256 (11)
H15A	0.3757	0.7333	1.0511	0.031*
N16	0.4098 (2)	0.6278 (2)	0.9496 (3)	0.0328 (12)
H16A	0.4360	0.6362	1.0079	0.039*
H16B	0.4182	0.5916	0.9083	0.039*
N17	0.5277 (3)	0.4141 (3)	0.5916 (4)	0.0421 (13)
N18	0.5183 (2)	0.9676 (3)	0.6417 (3)	0.0291 (11)
N19	−0.0127 (3)	0.0485 (3)	0.3698 (4)	0.0358 (12)
N20	−0.0031 (2)	0.6531 (3)	0.4316 (4)	0.0358 (12)
O1	0.4955 (2)	0.4005 (3)	0.6560 (3)	0.0628 (14)

O2	0.5329 (2)	0.3626 (3)	0.5256 (4)	0.0677 (15)
O3	0.5557 (2)	0.4799 (3)	0.5909 (3)	0.0544 (13)
O4	0.57090 (17)	0.9985 (2)	0.6837 (3)	0.0329 (10)
O5	0.46998 (18)	1.0110 (2)	0.6105 (3)	0.0406 (11)
O6	0.51370 (17)	0.8926 (2)	0.6304 (3)	0.0335 (10)
O7	−0.01433 (19)	0.1186 (2)	0.4029 (3)	0.0448 (11)
O8	0.0395 (2)	0.0142 (3)	0.3794 (3)	0.0516 (12)
O9	−0.0623 (2)	0.0145 (3)	0.3268 (3)	0.0648 (15)
O10	0.02421 (18)	0.7177 (2)	0.4717 (3)	0.0395 (11)
O11	−0.01805 (19)	0.6012 (2)	0.4904 (3)	0.0430 (11)
O12	−0.01414 (18)	0.6431 (2)	0.3370 (3)	0.0441 (11)
O1W	0.62343 (19)	0.4712 (3)	0.4129 (3)	0.0608 (13)
H1WA	0.6112	0.4562	0.3504	0.073*
H1WB	0.6057	0.4444	0.4533	0.073*
O2W	0.52013 (19)	0.6250 (3)	0.7187 (3)	0.0588 (13)
H2WA	0.5064	0.6175	0.7733	0.071*
H2WB	0.5496	0.5995	0.6990	0.071*
O3W	0.04209 (17)	0.3374 (2)	0.1575 (3)	0.0400 (10)
H3WA	0.0152	0.3325	0.1001	0.048*
H3WB	0.0337	0.3847	0.1746	0.048*
O4W	0.43806 (18)	0.7533 (2)	0.6735 (3)	0.0542 (12)
H4WA	0.4679	0.7266	0.6564	0.065*
H4WB	0.4545	0.7897	0.7161	0.065*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0256 (4)	0.0197 (3)	0.0261 (3)	−0.0050 (3)	0.0059 (3)	−0.0023 (3)
Zn2	0.0243 (4)	0.0183 (3)	0.0222 (3)	0.0012 (3)	0.0023 (3)	−0.0007 (3)
S1	0.0311 (10)	0.0296 (8)	0.0283 (7)	−0.0100 (7)	0.0039 (7)	0.0025 (6)
S2	0.0338 (10)	0.0279 (8)	0.0388 (8)	−0.0050 (7)	0.0116 (7)	−0.0111 (6)
S3	0.0340 (10)	0.0228 (7)	0.0260 (7)	−0.0015 (7)	0.0038 (6)	0.0007 (6)
S4	0.0302 (9)	0.0229 (7)	0.0279 (7)	0.0048 (7)	0.0005 (6)	−0.0041 (6)
C1	0.040 (4)	0.024 (3)	0.034 (3)	−0.002 (3)	0.001 (3)	−0.003 (3)
C2	0.059 (5)	0.025 (3)	0.028 (3)	0.016 (3)	0.006 (3)	−0.005 (3)
C3	0.065 (5)	0.021 (3)	0.036 (3)	0.007 (3)	0.025 (3)	0.004 (3)
C4	0.045 (4)	0.021 (3)	0.038 (3)	0.008 (3)	0.019 (3)	0.003 (3)
C5	0.035 (4)	0.017 (3)	0.034 (3)	0.004 (3)	0.019 (3)	0.001 (2)
C6	0.029 (4)	0.015 (3)	0.043 (3)	−0.005 (3)	0.015 (3)	−0.001 (3)
C8	0.023 (3)	0.020 (3)	0.025 (3)	0.002 (3)	0.008 (2)	−0.006 (2)
C9	0.038 (4)	0.018 (3)	0.025 (3)	−0.004 (3)	0.008 (3)	0.004 (2)
C10	0.032 (4)	0.031 (3)	0.026 (3)	0.010 (3)	0.012 (3)	0.012 (2)
C11	0.055 (5)	0.018 (3)	0.025 (3)	0.007 (3)	0.005 (3)	0.000 (2)
C12	0.041 (4)	0.019 (3)	0.028 (3)	−0.002 (3)	0.004 (3)	−0.003 (2)
C13	0.023 (4)	0.019 (3)	0.017 (3)	0.002 (3)	0.004 (2)	0.003 (2)
C14	0.030 (4)	0.021 (3)	0.023 (3)	−0.005 (3)	0.001 (3)	0.002 (2)
C16	0.029 (4)	0.024 (3)	0.034 (3)	0.002 (3)	0.009 (3)	−0.001 (2)
C17	0.027 (4)	0.022 (3)	0.035 (3)	0.005 (3)	0.004 (3)	−0.005 (3)

C18	0.025 (4)	0.023 (3)	0.044 (3)	−0.003 (3)	0.012 (3)	−0.005 (3)
C19	0.051 (4)	0.021 (3)	0.034 (3)	−0.013 (3)	0.022 (3)	−0.006 (3)
C20	0.040 (4)	0.026 (3)	0.023 (3)	−0.005 (3)	0.013 (3)	0.000 (2)
C21	0.023 (3)	0.014 (3)	0.027 (3)	0.002 (2)	0.008 (2)	−0.003 (2)
C22	0.031 (4)	0.024 (3)	0.022 (3)	0.002 (3)	0.006 (3)	0.001 (2)
C24	0.030 (4)	0.016 (3)	0.027 (3)	0.002 (3)	0.012 (3)	−0.004 (2)
C25	0.025 (4)	0.026 (3)	0.033 (3)	−0.002 (3)	0.007 (3)	0.003 (3)
C26	0.024 (4)	0.024 (3)	0.039 (3)	0.006 (3)	0.011 (3)	0.002 (3)
C27	0.034 (4)	0.022 (3)	0.043 (3)	0.001 (3)	0.015 (3)	−0.009 (3)
C28	0.037 (4)	0.022 (3)	0.038 (3)	−0.005 (3)	0.010 (3)	−0.011 (3)
C29	0.028 (4)	0.017 (3)	0.028 (3)	0.002 (3)	0.012 (3)	0.001 (2)
C30	0.033 (4)	0.024 (3)	0.021 (3)	0.000 (3)	0.007 (3)	−0.005 (2)
C32	0.019 (3)	0.020 (3)	0.035 (3)	0.000 (3)	0.010 (3)	0.001 (2)
N1	0.030 (3)	0.019 (2)	0.034 (3)	0.003 (2)	0.011 (2)	0.000 (2)
N2	0.027 (3)	0.016 (2)	0.029 (2)	−0.002 (2)	0.009 (2)	0.0015 (19)
N3	0.025 (3)	0.020 (2)	0.036 (3)	−0.009 (2)	0.005 (2)	−0.003 (2)
N4	0.021 (3)	0.025 (3)	0.034 (2)	−0.004 (2)	0.001 (2)	0.001 (2)
N5	0.024 (3)	0.019 (2)	0.025 (2)	0.001 (2)	0.007 (2)	−0.0008 (19)
N6	0.026 (3)	0.021 (2)	0.028 (2)	0.001 (2)	0.011 (2)	0.003 (2)
N7	0.023 (3)	0.028 (3)	0.035 (3)	−0.005 (2)	0.005 (2)	−0.006 (2)
N8	0.032 (3)	0.042 (3)	0.057 (3)	−0.006 (3)	0.017 (3)	−0.016 (3)
N9	0.020 (3)	0.019 (2)	0.031 (2)	−0.002 (2)	0.007 (2)	−0.0047 (19)
N10	0.020 (3)	0.017 (2)	0.022 (2)	−0.001 (2)	0.0064 (19)	−0.0004 (18)
N11	0.022 (3)	0.026 (3)	0.023 (2)	−0.010 (2)	0.000 (2)	0.0038 (19)
N12	0.030 (3)	0.026 (3)	0.039 (3)	−0.011 (2)	0.007 (2)	0.002 (2)
N13	0.023 (3)	0.018 (2)	0.029 (2)	0.001 (2)	0.009 (2)	−0.0018 (19)
N14	0.017 (3)	0.021 (2)	0.025 (2)	0.002 (2)	0.0043 (19)	−0.0006 (19)
N15	0.028 (3)	0.023 (2)	0.021 (2)	0.001 (2)	−0.004 (2)	−0.0029 (18)
N16	0.031 (3)	0.028 (3)	0.036 (3)	0.007 (2)	0.000 (2)	−0.010 (2)
N17	0.041 (4)	0.041 (3)	0.042 (3)	−0.006 (3)	0.006 (3)	−0.006 (3)
N18	0.026 (3)	0.031 (3)	0.028 (3)	−0.003 (3)	0.002 (2)	0.004 (2)
N19	0.037 (4)	0.031 (3)	0.039 (3)	−0.005 (3)	0.009 (3)	0.007 (2)
N20	0.032 (3)	0.031 (3)	0.041 (3)	0.010 (3)	0.000 (3)	−0.001 (2)
O1	0.063 (3)	0.077 (4)	0.059 (3)	−0.036 (3)	0.038 (3)	−0.026 (3)
O2	0.081 (4)	0.059 (3)	0.075 (3)	−0.013 (3)	0.042 (3)	−0.022 (3)
O3	0.053 (3)	0.046 (3)	0.061 (3)	−0.020 (3)	0.006 (2)	−0.003 (2)
O4	0.023 (2)	0.030 (2)	0.043 (2)	−0.0044 (19)	0.0008 (19)	0.0046 (18)
O5	0.028 (3)	0.033 (2)	0.054 (3)	0.005 (2)	−0.005 (2)	0.001 (2)
O6	0.038 (3)	0.019 (2)	0.045 (2)	−0.0062 (19)	0.012 (2)	−0.0087 (18)
O7	0.051 (3)	0.021 (2)	0.072 (3)	−0.004 (2)	0.036 (2)	−0.008 (2)
O8	0.049 (3)	0.047 (3)	0.058 (3)	0.019 (3)	0.011 (2)	0.006 (2)
O9	0.065 (3)	0.059 (3)	0.058 (3)	−0.045 (3)	−0.014 (3)	0.015 (2)
O10	0.047 (3)	0.027 (2)	0.037 (2)	−0.004 (2)	−0.007 (2)	0.0000 (18)
O11	0.046 (3)	0.037 (2)	0.046 (3)	−0.008 (2)	0.010 (2)	0.007 (2)
O12	0.046 (3)	0.046 (3)	0.033 (2)	0.008 (2)	−0.006 (2)	−0.005 (2)
O1W	0.066 (3)	0.076 (3)	0.040 (3)	−0.008 (3)	0.010 (2)	0.004 (2)
O2W	0.048 (3)	0.070 (3)	0.061 (3)	0.002 (3)	0.018 (2)	0.005 (2)
O3W	0.046 (3)	0.034 (2)	0.040 (2)	−0.001 (2)	0.012 (2)	−0.0074 (19)
O4W	0.046 (3)	0.053 (3)	0.055 (3)	−0.010 (2)	−0.008 (2)	0.004 (2)

Geometric parameters (Å, °)

Zn1—N6	2.133 (4)	C21—C22	1.463 (7)
Zn1—N2	2.133 (4)	C22—N10	1.283 (6)
Zn1—N5	2.196 (4)	C22—H22A	0.9300
Zn1—N1	2.211 (4)	C24—N12	1.319 (6)
Zn1—S1	2.4678 (15)	C24—N11	1.356 (6)
Zn1—S2	2.4860 (16)	C25—N13	1.331 (6)
Zn2—N10	2.165 (4)	C25—C26	1.389 (7)
Zn2—N14	2.165 (4)	C25—H25A	0.9300
Zn2—N13	2.178 (4)	C26—C27	1.372 (7)
Zn2—N9	2.203 (4)	C26—H26A	0.9300
Zn2—S4	2.4475 (15)	C27—C28	1.393 (7)
Zn2—S3	2.4733 (15)	C27—H27A	0.9300
S1—C8	1.692 (5)	C28—C29	1.380 (7)
S2—C16	1.689 (6)	C28—H28A	0.9300
S3—C24	1.688 (5)	C29—N13	1.356 (6)
S4—C32	1.690 (5)	C29—C30	1.464 (7)
C1—N1	1.319 (6)	C30—N14	1.270 (6)
C1—C2	1.386 (7)	C30—H30A	0.9300
C1—H1A	0.9300	C32—N16	1.304 (6)
C2—C3	1.385 (7)	C32—N15	1.369 (6)
C2—H2A	0.9300	N2—N3	1.361 (5)
C3—C4	1.372 (7)	N3—H3B	0.8600
C3—H3A	0.9300	N4—H4B	0.8600
C4—C5	1.388 (7)	N4—H4C	0.8600
C4—H4A	0.9300	N6—N7	1.367 (5)
C5—N1	1.349 (6)	N7—H7A	0.8600
C5—C6	1.445 (7)	N8—H8A	0.8600
C6—N2	1.273 (6)	N8—H8B	0.8600
C6—H6A	0.9300	N10—N11	1.359 (5)
C8—N4	1.314 (6)	N11—H11B	0.8600
C8—N3	1.353 (6)	N12—H12B	0.8600
C9—N5	1.322 (6)	N12—H12C	0.8600
C9—C10	1.404 (7)	N14—N15	1.348 (5)
C9—H9A	0.9300	N15—H15A	0.8600
C10—C11	1.375 (7)	N16—H16A	0.8600
C10—H10A	0.9300	N16—H16B	0.8600
C11—C12	1.371 (7)	N17—O1	1.233 (6)
C11—H11A	0.9300	N17—O2	1.249 (6)
C12—C13	1.375 (6)	N17—O3	1.250 (6)
C12—H12A	0.9300	N18—O4	1.252 (5)
C13—N5	1.347 (6)	N18—O5	1.256 (5)
C13—C14	1.452 (7)	N18—O6	1.258 (5)
C14—N6	1.273 (6)	N19—O9	1.229 (5)
C14—H14A	0.9300	N19—O8	1.238 (5)
C16—N8	1.329 (6)	N19—O7	1.249 (5)
C16—N7	1.354 (6)	N20—O12	1.236 (5)

C17—N9	1.328 (6)	N20—O11	1.252 (5)
C17—C18	1.387 (7)	N20—O10	1.281 (5)
C17—H17A	0.9300	O1W—H1WA	0.8500
C18—C19	1.359 (7)	O1W—H1WB	0.8501
C18—H18A	0.9300	O2W—H2WA	0.8499
C19—C20	1.394 (7)	O2W—H2WB	0.8500
C19—H19A	0.9300	O3W—H3WA	0.8502
C20—C21	1.383 (6)	O3W—H3WB	0.8500
C20—H20A	0.9300	O4W—H4WA	0.8500
C21—N9	1.347 (6)	O4W—H4WB	0.8502
N6—Zn1—N2	167.04 (16)	N10—C22—C21	116.6 (5)
N6—Zn1—N5	74.23 (16)	N10—C22—H22A	121.7
N2—Zn1—N5	97.52 (16)	C21—C22—H22A	121.7
N6—Zn1—N1	95.16 (16)	N12—C24—N11	116.2 (5)
N2—Zn1—N1	74.32 (16)	N12—C24—S3	121.4 (4)
N5—Zn1—N1	88.34 (15)	N11—C24—S3	122.4 (4)
N6—Zn1—S1	110.45 (11)	N13—C25—C26	123.0 (5)
N2—Zn1—S1	79.34 (12)	N13—C25—H25A	118.5
N5—Zn1—S1	91.99 (11)	C26—C25—H25A	118.5
N1—Zn1—S1	153.47 (13)	C27—C26—C25	119.1 (5)
N6—Zn1—S2	78.96 (12)	C27—C26—H26A	120.5
N2—Zn1—S2	108.58 (11)	C25—C26—H26A	120.5
N5—Zn1—S2	153.14 (12)	C26—C27—C28	118.9 (5)
N1—Zn1—S2	92.62 (11)	C26—C27—H27A	120.6
S1—Zn1—S2	98.79 (5)	C28—C27—H27A	120.6
N10—Zn2—N14	169.14 (15)	C29—C28—C27	118.6 (5)
N10—Zn2—N13	97.54 (15)	C29—C28—H28A	120.7
N14—Zn2—N13	73.92 (16)	C27—C28—H28A	120.7
N10—Zn2—N9	73.97 (15)	N13—C29—C28	122.7 (5)
N14—Zn2—N9	99.09 (15)	N13—C29—C30	115.1 (4)
N13—Zn2—N9	90.90 (15)	C28—C29—C30	122.1 (5)
N10—Zn2—S4	109.51 (11)	N14—C30—C29	116.6 (5)
N14—Zn2—S4	78.71 (11)	N14—C30—H30A	121.7
N13—Zn2—S4	152.61 (12)	C29—C30—H30A	121.7
N9—Zn2—S4	92.42 (11)	N16—C32—N15	116.1 (5)
N10—Zn2—S3	78.04 (11)	N16—C32—S4	121.2 (4)
N14—Zn2—S3	108.77 (11)	N15—C32—S4	122.7 (4)
N13—Zn2—S3	93.90 (11)	C1—N1—C5	118.7 (5)
N9—Zn2—S3	151.99 (12)	C1—N1—Zn1	127.7 (4)
S4—Zn2—S3	95.80 (5)	C5—N1—Zn1	113.5 (3)
C8—S1—Zn1	97.99 (18)	C6—N2—N3	121.0 (4)
C16—S2—Zn1	97.7 (2)	C6—N2—Zn1	118.6 (4)
C24—S3—Zn2	98.53 (19)	N3—N2—Zn1	120.4 (3)
C32—S4—Zn2	99.06 (19)	C8—N3—N2	119.7 (4)
N1—C1—C2	122.7 (6)	C8—N3—H3B	120.2
N1—C1—H1A	118.6	N2—N3—H3B	120.2
C2—C1—H1A	118.6	C8—N4—H4B	120.0
C3—C2—C1	119.0 (6)	C8—N4—H4C	120.0
C3—C2—H2A	120.5	H4B—N4—H4C	120.0

C1—C2—H2A	120.5	C9—N5—C13	118.6 (4)
C4—C3—C2	118.5 (5)	C9—N5—Zn1	126.8 (3)
C4—C3—H3A	120.7	C13—N5—Zn1	114.6 (3)
C2—C3—H3A	120.7	C14—N6—N7	120.2 (5)
C3—C4—C5	119.4 (6)	C14—N6—Zn1	118.6 (4)
C3—C4—H4A	120.3	N7—N6—Zn1	121.1 (3)
C5—C4—H4A	120.3	C16—N7—N6	118.8 (4)
N1—C5—C4	121.7 (5)	C16—N7—H7A	120.6
N1—C5—C6	116.2 (5)	N6—N7—H7A	120.6
C4—C5—C6	122.1 (5)	C16—N8—H8A	120.0
N2—C6—C5	117.2 (5)	C16—N8—H8B	120.0
N2—C6—H6A	121.4	H8A—N8—H8B	120.0
C5—C6—H6A	121.4	C17—N9—C21	118.1 (4)
N4—C8—N3	115.3 (5)	C17—N9—Zn2	127.2 (3)
N4—C8—S1	122.1 (4)	C21—N9—Zn2	114.7 (3)
N3—C8—S1	122.6 (4)	C22—N10—N11	120.9 (4)
N5—C9—C10	121.5 (5)	C22—N10—Zn2	117.9 (4)
N5—C9—H9A	119.3	N11—N10—Zn2	121.1 (3)
C10—C9—H9A	119.3	C24—N11—N10	118.5 (4)
C11—C10—C9	119.1 (5)	C24—N11—H11B	120.7
C11—C10—H10A	120.5	N10—N11—H11B	120.7
C9—C10—H10A	120.5	C24—N12—H12B	120.0
C12—C11—C10	119.3 (5)	C24—N12—H12C	120.0
C12—C11—H11A	120.4	H12B—N12—H12C	120.0
C10—C11—H11A	120.4	C25—N13—C29	117.7 (4)
C11—C12—C13	118.5 (5)	C25—N13—Zn2	126.7 (3)
C11—C12—H12A	120.7	C29—N13—Zn2	115.6 (3)
C13—C12—H12A	120.7	C30—N14—N15	120.2 (4)
N5—C13—C12	123.0 (5)	C30—N14—Zn2	118.6 (4)
N5—C13—C14	115.3 (4)	N15—N14—Zn2	121.1 (3)
C12—C13—C14	121.7 (5)	N14—N15—C32	118.4 (4)
N6—C14—C13	117.2 (5)	N14—N15—H15A	120.8
N6—C14—H14A	121.4	C32—N15—H15A	120.8
C13—C14—H14A	121.4	C32—N16—H16A	120.0
N8—C16—N7	115.1 (5)	C32—N16—H16B	120.0
N8—C16—S2	121.5 (4)	H16A—N16—H16B	120.0
N7—C16—S2	123.3 (4)	O1—N17—O2	120.8 (5)
N9—C17—C18	123.4 (5)	O1—N17—O3	120.7 (5)
N9—C17—H17A	118.3	O2—N17—O3	118.5 (6)
C18—C17—H17A	118.3	O4—N18—O5	120.5 (4)
C19—C18—C17	118.2 (5)	O4—N18—O6	120.0 (5)
C19—C18—H18A	120.9	O5—N18—O6	119.5 (5)
C17—C18—H18A	120.9	O9—N19—O8	120.5 (5)
C18—C19—C20	119.8 (5)	O9—N19—O7	120.2 (6)
C18—C19—H19A	120.1	O8—N19—O7	119.3 (5)
C20—C19—H19A	120.1	O12—N20—O11	121.5 (5)
C21—C20—C19	118.3 (5)	O12—N20—O10	120.1 (5)
C21—C20—H20A	120.9	O11—N20—O10	118.4 (5)
C19—C20—H20A	120.9	H1WA—O1W—H1WB	112.2

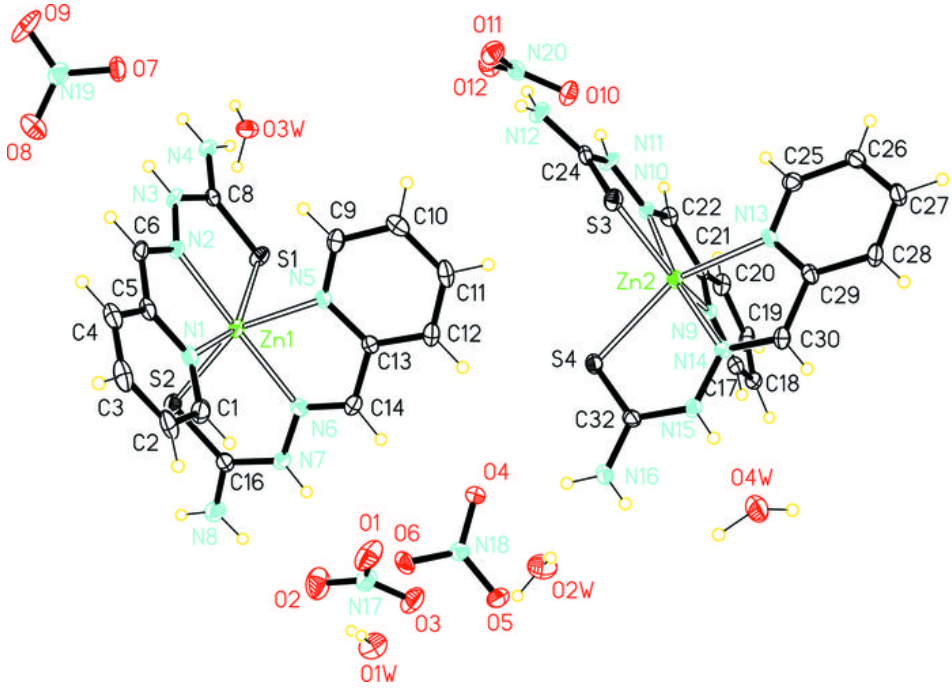
N9—C21—C20	122.1 (5)	H2WA—O2W—H2WB	127.8
N9—C21—C22	115.9 (4)	H3WA—O3W—H3WB	100.8
C20—C21—C22	121.9 (5)	H4WA—O4W—H4WB	108.9

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3B···O7	0.86	2.19	2.966 (6)	150
N4—H4B···O7	0.86	2.17	2.957 (6)	153
N4—H4C···O3W	0.86	2.03	2.840 (5)	157
N7—H7A···O1	0.86	1.96	2.813 (6)	172
N8—H8A···O2	0.86	2.08	2.906 (6)	160
N8—H8B···O6^{i}	0.86	2.04	2.870 (6)	163
N11—H11B···O10	0.86	1.87	2.710 (5)	167
N12—H12B···O11	0.86	2.02	2.876 (6)	173
N12—H12C···O8^{ii}	0.86	2.27	3.114 (6)	168
N15—H15A···O4W^{iii}	0.86	1.87	2.733 (5)	178
N16—H16A···O6^{iii}	0.86	2.11	2.909 (6)	155
N16—H16B···O4^{iv}	0.86	2.02	2.873 (5)	173
O1W—H1WA···O4^{v}	0.85	2.32	3.042 (5)	144
O1W—H1WB···O3	0.85	2.39	3.041 (6)	134
O2W—H2WA···O5^{iv}	0.85	2.33	2.927 (6)	128
O2W—H2WB···O3	0.85	2.47	3.141 (6)	136
O3W—H3WA···O10^{vi}	0.85	2.22	2.800 (5)	126
O3W—H3WB···O9^{vii}	0.85	2.24	2.978 (6)	145
O4W—H4WA···O2W	0.85	2.09	2.746 (6)	133
O4W—H4WB···O6	0.85	2.55	2.958 (5)	111

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*, −*y*+1/2, *z*+1/2; (iii) *x*, −*y*+3/2, *z*+1/2; (iv) −*x*+1, *y*−1/2, −*z*+3/2; (v) *x*, −*y*+3/2, *z*−1/2; (vi) −*x*, *y*−1/2, −*z*+1/2; (vii) −*x*, *y*+1/2, −*z*+1/2.

Fig. 1


O9
O7
N19
O8
O3W
N4
N3
C8
C6
N2
S1
C9
C10
C5
N5
C11
C4
N1
Zn1
C12
C13
S2
C3
C1
C14
C2
N6
N7
C16
N8
O11
N20
O12
O10
N12
N11
C24
N10
C25
C26
C27
S3
C22
N13
C21
C28
Zn2
C20
C29
C19
N9
C30
S4
N14
C17
C18
C32
N15
N16
O4W
O4
O1
O6
N18
O2
N17
O3
O5
O2W
O1W