Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dibromidobis(4-hydroxy-1,5-dimethyl-2-phenyl-3-pyrazolone)zinc(II)

Pascale Lemoine,[a]* Bernard Viossat,[a] Jean Daniel Brion[b] and Alain Bekaert[b]

[a]Laboratoire de Cristallographie et RMN biologiques, UMR 8015 CNRS, Faculté des Sciences Pharmaceutiques et Biologiques de Paris Descartes, 4 avenue de l'Observatoire, 75270 Paris Cedex 06, France, and [b]Université de Paris XI, Faculté des Sciences Pharmaceutiques et Biologiques, Laboratoire de Chimie Thérapeutique BioCIS, UPRES-A 8076 CNRS, 5 rue J. B. Clément, 92296 Châtenay-Malabry Cedex, France
Correspondence e-mail: lemoine@pharmacie.univ-paris5.fr

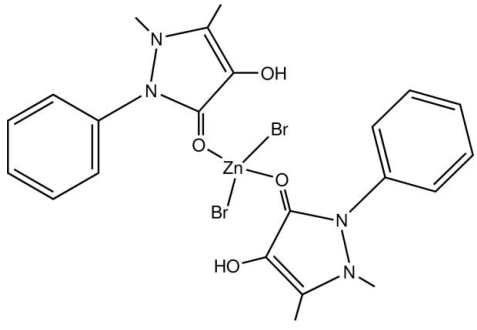
Received 14 May 2008; accepted 3 June 2008

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.009 Å; R factor = 0.035; wR factor = 0.094; data-to-parameter ratio = 24.2.

In the title compound, $[ZnBr_2(C_{11}H_{12}N_2O_2)_2]$, the Zn(II) ion is coordinated by two Br atoms and two O atoms from two 4-hydroxyantipyrine molecules *via* the carbonyl O atoms, which act as monodentate ligands, giving rise to a distorted tetrahedral geometry. The values of the bond angles at the Zn atom are in the range 99.4 (1) to 113.2 (1)°. The presence of O—H···O and O—H···Br intramolecular hydrogen bonds can explain the difference between the two Zn—O [1.961 (3)/2.015 (3) Å] and the two Zn—Br [2.350 (1)/2.378 (1) Å] bond lengths. The crystal structure is governed by C—H···O, C—H···Br and Zn—Br···Cg(π-ring) interactions.

Related literature

For related literature, see: Bekaert *et al.* (2003, 2007); Filiz *et al.* (2008); Lemoine *et al.* (2007); Matzke *et al.* (2000); Melov *et al.*, (1998); Panneerselvam *et al.* (1996); Tougu *et al.* (2008).



Experimental

Crystal data

$[ZnBr_2(C_{11}H_{12}N_2O_2)_2]$
M_r = 633.64
Tetragonal, $P4_1$
a = 9.824 (3) Å
c = 26.120 (3) Å
V = 2521 (1) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.18 mm^{-1}
T = 293 (2) K
0.17 × 0.16 × 0.15 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
Absorption correction: none
15417 measured reflections
7354 independent reflections
3152 reflections with $I > 2\sigma(I)$
R_{int} = 0.091
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.093
S = 0.90
7354 reflections
304 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Absolute structure: Flack (1983), 3602 Friedel pairs
Flack parameter: −0.015 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···O24	0.82	1.94	2.734 (5)	164
O25—H25···Br1	0.82	2.40	3.212 (4)	169
C10—H10···O5^{i}	0.93	2.47	3.378 (8)	165
C27—H27C···Br2^{ii}	0.96	2.81	3.686 (7)	151

Symmetry codes: (i) $x+1, y, z$; (ii) $-y+1, x-1, z+\frac{1}{4}$.

Table 2
Zn—Br···Cg(π-ring) interaction.

y—$X(I)$···$Cg(J)$	X···Cg	X-Perp	γ	Y—X···Cg
Zn1—Br1···$Cg1^{i}$	3.671 (2)	3.646	6.76	132.21 (4)

Symmetry code: (i) $1+y, 1-x, -\frac{1}{4}+z$. $Cg1$ is the centroid of atoms Cl/N2/N3/C4/C5.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2351).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Bekaert, A., Lemoine, P., Brion, J. D. & Viossat, B. (2003). *Acta Cryst.* E**59**, m574–m575.
Bekaert, A., Lemoine, P., Brion, J. D. & Viossat, B. (2007). *Acta Cryst.* E**63**, o3187–o3189.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf-Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Filiz, G., Price, K. A., Caragounis, A., Du, T., Crouch, P. J. & White, A. R. (2008). *Eur. Biophys. J.* **37**, 315–321.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Lemoine, P., Viossat, B., Brion, J. D. & Bekaert, A. (2007). *Acta Cryst.* E**63**, m2844–m2845.
Matzke, G. R., Frye, R. F., Early, J. J., Straka, R. J. & Carson, S. W. (2000). *Pharmacotherapy*, **20**, 182–190.
Melov, S., Schneider, J. A., Day, B. J., Hinerfeld, D., Coskun, P., Mirra, S. S., Crapo, J. D. & Wallace, D. (1998). *Nat. Genet.* **18**, 159–163.
Panneerselvam, K., Jayanthi, N., Rudiño-Piñera, E. & Soriano-García, M. (1996). *Acta Cryst.* C**52**, 1257–1258.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tougu, V., Karafin, A. & Palumaa, P. (2008). *J. Neurochem.* **104**, 1249–1259.

supporting information

Acta Cryst. (2008). E**64**, m891–m892 [doi:10.1107/S1600536808016838]

Dibromidobis(4-hydroxy-1,5-dimethyl-2-phenyl-3-pyrazolone)zinc(II)

Pascale Lemoine, Bernard Viossat, Jean Daniel Brion and Alain Bekaert

S1. Comment

Metals like Zn are expected to be involved in neurodegenerative diseases such as Alzheimer or Parkinson leading to neurofibrillary tangles degeneration and tau protein accumulation (Filiz *et al.*,2008; Tougu *et al.*,2008). These amyloi¨d plaques in the cortical brain are the sign of cerebral aging and associated with a neuronic a high level of metals. Much work (Melov *et al.*, 1998) is now devoted to theses diseases since no real drug is available up to date. As researchers postulate that soft chelating drugs could interfere with free metal accumulation and neuronal collapsus, our idea was that phenazone (antipyrine), a well known antipyretic brain available drug, could become a soft chelating molecule upon hydroxylation in the 4-hydroxy derivative. For this reason and our knowledge in metal amide complexes, (Bekaert *et al.*, 2007; Lemoine *et al.*, 2007) we have prepared a new cristalline complex including Zn and 4-hydroxy-1,5-dimethyl-2-phenyl-3-pyrazolone (4-hydroxyantipyrine) which is of considerable interest as a antipyrine primary metabolite and which is the object of many biological studies the latter years, by example in the evaluation of the influence of diabete mellitus on antipyrine metabolism (Matzke *et al.*, 2000). The hydroxyamide structure which is close to lactamide let us to test it as a metal pinch. Following our work concerning lactamide and zinc(II) complex (Bekaert *et al.*, 2003), we now report a new zinc complex with 4-hydroxyantipyrine.

The title compound contains one monomeric tetrahedral zinc complex, $[Zn(C_{22}H_{24}N_4O_4)Br_2]$. The Zn atom is surrounded by two monodentate 4-hydroxyantipyrine ligands *via* the carbonyl O atom O4 (or O24) in the sp^2 lone-pair direction and two Br ligands (Fig. 1). The complex exhibits a distorted tetrahedral geometry around the zincII atom. The degree of deviation from an ideal tetrahedron is appreciable with the angles around Zn atom ranging from 99.4 (1) to 113.2 (1) °. The Zn—O and Zn—Br distances in the coordination polyhedron are 1.961 (3)/2.015 (3) Å and 2.351 (1)/2.379 (1)Å, respectively, in good agreement with those found in similar Zn^{II}tetrahedral coordination (Bekaert *et al.*, 2003). The difference between the two Zn—O (or the two Zn—Br) bond lengths can be explained by the presence of the O5—H5···O24 (or O25—H25···Br1) intramolecular hydrogen bond (Table 1) which causes the stretching of the Zn—O24 (or Zn—Br1) bond. Each hydroxyantipyrine ligand consists of a pyrazole P1 (Cl/N2—N3/C4—C5) [or P3 (C2l/N22—N23/C24—C25)] and a phenyl ring P2 (C8—C13) [or P4 (C28—C33)] which are planar with maximum deviation of 0.017 (3) Å for N2 (first ligand) and 0.021 (3) Å for N23 (second ligand). The dihedral angles are 65.2 (2)° between P1 and P2 and 81.6 (2)° for P3 and P4, these values are significantly different from those reported in 4-hydroxyantipyrine [42.5 (1)°] (Panneerselvam *et al.*,1996).

The crystal packing is governed by weak C—H···O and Zn—Br···*Cg1*(centroid of the P1 plane) interactions (Tables1 and 2).

S2. Experimental

The title compound, dibromido-bis[4-hydroxyantipyrine]zinc(II), was prepared by mixing 1.02 g (5 mmole) of 4-hydroxyantipyrine dissolved in hot acetic acid (10 ml, 353 K) and 10 ml of a solution of ZnBr2 (0.496 g, 2 mmole) in

boiling acetic acid. Upon slow cooling, crystal suitable for X-ray diffraction were recovered.

S3. Refinement

All H atoms were positioned geometrically and treated as riding on their parent atoms with distances C—H = 0.96 Å (CH_3) and U_{iso}(H) = 1.5 times U_{eq}(C) or 0.93 Å (aromatic) with U_{iso}(H) = 1.2 times U_{eq}(C) and O—H= 0.82Å with U_{iso}(H) = 1.5 times U_{eq}(O).

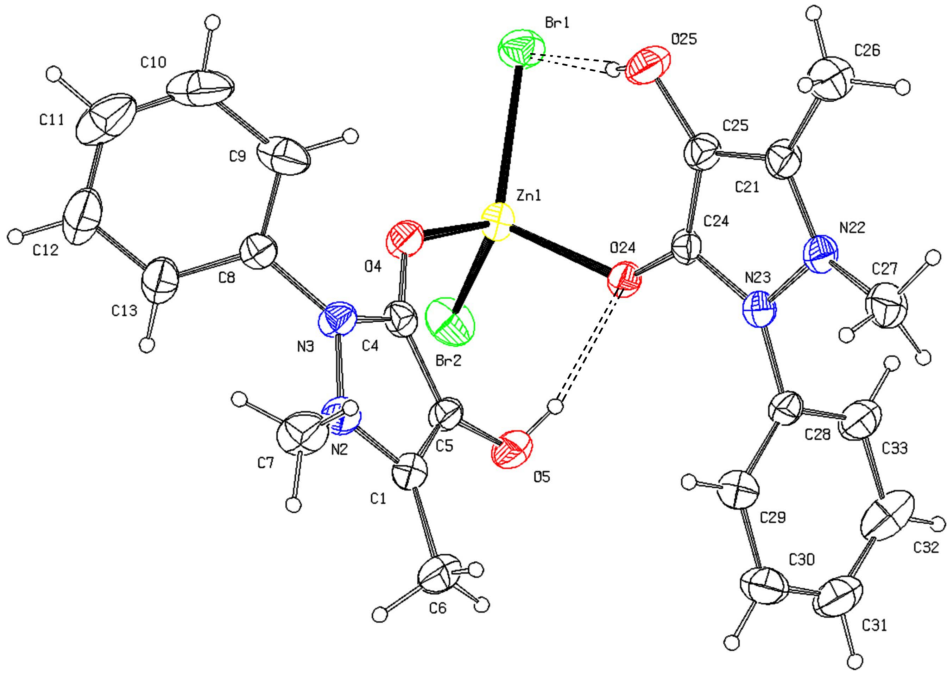


Figure 1

Molecular view of the complex with the atom-labelling scheme. Ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. H atoms are represented as small spheres of arbitrary radii.

Dibromidobis(4-hydroxy-1,5-dimethyl-2-phenyl-3-pyrazolone)zinc(II)

Crystal data

$[ZnBr_2(C_{11}H_{12}N_2O_2)_2]$
M_r = 633.64
Tetragonal, $P4_1$
Hall symbol: P4w
a = 9.824 (3) Å
c = 26.120 (3) Å
V = 2521 (1) Å^3
Z = 4
F(000) = 1264

D_x = 1.670 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 2.2–7.0°
μ = 4.18 mm^{-1}
T = 293 K
Parallelepiped, colourless
0.18 × 0.16 × 0.15 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega - 2\theta$ scans
15417 measured reflections

7354 independent reflections
3152 reflections with $I > 2\sigma(I)$
R_{int} = 0.091
θ_{max} = 30.1°, θ_{min} = 2.2°
h = −13→13
k = 0→13

$l = -36 \rightarrow 36$
3 standard reflections every 60 min
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.093$
$S = 0.90$
7354 reflections
304 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.023$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Absolute structure: Flack (1983), 3602 Friedel pairs
Absolute structure parameter: −0.015 (9)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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	0.74076 (5)	0.20414 (5)	0.423054 (19)	0.05571 (13)
Br1	0.88194 (6)	0.16046 (6)	0.35092 (2)	0.07972 (17)
Br2	0.57242 (7)	0.36720 (6)	0.40493 (2)	0.0908 (2)
C1	0.6782 (5)	0.2246 (5)	0.6042 (2)	0.0645 (13)
N2	0.8063 (4)	0.2622 (5)	0.61659 (16)	0.0699 (11)
N3	0.8827 (4)	0.2682 (4)	0.57175 (14)	0.0579 (9)
O4	0.8439 (3)	0.2507 (3)	0.48491 (13)	0.0627 (8)
C4	0.7980 (5)	0.2417 (4)	0.53136 (18)	0.0531 (11)
O5	0.5526 (3)	0.1862 (4)	0.52624 (16)	0.0774 (10)
H5	0.5683	0.1309	0.5035	0.116*
C5	0.6701 (4)	0.2140 (4)	0.5522 (2)	0.0574 (12)
C6	0.5746 (6)	0.1951 (7)	0.6436 (2)	0.097 (2)
H6A	0.5993	0.1139	0.6618	0.146*
H6B	0.4877	0.1824	0.6275	0.146*
H6C	0.5694	0.2700	0.6672	0.146*
C7	0.8723 (6)	0.2520 (7)	0.6664 (2)	0.0960 (18)
H7A	0.8082	0.2746	0.6928	0.144*
H7B	0.9477	0.3140	0.6677	0.144*
H7C	0.9045	0.1607	0.6714	0.144*
C8	1.0114 (4)	0.3326 (5)	0.57024 (18)	0.0565 (11)
C9	1.1196 (6)	0.2603 (7)	0.5512 (2)	0.094 (2)

H9	1.1110	0.1706	0.5403	0.113*
C10	1.2471 (7)	0.3318 (13)	0.5490 (3)	0.135 (4)
H10	1.3244	0.2882	0.5367	0.162*
C11	1.2545 (10)	0.4602 (14)	0.5647 (3)	0.140 (4)
H11	1.3380	0.5045	0.5626	0.168*
C12	1.1441 (9)	0.5314 (8)	0.5840 (3)	0.111 (3)
H12	1.1530	0.6205	0.5956	0.133*
C13	1.0223 (6)	0.4661 (6)	0.5853 (2)	0.0779 (15)
H13	0.9453	0.5123	0.5966	0.093*
C21	0.8032 (5)	−0.2887 (4)	0.4583 (2)	0.0630 (12)
N22	0.6796 (4)	−0.3069 (4)	0.47977 (18)	0.0638 (11)
N23	0.6143 (4)	−0.1837 (4)	0.47984 (16)	0.0595 (10)
O24	0.6506 (3)	0.0316 (3)	0.44738 (13)	0.0597 (8)
C24	0.6943 (4)	−0.0888 (4)	0.45531 (17)	0.0487 (10)
O25	0.9281 (3)	−0.1073 (3)	0.41933 (19)	0.0825 (10)
H25	0.9098	−0.0349	0.4053	0.124*
C25	0.8144 (4)	−0.1576 (5)	0.4424 (2)	0.0602 (12)
C26	0.9040 (6)	−0.4025 (5)	0.4535 (3)	0.099 (2)
H26A	0.9660	−0.3830	0.4260	0.148*
H26B	0.8568	−0.4859	0.4465	0.148*
H26C	0.9539	−0.4112	0.4849	0.148*
C27	0.6348 (7)	−0.4141 (5)	0.5139 (3)	0.0872 (18)
H27A	0.6787	−0.4979	0.5047	0.131*
H27B	0.5380	−0.4247	0.5111	0.131*
H27C	0.6581	−0.3907	0.5485	0.131*
C28	0.4741 (5)	−0.1712 (4)	0.49287 (19)	0.0572 (12)
C29	0.4387 (6)	−0.1184 (6)	0.5390 (3)	0.0860 (18)
H29	0.5048	−0.0915	0.5624	0.103*
C30	0.3006 (9)	−0.1055 (7)	0.5503 (3)	0.110 (3)
H30	0.2737	−0.0673	0.5813	0.132*
C31	0.2057 (7)	−0.1483 (7)	0.5167 (4)	0.107 (3)
H31	0.1142	−0.1402	0.5253	0.128*
C32	0.2391 (6)	−0.2030 (8)	0.4702 (3)	0.108 (2)
H32	0.1727	−0.2318	0.4472	0.129*
C33	0.3770 (6)	−0.2138 (6)	0.4589 (3)	0.0827 (16)
H33	0.4037	−0.2506	0.4277	0.099*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0566 (3)	0.0519 (3)	0.0587 (3)	−0.0067 (2)	−0.0048 (2)	0.0016 (2)
Br1	0.0845 (4)	0.0840 (4)	0.0706 (4)	0.0026 (3)	0.0170 (3)	0.0095 (3)
Br2	0.0966 (4)	0.0866 (4)	0.0893 (5)	0.0281 (3)	−0.0168 (3)	−0.0011 (3)
C1	0.064 (3)	0.062 (3)	0.068 (4)	−0.011 (2)	0.008 (3)	−0.009 (2)
N2	0.077 (3)	0.077 (3)	0.056 (3)	−0.012 (2)	0.012 (2)	−0.005 (2)
N3	0.053 (2)	0.073 (2)	0.048 (3)	−0.0083 (17)	0.0001 (18)	0.0005 (18)
O4	0.0571 (18)	0.073 (2)	0.058 (2)	−0.0122 (15)	0.0017 (15)	−0.0002 (16)
C4	0.063 (3)	0.043 (2)	0.053 (3)	0.0022 (19)	0.001 (2)	0.000 (2)

O5	0.0492 (19)	0.093 (3)	0.090 (3)	−0.0133 (17)	0.0043 (18)	−0.013 (2)
C5	0.041 (3)	0.051 (3)	0.080 (4)	−0.0038 (19)	0.008 (2)	−0.001 (2)
C6	0.088 (4)	0.109 (4)	0.095 (5)	−0.034 (3)	0.034 (4)	−0.013 (4)
C7	0.101 (4)	0.138 (5)	0.049 (4)	−0.019 (4)	0.007 (3)	0.002 (3)
C8	0.055 (3)	0.062 (3)	0.052 (3)	−0.002 (2)	−0.001 (2)	0.001 (2)
C9	0.067 (4)	0.136 (6)	0.078 (4)	0.027 (4)	−0.004 (3)	−0.034 (4)
C10	0.058 (4)	0.255 (11)	0.092 (6)	0.006 (5)	0.010 (3)	−0.048 (7)
C11	0.113 (7)	0.249 (12)	0.057 (5)	−0.082 (8)	0.006 (4)	0.001 (6)
C12	0.142 (7)	0.107 (5)	0.084 (5)	−0.064 (5)	0.000 (5)	0.000 (4)
C13	0.091 (4)	0.072 (3)	0.071 (4)	−0.023 (3)	−0.002 (3)	0.001 (3)
C21	0.055 (3)	0.050 (3)	0.084 (4)	0.003 (2)	−0.003 (3)	0.003 (2)
N22	0.064 (3)	0.041 (2)	0.086 (3)	0.0001 (18)	0.010 (2)	0.0034 (19)
N23	0.062 (2)	0.044 (2)	0.072 (3)	−0.0030 (17)	0.0102 (19)	−0.0017 (18)
O24	0.0507 (16)	0.0470 (16)	0.081 (2)	−0.0025 (13)	0.0073 (15)	−0.0007 (15)
C24	0.048 (2)	0.044 (2)	0.053 (3)	−0.0052 (19)	−0.0045 (19)	−0.0060 (19)
O25	0.0525 (17)	0.073 (2)	0.122 (3)	0.0007 (15)	0.021 (2)	0.020 (2)
C25	0.052 (3)	0.059 (3)	0.069 (3)	−0.001 (2)	−0.001 (2)	0.001 (2)
C26	0.086 (4)	0.059 (3)	0.150 (7)	0.019 (3)	0.024 (4)	0.020 (4)
C27	0.110 (5)	0.055 (3)	0.097 (5)	0.001 (3)	0.017 (4)	0.009 (3)
C28	0.058 (3)	0.048 (2)	0.066 (3)	−0.006 (2)	0.014 (2)	0.005 (2)
C29	0.086 (4)	0.083 (4)	0.089 (5)	−0.010 (3)	0.024 (3)	−0.017 (3)
C30	0.119 (6)	0.075 (4)	0.136 (7)	0.006 (4)	0.066 (5)	−0.007 (4)
C31	0.068 (4)	0.083 (4)	0.170 (9)	0.002 (3)	0.037 (5)	0.023 (5)
C32	0.069 (4)	0.129 (6)	0.125 (7)	−0.021 (4)	−0.006 (4)	0.044 (5)
C33	0.068 (3)	0.093 (4)	0.088 (5)	−0.017 (3)	0.011 (3)	0.002 (3)

Geometric parameters (Å, º)

Zn1—O4	1.961 (3)	C12—H12	0.9300
Zn1—O24	2.015 (3)	C13—H13	0.9300
Zn1—Br2	2.3505 (10)	C21—N22	1.349 (6)
Zn1—Br1	2.3786 (8)	C21—C25	1.357 (7)
C1—N2	1.350 (6)	C21—C26	1.498 (7)
C1—C5	1.365 (7)	N22—N23	1.370 (5)
C1—C6	1.477 (7)	N22—C27	1.448 (7)
N2—N3	1.392 (5)	N23—C24	1.378 (5)
N2—C7	1.457 (7)	N23—C28	1.424 (6)
N3—C4	1.369 (6)	O24—C24	1.275 (5)
N3—C8	1.415 (6)	C24—C25	1.400 (6)
O4—C4	1.297 (5)	O25—C25	1.363 (6)
C4—C5	1.396 (7)	O25—H25	0.8200
O5—C5	1.366 (6)	C26—H26A	0.9600
O5—H5	0.8200	C26—H26B	0.9600
C6—H6A	0.9600	C26—H26C	0.9600
C6—H6B	0.9600	C27—H27A	0.9600
C6—H6C	0.9600	C27—H27B	0.9600
C7—H7A	0.9600	C27—H27C	0.9600
C7—H7B	0.9600	C28—C29	1.356 (7)

C7—H7C	0.9600	C28—C33	1.368 (8)
C8—C9	1.372 (7)	C29—C30	1.395 (9)
C8—C13	1.373 (7)	C29—H29	0.9300
C9—C10	1.437 (11)	C30—C31	1.349 (12)
C9—H9	0.9300	C30—H30	0.9300
C10—C11	1.328 (14)	C31—C32	1.368 (11)
C10—H10	0.9300	C31—H31	0.9300
C11—C12	1.386 (13)	C32—C33	1.390 (9)
C11—H11	0.9300	C32—H32	0.9300
C12—C13	1.358 (9)	C33—H33	0.9300

O4—Zn1—O24	99.41 (13)	C12—C13—C8	120.9 (6)
O4—Zn1—Br2	111.74 (10)	C12—C13—H13	119.6
O24—Zn1—Br2	109.12 (8)	C8—C13—H13	119.6
O4—Zn1—Br1	113.16 (10)	N22—C21—C25	109.0 (4)
O24—Zn1—Br1	110.75 (9)	N22—C21—C26	122.0 (4)
Br2—Zn1—Br1	111.94 (3)	C25—C21—C26	129.0 (5)
N2—C1—C5	108.3 (4)	C21—N22—N23	107.8 (3)
N2—C1—C6	121.9 (5)	C21—N22—C27	128.8 (4)
C5—C1—C6	129.7 (5)	N23—N22—C27	119.9 (4)
C1—N2—N3	108.2 (4)	N22—N23—C24	109.2 (3)
C1—N2—C7	127.6 (4)	N22—N23—C28	122.0 (4)
N3—N2—C7	120.9 (4)	C24—N23—C28	127.2 (4)
C4—N3—N2	108.2 (4)	C24—O24—Zn1	133.1 (3)
C4—N3—C8	127.4 (4)	O24—C24—N23	120.7 (4)
N2—N3—C8	121.6 (4)	O24—C24—C25	133.8 (4)
C4—O4—Zn1	125.1 (3)	N23—C24—C25	105.4 (4)
O4—C4—N3	119.8 (4)	C25—O25—H25	109.5
O4—C4—C5	133.7 (4)	C21—C25—O25	123.1 (4)
N3—C4—C5	106.5 (4)	C21—C25—C24	108.5 (4)
C5—O5—H5	109.5	O25—C25—C24	128.4 (4)
C1—C5—O5	123.9 (4)	C21—C26—H26A	109.5
C1—C5—C4	108.7 (4)	C21—C26—H26B	109.5
O5—C5—C4	127.3 (5)	H26A—C26—H26B	109.5
C1—C6—H6A	109.5	C21—C26—H26C	109.5
C1—C6—H6B	109.5	H26A—C26—H26C	109.5
H6A—C6—H6B	109.5	H26B—C26—H26C	109.5
C1—C6—H6C	109.5	N22—C27—H27A	109.5
H6A—C6—H6C	109.5	N22—C27—H27B	109.5
H6B—C6—H6C	109.5	H27A—C27—H27B	109.5
N2—C7—H7A	109.5	N22—C27—H27C	109.5
N2—C7—H7B	109.5	H27A—C27—H27C	109.5
H7A—C7—H7B	109.5	H27B—C27—H27C	109.5
N2—C7—H7C	109.5	C29—C28—C33	120.9 (5)
H7A—C7—H7C	109.5	C29—C28—N23	119.6 (5)
H7B—C7—H7C	109.5	C33—C28—N23	119.5 (4)
C9—C8—C13	122.5 (5)	C28—C29—C30	118.2 (7)
C9—C8—N3	118.1 (5)	C28—C29—H29	120.9

C13—C8—N3	119.2 (4)	C30—C29—H29	120.9
C8—C9—C10	115.8 (7)	C31—C30—C29	120.4 (7)
C8—C9—H9	122.1	C31—C30—H30	119.8
C10—C9—H9	122.1	C29—C30—H30	119.8
C11—C10—C9	120.0 (7)	C30—C31—C32	122.4 (6)
C11—C10—H10	120.0	C30—C31—H31	118.8
C9—C10—H10	120.0	C32—C31—H31	118.8
C10—C11—C12	123.3 (7)	C31—C32—C33	116.9 (7)
C10—C11—H11	118.4	C31—C32—H32	121.6
C12—C11—H11	118.4	C33—C32—H32	121.6
C13—C12—C11	117.4 (7)	C28—C33—C32	121.2 (7)
C13—C12—H12	121.3	C28—C33—H33	119.4
C11—C12—H12	121.3	C32—C33—H33	119.4

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O24	0.82	1.94	2.734 (5)	164
O25—H25···Br1	0.82	2.40	3.212 (4)	169
C10—H10···O5^{i}	0.93	2.47	3.378 (8)	165
C27—H27*C*···Br2^{ii}	0.96	2.81	3.686 (7)	151

Symmetry codes: (i) $x+1, y, z$; (ii) $-y+1, x-1, z+1/4$.