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Aquabis(*o*-phenylenediamine-κ^2N,N')-(*o*-phenylenediamine-κN)zinc(II) bis(*p*-toluenesulfonate) trihydrate

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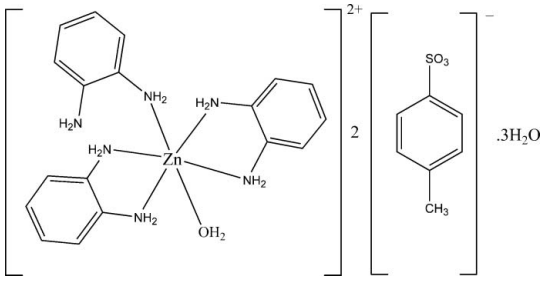
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.009 Å; R factor = 0.056; wR factor = 0.158; data-to-parameter ratio = 13.9.

In the title compound, $[Zn(C_6H_8N_2)_3(H_2O)](C_7H_7SO_3)_2\cdot 3H_2O$, the Zn atom has a slightly tetragonally distorted octahedral geometry, with four shorter equatorial Zn—N and Zn—O bonds [2.153 (4)–2.189 (3) Å] and two longer axial Zn—N bonds [2.239 (4) and 2.243 (4) Å]. The crystal packing is stabilized by weak intermolecular N—H···O hydrogen bonds.

Related literature

For related literature, see: Gunderman *et al.* (1997); Milliken *et al.* (2003); Ovalle-Marroquín *et al.* (2002); Warren (1977).



Experimental

Crystal data

$[Zn(C_6H_8N_2)_3(H_2O)](C_7H_7SO_3)_2\cdot 3H_2O$
M_r = 804.24
Triclinic, $P\overline{1}$
a = 7.498 (3) Å
b = 14.017 (5) Å
c = 19.455 (7) Å
α = 107.846 (4)°
β = 94.850 (5)°
γ = 104.759 (4)°
V = 1852.5 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.84 mm^{-1}
T = 298 (2) K
0.23 × 0.20 × 0.13 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.831, T_{max} = 0.899
9725 measured reflections
6412 independent reflections
3908 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.158
S = 1.01
6412 reflections
460 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^{i}	0.90	2.26	3.049 (6)	147
N1—H1B···O9^{ii}	0.90	2.14	3.037 (7)	174
N2—H2A···O1^{iii}	0.90	2.07	2.957 (6)	169
N2—H2B···O2^{i}	0.90	2.08	2.971 (6)	168
N3—H3A···O5^{iv}	0.90	2.23	3.114 (6)	168
N3—H3B···O4^{v}	0.90	2.26	3.128 (6)	162
N4—H4A···O6^{v}	0.90	2.20	3.015 (6)	149
N4—H4B···O10^{i}	0.90	2.08	2.966 (6)	170
N5—H5A···O1^{iii}	0.90	2.27	3.147 (6)	166
N5—H5A···S1^{iii}	0.90	2.87	3.718 (5)	158
N5—H5B···O6^{iv}	0.90	2.24	3.136 (6)	173
N6—H6A···O1^{iii}	0.86	2.20	3.052 (6)	172
N6—H6B···O10^{vi}	0.86	2.42	3.168 (6)	146
O7—H33···O3^{iii}	0.85	2.03	2.842 (6)	161
O7—H34···O5^{iv}	0.85	2.57	3.401 (6)	166
O9—H38···O4^{iii}	0.85	2.12	2.680 (7)	123
O10—H40···N6^{i}	0.85	2.15	2.960 (7)	159

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Version 1.64.05; Farrugia, 1999); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2049).

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supplementary materials

Acta Cryst. (2007). E**63**, m2930 [**doi:10.1107/S1600536807052075**]

Aquabis(*o*-phenylenediamine-κ^2N,N')(*o*-phenylenediamine-κN)zinc(II) bis(*p*-toluenesulfonate) trihydrate

B. Qian, W.-X. Ma, L.-D. Lu, X.-J. Yang and X. Wang

Comment

Transition-metal complexes of the *o*-$C_6H_4(NH_2)_2$(*o*-phenylenediamine) ligand are of particular interest due to their oxidation-reduction propensities (Warren,1977; Milliken *et al.*,2003). The zinc complex of this ligand system has been synthesized using dibenzoylmethane, *o*-phenylenediamine and zinc(II) acetate (Ovalle-Marroquín, *et al.*,2002). Arenesulfonate anions are widely used industrially as surfactants and dyes (Gunderman *et al.*,1997). Sulfonate anions can compete with water molecules by introducing other organic ligands as auxiliiaries to the metal centers. In order to explore the structural changes in the zinc complex of the *o*-phenylenediamine ligand with *p*-toluenesulfonate, the X-ray analysis of the title compound, $[Zn(C_6H_8N_2)_3(H_2O)](C_7H_7SO_3)_2{\cdot}3H_2O$(I), was undertaken.

Fig.1 shows the molecular structure of the title compound. The Zn(II) center is coordinated octahedrally by five N-atoms and one O-atom. It is interesting to note that there are two types of *o*-phenylenediamine ligand present, one is coordinated as bidentate and another as monodentate. This is probably due to the steric interactions within the rigid ligands. The bond length of Zn(1)—N(1),Zn(1)—N(2),Zn(1)—N(3),Zn(1)—N(4), Zn(1)—N(5),Zn(1)—O(7) are 2.239 (4) Å, 2.153 (4) Å, 2.168 (4) Å, 2.162 (4) Å, 2.243 (4) Å, 2.189 (3) Å, respectively. N(1) and N(5) occupied the axial positions.

As shown in Fig.2, all of the SO_3^- O-atoms, water molecules and the amino H-atoms are involved in hydrogen bonds with each other, resulting extended structures. The crystalline water molecules fill in the gaps formed by the two *p*-toluenesulfonate molecules and two complex cations, anchored by forming hydrogen bonds with the SO_3^- O-atoms.

Experimental

To a stirred solution of *p*-toluenesulfonic acid ($C_7H_8O_3S{\cdot}H_2O$, 0.380 g, 2.0 mmol) in water (10 ml), ZnO (0.081 g, 1.0 mmol) was added with heating in 50 °C, until all of the solid dissolved. To this solution was added *o*-phenylenediamine (0.618 g, 6.0 mmol) in methanol (20 ml) with heating and stirring for another 3 h. Colorless crystals of (I) suitable for X-ray diffraction were obtained after 7 days.

Refinement

All H atoms attached to C,*N* and O atoms were fixed geometrically and treated as riding with C—H=0.96Å (methyl),0.93Å (aromatic C—H), 0.90Å (NH_2),and 0.85Å (OH) with U_{iso}(H)=1.2U_{eq} (NH_2,aromatic C—H) and U_{iso}(H)=1.5U_{eq} (OH,CH_3).

Figures

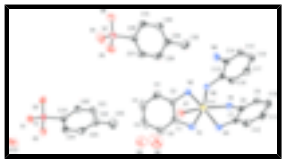


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

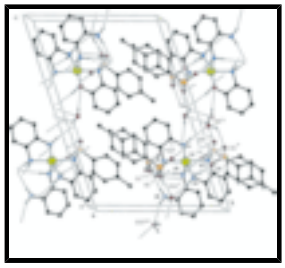


Fig. 2. A perspective view of the crystal packing of (I). The hydrogen-bond contacts are shown as dashed lines. Hydrogen atoms have been ommited for clarity.

Aquabis(*o*-phenylenediamine-κ^2*N*,*N*')(*o*- phenylenediamine-κ*N*)zinc(II) bis(*p*-toluenesulfonate) trihydrate

Crystal data

$[Zn(C_6H_8N_2)_3(H_2O)](C_7H_7SO_3)_2\cdot 3H_2O$	$Z = 2$
$M_r = 804.24$	$F_{000} = 844$
Triclinic, $P\bar{1}$	$D_x = 1.442$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.498$ (3) Å	Cell parameters from 2226 reflections
$b = 14.017$ (5) Å	$\theta = 2.2$–22.2º
$c = 19.455$ (7) Å	$\mu = 0.84$ mm^{-1}
$\alpha = 107.846$ (4)º	$T = 298$ (2) K
$\beta = 94.850$ (5)º	Prism, colorless
$\gamma = 104.759$ (4)º	0.23 × 0.20 × 0.13 mm
$V = 1852.5$ (12) Å^3	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	6412 independent reflections
Radiation source: fine-focus sealed tube	3908 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.032$
$T = 298(2)$ K	$\theta_{max} = 25.0$º
φ and ω scans	$\theta_{min} = 1.6$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -8\rightarrow7$
$T_{min} = 0.831$, $T_{max} = 0.899$	$k = -13\rightarrow16$
9725 measured reflections	$l = -23\rightarrow23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.056$	H-atom parameters constrained
$wR(F^2) = 0.158$	$w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 1.0494P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
6412 reflections	$\Delta\rho_{max} = 0.95$ e Å^{-3}
460 parameters	$\Delta\rho_{min} = -0.65$ 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}
Zn1	1.03676 (8)	0.79056 (4)	0.26307 (3)	0.0404 (2)
N1	1.2511 (6)	0.8017 (3)	0.3550 (2)	0.0464 (11)
H1A	1.3531	0.7877	0.3382	0.056*
H1B	1.2862	0.8662	0.3892	0.056*
N2	0.9884 (5)	0.6316 (3)	0.26146 (19)	0.0386 (9)
H2A	0.8696	0.5934	0.2401	0.046*
H2B	1.0663	0.6018	0.2359	0.046*
N3	1.1269 (5)	0.9559 (3)	0.2764 (2)	0.0418 (10)
H3A	1.0410	0.9870	0.2939	0.050*
H3B	1.2368	0.9885	0.3077	0.050*
N4	1.2232 (6)	0.7982 (3)	0.1847 (2)	0.0439 (10)
H4A	1.3432	0.8161	0.2068	0.053*
H4B	1.1962	0.7358	0.1486	0.053*
N5	0.7684 (5)	0.7547 (3)	0.18667 (19)	0.0372 (9)
H5A	0.6971	0.6935	0.1883	0.045*
H5B	0.7147	0.8033	0.2097	0.045*
N6	0.7667 (6)	0.5687 (3)	0.0708 (2)	0.0549 (12)
H6A	0.7127	0.5524	0.1046	0.082*

H6B	0.7363	0.5121	0.0332	0.082*
O1	0.4148 (5)	0.4665 (3)	0.80089 (18)	0.0515 (9)
O2	0.7405 (5)	0.4752 (3)	0.80434 (19)	0.0569 (10)
O3	0.5072 (5)	0.3368 (3)	0.70899 (19)	0.0566 (10)
O4	0.5412 (6)	0.0776 (3)	0.3546 (2)	0.0774 (13)
O5	0.8561 (6)	0.0645 (3)	0.3599 (2)	0.0788 (13)
O6	0.6087 (5)	−0.0614 (3)	0.26375 (19)	0.0641 (11)
O7	0.8509 (5)	0.8151 (3)	0.34339 (17)	0.0519 (9)
H33	0.7414	0.7744	0.3384	0.078*
H34	0.8315	0.8728	0.3448	0.078*
O8	0.9193 (11)	0.9066 (6)	0.5003 (4)	0.182 (3)
H35	1.0054	0.9523	0.5343	0.273*
H36	0.9694	0.8824	0.4637	0.273*
O9	0.6182 (9)	0.9741 (4)	0.5385 (3)	0.140 (2)
H37	0.6603	0.9468	0.5004	0.210*
H38	0.5302	0.9256	0.5429	0.210*
O10	0.8297 (6)	0.4120 (3)	0.9249 (2)	0.0756 (12)
H39	0.7974	0.4234	0.8860	0.113*
H40	0.9488	0.4338	0.9336	0.113*
S1	0.55943 (17)	0.44501 (10)	0.75802 (7)	0.0422 (3)
S2	0.6815 (2)	0.04591 (12)	0.31382 (7)	0.0536 (4)
C1	1.1581 (7)	0.7238 (4)	0.3850 (3)	0.0420 (12)
C2	1.0222 (6)	0.6357 (4)	0.3364 (2)	0.0373 (11)
C3	0.9242 (7)	0.5613 (4)	0.3613 (3)	0.0517 (14)
H3	0.8349	0.5018	0.3287	0.062*
C4	0.9569 (9)	0.5735 (6)	0.4346 (4)	0.0694 (18)
H4	0.8888	0.5223	0.4513	0.083*
C5	1.0880 (10)	0.6599 (6)	0.4829 (3)	0.0714 (19)
H5	1.1089	0.6674	0.5323	0.086*
C6	1.1897 (9)	0.7362 (5)	0.4587 (3)	0.0595 (15)
H6	1.2788	0.7954	0.4917	0.071*
C7	1.1473 (6)	0.9602 (4)	0.2036 (3)	0.0410 (12)
C8	1.1933 (6)	0.8772 (4)	0.1559 (3)	0.0401 (12)
C9	1.2048 (7)	0.8722 (4)	0.0853 (3)	0.0521 (14)
H9	1.2355	0.8166	0.0535	0.063*
C10	1.1708 (8)	0.9500 (5)	0.0614 (3)	0.0664 (17)
H10	1.1768	0.9464	0.0131	0.080*
C11	1.1282 (8)	1.0324 (5)	0.1087 (4)	0.0663 (17)
H11	1.1077	1.0853	0.0926	0.080*
C12	1.1153 (7)	1.0382 (4)	0.1799 (3)	0.0541 (14)
H12	1.0854	1.0943	0.2117	0.065*
C13	0.7324 (6)	0.7456 (4)	0.1103 (2)	0.0359 (11)
C14	0.7316 (7)	0.6549 (4)	0.0545 (3)	0.0423 (12)
C15	0.7034 (8)	0.6532 (4)	−0.0173 (3)	0.0546 (14)
H15	0.7030	0.5936	−0.0553	0.066*
C16	0.6761 (8)	0.7372 (5)	−0.0332 (3)	0.0634 (16)
H16	0.6581	0.7342	−0.0818	0.076*
C17	0.6749 (8)	0.8256 (4)	0.0211 (3)	0.0585 (15)
H17	0.6557	0.8825	0.0100	0.070*

C18	0.7023 (7)	0.8292 (4)	0.0929 (3)	0.0441 (12)
H18	0.7006	0.8891	0.1302	0.053*
C19	0.5793 (6)	0.5248 (4)	0.7027 (3)	0.0391 (12)
C20	0.6237 (7)	0.4905 (4)	0.6339 (3)	0.0451 (13)
H20	0.6394	0.4242	0.6158	0.054*
C21	0.6448 (8)	0.5545 (4)	0.5918 (3)	0.0534 (14)
H21	0.6749	0.5304	0.5455	0.064*
C22	0.6224 (7)	0.6542 (4)	0.6169 (3)	0.0510 (14)
C23	0.5767 (7)	0.6860 (4)	0.6857 (3)	0.0551 (14)
H23	0.5591	0.7519	0.7036	0.066*
C24	0.5563 (7)	0.6237 (4)	0.7289 (3)	0.0495 (14)
H24	0.5273	0.6479	0.7754	0.059*
C25	0.6477 (9)	0.7232 (5)	0.5713 (3)	0.0736 (18)
H25A	0.5289	0.7132	0.5430	0.110*
H25B	0.7329	0.7056	0.5388	0.110*
H25C	0.6976	0.7951	0.6026	0.110*
C26	0.7308 (7)	0.1268 (4)	0.2598 (3)	0.0463 (13)
C27	0.8698 (8)	0.2216 (5)	0.2859 (3)	0.0607 (16)
H27	0.9392	0.2435	0.3328	0.073*
C28	0.9073 (8)	0.2843 (5)	0.2432 (4)	0.0667 (18)
H28	1.0026	0.3476	0.2619	0.080*
C29	0.8069 (8)	0.2556 (4)	0.1736 (3)	0.0566 (15)
C30	0.6659 (8)	0.1609 (4)	0.1480 (3)	0.0570 (15)
H30	0.5946	0.1399	0.1015	0.068*
C31	0.6290 (7)	0.0970 (4)	0.1903 (3)	0.0532 (14)
H31	0.5346	0.0334	0.1716	0.064*
C32	0.8473 (10)	0.3246 (5)	0.1275 (4)	0.086 (2)
H32A	0.7322	0.3200	0.0993	0.129*
H32B	0.9293	0.3018	0.0950	0.129*
H32C	0.9063	0.3959	0.1588	0.129*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0418 (4)	0.0408 (4)	0.0418 (4)	0.0152 (3)	0.0085 (3)	0.0159 (3)
N1	0.040 (2)	0.043 (2)	0.051 (3)	0.012 (2)	−0.002 (2)	0.011 (2)
N2	0.036 (2)	0.045 (2)	0.034 (2)	0.0144 (19)	0.0024 (18)	0.0113 (18)
N3	0.037 (2)	0.037 (2)	0.046 (2)	0.0110 (18)	0.0051 (19)	0.0058 (19)
N4	0.041 (2)	0.041 (2)	0.049 (2)	0.016 (2)	0.011 (2)	0.0106 (19)
N5	0.039 (2)	0.039 (2)	0.037 (2)	0.0146 (18)	0.0078 (18)	0.0143 (18)
N6	0.079 (3)	0.045 (3)	0.046 (3)	0.028 (2)	0.016 (2)	0.015 (2)
O1	0.042 (2)	0.066 (2)	0.050 (2)	0.0176 (18)	0.0210 (17)	0.0211 (18)
O2	0.037 (2)	0.083 (3)	0.058 (2)	0.0204 (19)	0.0078 (18)	0.033 (2)
O3	0.065 (3)	0.043 (2)	0.063 (2)	0.0142 (18)	0.023 (2)	0.0183 (18)
O4	0.074 (3)	0.108 (3)	0.071 (3)	0.052 (3)	0.038 (2)	0.033 (2)
O5	0.057 (3)	0.114 (4)	0.062 (3)	0.034 (2)	−0.006 (2)	0.022 (2)
O6	0.073 (3)	0.062 (3)	0.056 (2)	0.026 (2)	0.004 (2)	0.015 (2)
O7	0.047 (2)	0.064 (2)	0.052 (2)	0.0278 (18)	0.0117 (18)	0.0197 (18)

O8	0.189 (6)	0.212 (6)	0.144 (5)	0.077 (5)	0.034 (5)	0.044 (5)
O9	0.163 (6)	0.109 (4)	0.124 (5)	0.014 (4)	0.026 (4)	0.030 (4)
O10	0.098 (3)	0.075 (3)	0.058 (2)	0.039 (3)	0.012 (2)	0.018 (2)
S1	0.0348 (7)	0.0499 (8)	0.0445 (7)	0.0127 (6)	0.0114 (6)	0.0180 (6)
S2	0.0449 (9)	0.0709 (10)	0.0451 (8)	0.0280 (7)	0.0071 (7)	0.0111 (7)
C1	0.048 (3)	0.050 (3)	0.040 (3)	0.028 (3)	0.011 (2)	0.020 (2)
C2	0.034 (3)	0.044 (3)	0.040 (3)	0.018 (2)	0.007 (2)	0.019 (2)
C3	0.047 (3)	0.056 (3)	0.064 (4)	0.020 (3)	0.014 (3)	0.033 (3)
C4	0.073 (5)	0.094 (5)	0.073 (4)	0.043 (4)	0.033 (4)	0.053 (4)
C5	0.099 (5)	0.098 (5)	0.044 (3)	0.055 (5)	0.027 (4)	0.038 (4)
C6	0.074 (4)	0.063 (4)	0.046 (3)	0.034 (3)	0.007 (3)	0.014 (3)
C7	0.032 (3)	0.042 (3)	0.050 (3)	0.008 (2)	0.007 (2)	0.018 (2)
C8	0.031 (3)	0.040 (3)	0.044 (3)	0.004 (2)	0.002 (2)	0.013 (2)
C9	0.047 (3)	0.056 (3)	0.044 (3)	0.004 (3)	0.008 (3)	0.014 (3)
C10	0.059 (4)	0.085 (5)	0.056 (4)	0.006 (4)	0.007 (3)	0.039 (4)
C11	0.055 (4)	0.072 (4)	0.087 (5)	0.010 (3)	0.004 (3)	0.056 (4)
C12	0.046 (3)	0.046 (3)	0.073 (4)	0.014 (3)	0.009 (3)	0.024 (3)
C13	0.028 (3)	0.041 (3)	0.038 (3)	0.007 (2)	0.005 (2)	0.016 (2)
C14	0.042 (3)	0.042 (3)	0.040 (3)	0.011 (2)	0.002 (2)	0.012 (2)
C15	0.067 (4)	0.057 (4)	0.035 (3)	0.019 (3)	0.007 (3)	0.009 (3)
C16	0.078 (4)	0.077 (4)	0.041 (3)	0.022 (4)	0.007 (3)	0.028 (3)
C17	0.068 (4)	0.059 (4)	0.054 (3)	0.017 (3)	0.004 (3)	0.030 (3)
C18	0.042 (3)	0.045 (3)	0.042 (3)	0.012 (2)	0.003 (2)	0.013 (2)
C19	0.025 (3)	0.046 (3)	0.045 (3)	0.010 (2)	0.008 (2)	0.013 (2)
C20	0.048 (3)	0.050 (3)	0.043 (3)	0.026 (3)	0.014 (2)	0.014 (2)
C21	0.066 (4)	0.068 (4)	0.045 (3)	0.037 (3)	0.021 (3)	0.027 (3)
C22	0.039 (3)	0.056 (3)	0.065 (4)	0.019 (3)	0.006 (3)	0.027 (3)
C23	0.053 (4)	0.043 (3)	0.069 (4)	0.018 (3)	0.009 (3)	0.016 (3)
C24	0.049 (3)	0.046 (3)	0.049 (3)	0.018 (3)	0.015 (3)	0.006 (3)
C25	0.086 (5)	0.080 (4)	0.083 (4)	0.040 (4)	0.019 (4)	0.053 (4)
C26	0.032 (3)	0.053 (3)	0.046 (3)	0.017 (3)	0.003 (2)	0.003 (2)
C27	0.040 (3)	0.062 (4)	0.057 (4)	0.012 (3)	−0.004 (3)	−0.006 (3)
C28	0.040 (3)	0.051 (4)	0.087 (5)	0.004 (3)	0.012 (3)	0.000 (3)
C29	0.042 (3)	0.048 (3)	0.070 (4)	0.008 (3)	0.013 (3)	0.011 (3)
C30	0.052 (4)	0.058 (4)	0.053 (3)	0.010 (3)	0.000 (3)	0.014 (3)
C31	0.037 (3)	0.052 (3)	0.056 (3)	0.007 (3)	−0.001 (3)	0.006 (3)
C32	0.081 (5)	0.067 (4)	0.100 (5)	0.002 (4)	0.019 (4)	0.029 (4)

Geometric parameters (Å, °)

Zn1—N2	2.154 (4)	C6—H6	0.9300
Zn1—N4	2.162 (4)	C7—C12	1.374 (7)
Zn1—N3	2.168 (4)	C7—C8	1.389 (6)
Zn1—O7	2.188 (3)	C8—C9	1.365 (7)
Zn1—N1	2.241 (4)	C9—C10	1.380 (8)
Zn1—N5	2.243 (4)	C9—H9	0.9300
N1—C1	1.446 (6)	C10—C11	1.367 (8)
N1—H1A	0.9000	C10—H10	0.9300
N1—H1B	0.9000	C11—C12	1.376 (8)

N2—C2	1.440 (6)	C11—H11	0.9300
N2—H2A	0.9000	C12—H12	0.9300
N2—H2B	0.9000	C13—C18	1.381 (6)
N3—C7	1.456 (6)	C13—C14	1.394 (6)
N3—H3A	0.9000	C14—C15	1.385 (7)
N3—H3B	0.9000	C15—C16	1.364 (8)
N4—C8	1.440 (6)	C15—H15	0.9300
N4—H4A	0.9000	C16—C17	1.363 (7)
N4—H4B	0.9000	C16—H16	0.9300
N5—C13	1.447 (5)	C17—C18	1.376 (7)
N5—H5A	0.9000	C17—H17	0.9300
N5—H5B	0.9000	C18—H18	0.9300
N6—C14	1.419 (6)	C19—C20	1.376 (6)
N6—H6A	0.8600	C19—C24	1.384 (6)
N6—H6B	0.8599	C20—C21	1.378 (7)
O1—S1	1.459 (3)	C20—H20	0.9300
O2—S1	1.450 (4)	C21—C22	1.391 (7)
O3—S1	1.453 (3)	C21—H21	0.9300
O4—S2	1.448 (4)	C22—C23	1.378 (7)
O5—S2	1.440 (4)	C22—C25	1.489 (7)
O6—S2	1.450 (4)	C23—C24	1.377 (7)
O7—H33	0.8500	C23—H23	0.9300
O7—H34	0.8500	C24—H24	0.9300
O8—H36	0.8500	C25—H25A	0.9600
O8—H35	0.8500	C25—H25B	0.9600
O8—H36	0.8500	C25—H25C	0.9600
O9—H37	0.8500	C26—C27	1.379 (7)
O9—H38	0.8500	C26—C31	1.380 (7)
O10—H39	0.8498	C27—C28	1.379 (8)
O10—H40	0.8501	C27—H27	0.9300
S1—C19	1.764 (5)	C28—C29	1.380 (8)
S2—C26	1.763 (6)	C28—H28	0.9300
C1—C6	1.384 (7)	C29—C30	1.384 (7)
C1—C2	1.391 (6)	C29—C32	1.503 (8)
C2—C3	1.357 (6)	C30—C31	1.385 (7)
C3—C4	1.376 (8)	C30—H30	0.9300
C3—H3	0.9300	C31—H31	0.9300
C4—C5	1.362 (9)	C32—H32A	0.9600
C4—H4	0.9300	C32—H32B	0.9600
C5—C6	1.378 (8)	C32—H32C	0.9600
C5—H5	0.9300		
N2—Zn1—N4	102.12 (14)	C12—C7—C8	120.1 (5)
N2—Zn1—N3	170.84 (14)	C12—C7—N3	123.5 (5)
N4—Zn1—N3	76.62 (14)	C8—C7—N3	116.4 (4)
N2—Zn1—O7	89.45 (14)	C9—C8—C7	120.1 (5)
N4—Zn1—O7	168.41 (13)	C9—C8—N4	123.2 (5)
N3—Zn1—O7	92.07 (13)	C7—C8—N4	116.7 (4)
N2—Zn1—N1	75.34 (14)	C8—C9—C10	119.8 (5)
N4—Zn1—N1	96.55 (16)	C8—C9—H9	120.1

N3—Zn1—N1	95.71 (15)	C10—C9—H9	120.1
O7—Zn1—N1	86.97 (14)	C11—C10—C9	119.8 (5)
N2—Zn1—N5	94.31 (14)	C11—C10—H10	120.1
N4—Zn1—N5	97.55 (14)	C9—C10—H10	120.1
N3—Zn1—N5	94.84 (14)	C10—C11—C12	121.0 (5)
O7—Zn1—N5	80.68 (13)	C10—C11—H11	119.5
N1—Zn1—N5	164.02 (14)	C12—C11—H11	119.5
C1—N1—Zn1	104.7 (3)	C7—C12—C11	119.1 (5)
C1—N1—H1A	110.8	C7—C12—H12	120.4
Zn1—N1—H1A	110.8	C11—C12—H12	120.4
C1—N1—H1B	110.8	C18—C13—C14	119.7 (4)
Zn1—N1—H1B	110.8	C18—C13—N5	119.1 (4)
H1A—N1—H1B	108.9	C14—C13—N5	121.2 (4)
C2—N2—Zn1	107.4 (3)	C15—C14—C13	118.1 (5)
C2—N2—H2A	110.2	C15—C14—N6	120.9 (5)
Zn1—N2—H2A	110.2	C13—C14—N6	121.0 (4)
C2—N2—H2B	110.2	C16—C15—C14	121.3 (5)
Zn1—N2—H2B	110.2	C16—C15—H15	119.3
H2A—N2—H2B	108.5	C14—C15—H15	119.3
C7—N3—Zn1	105.7 (3)	C17—C16—C15	120.9 (5)
C7—N3—H3A	110.6	C17—C16—H16	119.6
Zn1—N3—H3A	110.6	C15—C16—H16	119.6
C7—N3—H3B	110.6	C16—C17—C18	119.0 (5)
Zn1—N3—H3B	110.6	C16—C17—H17	120.5
H3A—N3—H3B	108.7	C18—C17—H17	120.5
C8—N4—Zn1	105.7 (3)	C17—C18—C13	121.1 (5)
C8—N4—H4A	110.6	C17—C18—H18	119.4
Zn1—N4—H4A	110.6	C13—C18—H18	119.4
C8—N4—H4B	110.6	C20—C19—C24	119.4 (5)
Zn1—N4—H4B	110.6	C20—C19—S1	120.3 (4)
H4A—N4—H4B	108.7	C24—C19—S1	120.3 (4)
C13—N5—Zn1	131.3 (3)	C19—C20—C21	120.0 (5)
C13—N5—H5A	104.4	C19—C20—H20	120.0
Zn1—N5—H5A	104.4	C21—C20—H20	120.0
C13—N5—H5B	104.4	C20—C21—C22	121.8 (5)
Zn1—N5—H5B	104.4	C20—C21—H21	119.1
H5A—N5—H5B	105.6	C22—C21—H21	119.1
C14—N6—H6A	115.8	C23—C22—C21	116.8 (5)
C14—N6—H6B	113.1	C23—C22—C25	121.9 (5)
H6A—N6—H6B	106.2	C21—C22—C25	121.3 (5)
Zn1—O7—H33	124.3	C24—C23—C22	122.4 (5)
Zn1—O7—H34	104.2	C24—C23—H23	118.8
H33—O7—H34	103.4	C22—C23—H23	118.8
H36—O8—H35	108.1	C23—C24—C19	119.6 (5)
H35—O8—H36	108.1	C23—C24—H24	120.2
H37—O9—H38	106.8	C19—C24—H24	120.2
H39—O10—H40	105.2	C22—C25—H25A	109.5
O2—S1—O3	111.8 (2)	C22—C25—H25B	109.5
O2—S1—O1	111.8 (2)	H25A—C25—H25B	109.5

O3—S1—O1	112.2 (2)	C22—C25—H25C	109.5
O2—S1—C19	107.2 (2)	H25A—C25—H25C	109.5
O3—S1—C19	107.1 (2)	H25B—C25—H25C	109.5
O1—S1—C19	106.3 (2)	C27—C26—C31	118.2 (5)
O5—S2—O4	113.2 (2)	C27—C26—S2	121.2 (4)
O5—S2—O6	112.6 (3)	C31—C26—S2	120.5 (4)
O4—S2—O6	111.2 (3)	C28—C27—C26	120.8 (5)
O5—S2—C26	106.2 (3)	C28—C27—H27	119.6
O4—S2—C26	106.1 (2)	C26—C27—H27	119.6
O6—S2—C26	107.0 (2)	C27—C28—C29	121.7 (5)
C6—C1—C2	119.8 (5)	C27—C28—H28	119.2
C6—C1—N1	123.4 (5)	C29—C28—H28	119.2
C2—C1—N1	116.7 (4)	C28—C29—C30	117.3 (6)
C3—C2—C1	120.0 (5)	C28—C29—C32	121.5 (5)
C3—C2—N2	123.4 (5)	C30—C29—C32	121.2 (6)
C1—C2—N2	116.6 (4)	C29—C30—C31	121.3 (5)
C2—C3—C4	120.1 (6)	C29—C30—H30	119.3
C2—C3—H3	119.9	C31—C30—H30	119.3
C4—C3—H3	119.9	C26—C31—C30	120.7 (5)
C5—C4—C3	120.6 (6)	C26—C31—H31	119.6
C5—C4—H4	119.7	C30—C31—H31	119.6
C3—C4—H4	119.7	C29—C32—H32A	109.5
C4—C5—C6	120.2 (6)	C29—C32—H32B	109.5
C4—C5—H5	119.9	H32A—C32—H32B	109.5
C6—C5—H5	119.9	C29—C32—H32C	109.5
C5—C6—C1	119.3 (6)	H32A—C32—H32C	109.5
C5—C6—H6	120.3	H32B—C32—H32C	109.5
C1—C6—H6	120.3		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O3^{i}	0.90	2.26	3.049 (6)	147
N1—H1B···O9^{ii}	0.90	2.14	3.037 (7)	174
N2—H2A···O1^{iii}	0.90	2.07	2.957 (6)	169
N2—H2B···O2^{i}	0.90	2.08	2.971 (6)	168
N3—H3A···O5^{iv}	0.90	2.23	3.114 (6)	168
N3—H3B···O4^{v}	0.90	2.26	3.128 (6)	162
N4—H4A···O6^{v}	0.90	2.20	3.015 (6)	149
N4—H4B···O10^{i}	0.90	2.08	2.966 (6)	170
N5—H5A···O1^{iii}	0.90	2.27	3.147 (6)	166
N5—H5A···S1^{iii}	0.90	2.87	3.718 (5)	158
N5—H5B···O6^{iv}	0.90	2.24	3.136 (6)	173
N6—H6A···O1^{iii}	0.86	2.20	3.052 (6)	172
N6—H6B···O10^{vi}	0.86	2.42	3.168 (6)	146
O7—H33···O3^{iii}	0.85	2.03	2.842 (6)	161

O7—H34···O5^{iv}	0.85	2.57	3.401 (6)	166
O8—H36···O7	0.85	2.24	2.868 (6)	130
O9—H37···O8	0.85	2.16	2.736 (11)	125
O9—H38···O4^{iii}	0.85	2.12	2.680 (7)	123
O10—H39···O2	0.85	2.00	2.836 (6)	170
O10—H40···N6^{i}	0.85	2.15	2.960 (7)	159

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

Fig. 1

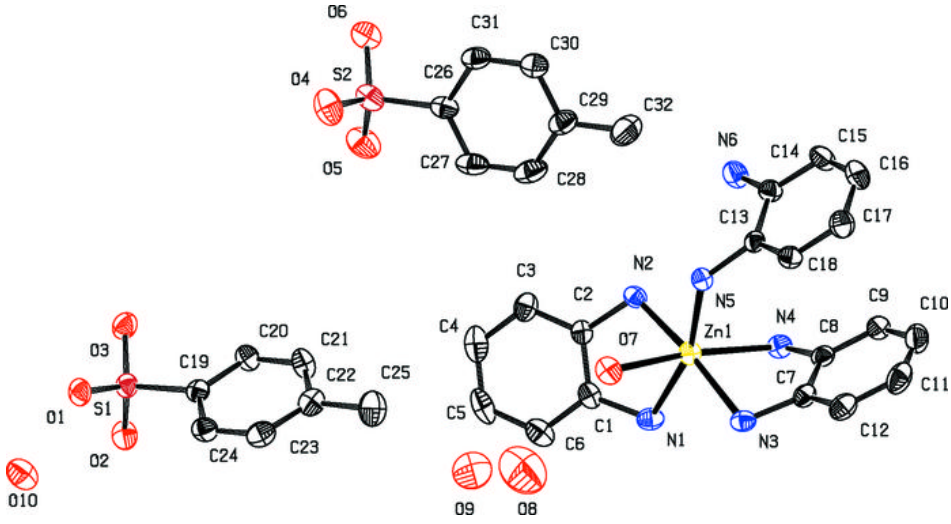
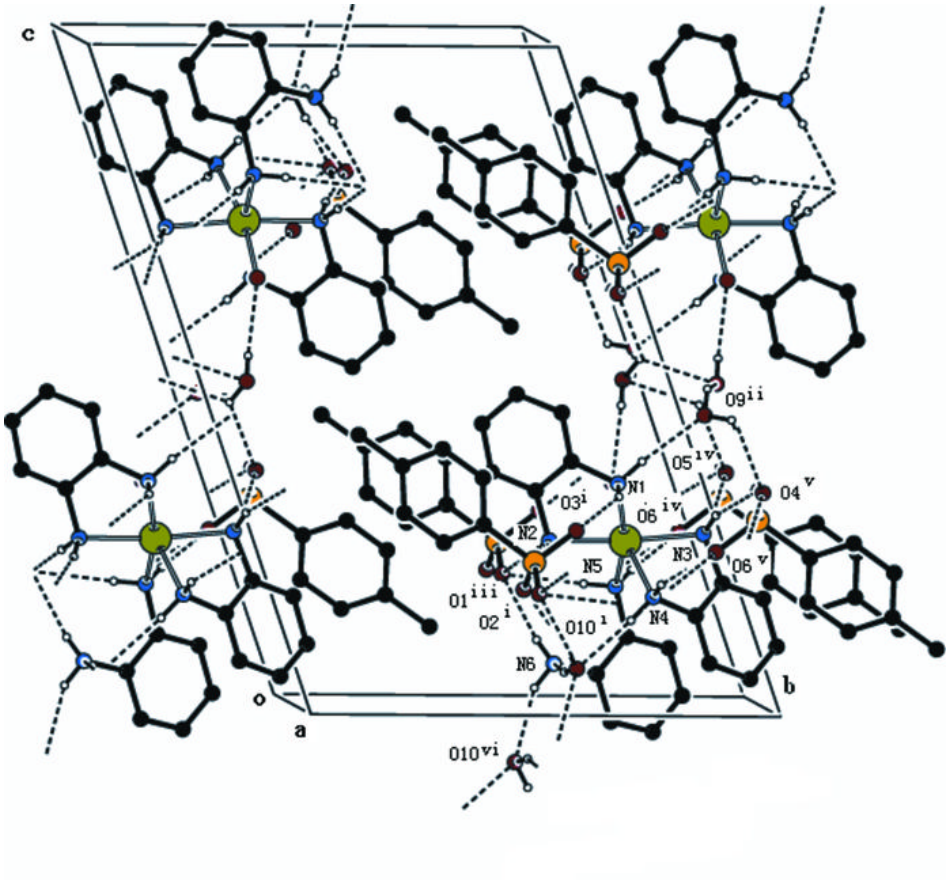

O6
C31
C30
O4
S2
C26
C29
C32
O5
C27
C28
N6
C14
C15
C16
C13
C17
C18
C3
N2
C2
N5
C9
C10
C4
Zn1
N4
C8
O3
C20
C21
C19
O7
C7
C11
C22
C25
O1
S1
C5
C1
N1
N3
C12
O2
C24
C23
C6
O10
O9
O8

Fig. 2


c
o
a
b
O9ii
O5iv
O4v
O3i
N1
O6iv
N2
N3
O6v
N5
O1iii
O2i
O10i
N4
N6
O10vi