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Dibromido-2κ^2*Br*-bis(4-methylpyridine-1κ*N*){μ-2,2′-[propane-1,3-diylbis(nitrilomethylidyne)]diphenolato-1κ^4*O*,*N*,*N*′,*O*′:2κ^2*O*,*O*′}nickel(II)zinc(II)

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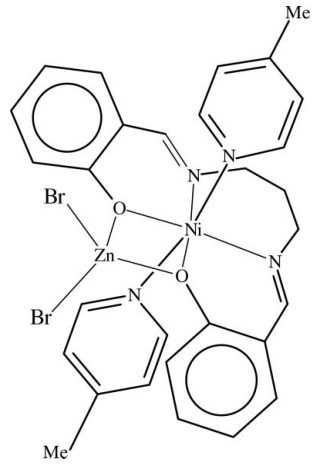
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.029 Å; R factor = 0.066; wR factor = 0.206; data-to-parameter ratio = 9.6.

The molecule of the title compound, [NiZnBr$_2$(C$_{17}$H$_{16}$N$_2$O$_2$)(C$_6$H$_7$N)$_2$], contains a heterodinuclear arrangement. The two metal ions are bridged *via* phenol O atoms of the propane-1,3-diylbis(nitrilomethylidyne)]diphenolate (salpd^{2-}) ligand. The two bridging O atoms of salpd^{2-} and two Br atoms constitute a distorted tetrahedral coordination environment around the Zn^{II} ion, while the Ni^{II} ion has a distorted octahedral coordination environment formed by two O and two N atoms of salpd^{2-} in the equatorial plane and two N atoms of two 4-methylpyridine ligands in the axial positions. In the crystal structure, weak intermolecular C—H···Br hydrogen bonds link the molecules into chains along the *c* axis. Weak intramolecular C—H···O and C—H···N hydrogen bonds are also present.

Related literature

For general background, see: Bertini *et al.* (1994). For related structures, see: Tatar *et al.* (2002); Tatar (2002); Tatar Yıldırım *et al.* (2007); Svoboda *et al.* (2001); Arıcı *et al.* (2001). For ring conformation puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

[NiZnBr$_2$(C$_{17}$H$_{16}$N$_2$O$_2$)(C$_6$H$_7$N)$_2$]
M_r = 750.45
Monoclinic, *Cc*
a = 19.357 (3) Å
b = 9.2130 (7) Å
c = 18.3269 (15) Å
β = 114.382 (10)°
V = 2976.9 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.16 mm^{-1}
T = 294 (2) K
0.20 × 0.15 × 0.15 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.478, T_{max} = 0.536
3381 measured reflections
3379 independent reflections
2118 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.206
S = 1.04
3379 reflections
353 parameters
H-atom parameters not refined
$\Delta\rho_{max}$ = 1.30 e Å^{-3}
$\Delta\rho_{min}$ = −1.42 e Å^{-3}
Absolute structure: Flack (1983), with 95 Friedel pairs
Flack parameter: 0.25 (7)

Table 1
Selected geometric parameters (Å, °).

Zn—Br1	2.400 (10)	Ni—O2	2.000 (10)
Zn—Br2	2.372 (3)	Ni—N1	2.054 (14)
Zn—O1	1.992 (9)	Ni—N2	2.063 (12)
Zn—O2	1.979 (10)	Ni—N3	2.180 (12)
Ni—O1	2.060 (10)	Ni—N4	2.243 (13)
O2—Zn—O1	81.7 (4)	O1—Ni—N2	170.1 (5)
O2—Zn—Br2	115.7 (3)	O2—Ni—N3	89.1 (5)
O1—Zn—Br2	120.2 (3)	N1—Ni—N3	92.1 (5)
O2—Zn—Br1	114.2 (4)	O1—Ni—N3	90.6 (4)
O1—Zn—Br1	123.3 (4)	N2—Ni—N3	90.0 (5)
Br2—Zn—Br1	101.6 (3)	O2—Ni—N4	89.8 (5)
O2—Ni—N1	169.1 (5)	N1—Ni—N4	88.9 (5)
O2—Ni—O1	79.5 (4)	O1—Ni—N4	88.5 (4)
N1—Ni—O1	89.6 (4)	N2—Ni—N4	90.8 (5)
O2—Ni—N2	90.6 (5)	N3—Ni—N4	178.7 (5)
N1—Ni—N2	100.3 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···Br2^{i}	0.93	2.93	3.78 (2)	153
C23—H23A···Br1^{ii}	0.96	2.91	3.79 (3)	153
C24—H24···O1	0.93	2.54	3.09 (4)	118
C28—H28···N2	0.93	2.60	3.18 (4)	121

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

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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2335).

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supplementary materials

Acta Cryst. (2007). E**63**, m2676-m2677 [**doi:10.1107/S1600536807048581**]

Dibromido-2κ^2*Br*-bis(4-methylpyridine-1κ*N*){μ-2,2'-[propane-1,3-diylbis(nitrilomethylidyne)]diphenolato-1κ^4*O*,*N*,*N*',*O*':2κ^2*O*,*O*'}nickel(II)zinc(II)

L. Tatar Yildirim and O. Atakol

Comment

Zinc and nickel elements are important essential rare elements for living beings (Bertini *et al.*, 1994), in this respect the zinc and nickel compounds are very important in medicine. Some dinuclear zinc-nickel metal compounds of Schiff-base ligands have been studied in our laboratory (Tatar Yıldırım *et al.*, 2007; Tatar, 2002; Tatar *et al.*, 2002; Arıcı *et al.*, 2001). We report herein the structure of the title compound, (I), a new hetero-dinuclear $[ZnBr_2Ni(salpd^{2-})(C_6H_7N)_2]$ complex [where $salpd^{2-}$ is *N*,*N*'-bis- (salicylidene)-1,3-propanediamine].

In the molecule of the title compound, (I), (Fig. 1) the bond lengths and angles (Table 1) are generally in good agreement with the corresponding values in similar oxygen-bridged dinuclear complexes reported, previously (Tatar *et al.*, 2007; Tatar, 2002; Tatar, Atakol *et al.*, 2002; Svoboda *et al.*, 2001; Arıcı *et al.*, 2001). The two bridging O atoms of salpd2- ligand and two Br atoms constitute a distorted tetrahedral coordination environment around the Zn^{II} ion, while the Ni^{II} ion has a distorted octahedral coordination environment formed by two O and two N atoms of $salpd^{2-}$ ligand in the equatorial plane and two N atoms of two methylpyridine ligands in the axial positions (Table 1). The Ni atom is −0.017 (2) Å away from the equatorial plane. The Zn···Ni distance is 3.062 (3) Å. The dihedral angle between (O1/Zn/O2) and (Br1/Zn/Br2) planes is 88.1 (3)°.

Rings B (Ni/O1/N1/C1/C6/C7), C (Ni/N1/N2/C8—C10) and D (Ni/O2/N2/C11/C12/C17) are not planar, having total puckering amplitudes, Q_T, of 0.190 (2), 1.143 (3) and 0.248 (2) Å, respectively [φ = 128.66 (5)°, θ = 92.56 (4)°; φ = 102.38 (6)°, θ = 85.87 (5)° and φ = 15.97 (6)°, θ = 43.44 (5)°, respectively] (Cremer & Pople, 1975). Rings B and D have flattened boat conformations, while ring A adopts a twisted conformation. Rings A (C1—C6), E (C12—C17), F (N3/C18—C22) and G (N4/C24—C28) are, of course, planar and the dihedral angles between them are A/E = 6.02 (3)° and F/G = 22.77 (2)°.

In the crystal structure, weak intermolecular C—H···Br hydrogen bonds (Table 2) link the molecules into chains along the *c* axis (Fig. 2); weak intramolecular C—H···O and C—H···N hydrogen bonds are also present.

Experimental

For the preparation of the title compound, (I), *N*,*N*'-bis(salicylidene)-1,3 -propanediamine (1.410 g, 5 mmol) was dissolved in hot EtOH (50 ml), and then added to a solution of $NiCl_2·6H_2O$ (1.185 g, 5 mmol) in hot water (30 ml) and ammonia (10 ml, 20%). The mixture was kept on the bench for 1–2 h. The pink precipitate was filtered and dried in an oven at 423 K. This complex (0.338 g, 1 mmol) was dissolved in hot dioxane (50 ml) and 4-methylpyridine (0.5 ml), and then added to a solution of $ZnBr_2$ (0.226 g, 1 mmol) in hot MeOH (20 ml). The resulting mixture was set aside for 2 d and the precipitated crystals were filtered and dried on air.

Refinement

The highest peak in the final difference electron-density map is located 1.81 Å from the Br1 atom. H atoms were positioned geometrically, with C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C), where x = 1.5 for methyl H, and x = 1.2 for all other H atoms.

Figures

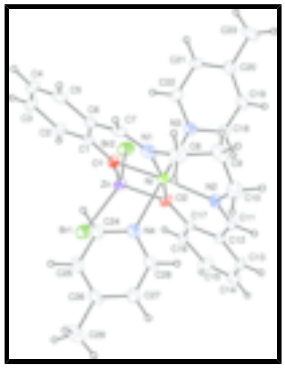

Fig. 1. The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

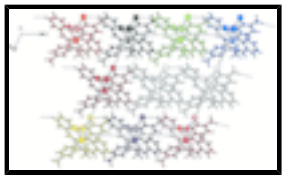

Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

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Crystal data

$[NiZnBr_2(C_{17}H_{16}N_2O_2)(C_6H_7N)_2]$	F_{000} = 1504
M_r = 750.45	D_x = 1.674 Mg m^{-3}
Monoclinic, *Cc*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: C -2yc	Cell parameters from 15 reflections
a = 19.357 (3) Å	θ = 10.2–11.6º
b = 9.2130 (7) Å	μ = 4.16 mm^{-1}
c = 18.3269 (15) Å	*T* = 294 (2) K
β = 114.382 (10)º	Prism, pink
V = 2976.9 (6) Å^3	0.20 × 0.15 × 0.15 mm
Z = 4	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	θ_{max} = 27.1º

non–profiled ω scans	θ_{min} = 2.3°
Absorption correction: ψ scan (North *et al.*, 1968)	h = −24→0
T_{min} = 0.478, T_{max} = 0.536	k = −11→0
3381 measured reflections	l = −21→23
3379 independent reflections	3 standard reflections
2118 reflections with $I > 2\sigma(I)$	every 120 min
R_{int} = 0.050	intensity decay: 2%

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)]$ = 0.066	$w = 1/[\sigma^2(F_o^2) + (0.1221P)^2 + 7.1119P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.206	$(\Delta/\sigma)_{max} < 0.001$
S = 1.04	$\Delta\rho_{max}$ = 1.30 e Å^{-3}
3379 reflections	$\Delta\rho_{min}$ = −1.42 e Å^{-3}
353 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 95 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.25 (7)

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}
Br1	0.9306 (8)	0.0500 (10)	0.8991 (6)	0.0763 (6)
Br2	0.82738 (13)	0.2500 (2)	0.99821 (11)	0.0761 (6)
Zn	0.94119 (8)	0.26209 (17)	0.97905 (8)	0.0440 (4)
Ni	1.05439 (11)	0.51344 (17)	1.01890 (11)	0.0402 (4)
O1	1.0376 (5)	0.3234 (10)	1.0686 (5)	0.041 (2)
O2	0.9577 (6)	0.4444 (11)	0.9314 (5)	0.045 (2)
N1	1.1532 (7)	0.5472 (14)	1.1188 (8)	0.052 (3)
N2	1.0548 (8)	0.6930 (12)	0.9518 (8)	0.051 (3)
N3	0.9881 (7)	0.6331 (12)	1.0703 (7)	0.044 (3)

N4	1.1205 (7)	0.3862 (13)	0.9650 (8)	0.050 (3)
C1	1.0756 (9)	0.2743 (14)	1.1395 (9)	0.045 (4)
C2	1.0492 (11)	0.1485 (18)	1.1622 (9)	0.059 (4)
H2	1.0062	0.1023	1.1255	0.07*
C3	1.0881 (12)	0.089 (2)	1.2422 (11)	0.076 (5)
H3	1.0708	0.0052	1.2575	0.091*
C4	1.1524 (12)	0.162 (2)	1.2954 (9)	0.068 (5)
H4	1.1773	0.1271	1.3475	0.081*
C5	1.1783 (10)	0.278 (2)	1.2733 (10)	0.064 (5)
H5	1.223	0.3193	1.3099	0.077*
C6	1.1416 (8)	0.3440 (16)	1.1959 (8)	0.046 (3)
C7	1.1783 (9)	0.4710 (17)	1.1806 (9)	0.049 (4)
H7	1.2248	0.4979	1.2206	0.059*
C8	1.1958 (9)	0.678 (2)	1.1167 (11)	0.071 (5)
H8A	1.2263	0.6562	1.0875	0.085*
H8B	1.2302	0.7026	1.1712	0.085*
C9	1.1480 (11)	0.8090 (19)	1.0793 (13)	0.075 (6)
H9A	1.1794	0.8951	1.0971	0.09*
H9B	1.1083	0.8161	1.0984	0.09*
C10	1.1114 (12)	0.807 (2)	0.9876 (13)	0.076 (5)
H10A	1.0875	0.9005	0.9687	0.091*
H10B	1.1511	0.7957	0.9687	0.091*
C11	1.0092 (11)	0.7073 (16)	0.8786 (10)	0.054 (4)
H11	1.0164	0.7906	0.8539	0.065*
C12	0.9484 (8)	0.6153 (16)	0.8280 (8)	0.043 (3)
C13	0.9113 (11)	0.6499 (18)	0.7485 (11)	0.061 (4)
H13	0.928	0.7312	0.7304	0.073*
C14	0.8516 (10)	0.574 (2)	0.6936 (11)	0.065 (4)
H14	0.8291	0.6001	0.6397	0.078*
C15	0.8280 (9)	0.461 (2)	0.7228 (9)	0.064 (5)
H15	0.7861	0.4092	0.688	0.077*
C16	0.8633 (9)	0.4150 (17)	0.8041 (9)	0.053 (4)
H16	0.8454	0.3349	0.822	0.063*
C17	0.9239 (9)	0.4915 (16)	0.8546 (8)	0.043 (4)
C18	0.9394 (9)	0.7358 (16)	1.0269 (10)	0.053 (4)
H18	0.9305	0.7469	0.9733	0.064*
C19	0.9030 (10)	0.8235 (18)	1.0583 (11)	0.060 (4)
H19	0.8689	0.8915	1.0254	0.073*
C20	0.9143 (11)	0.8160 (17)	1.1361 (12)	0.065 (5)
C21	0.9650 (11)	0.7132 (18)	1.1828 (10)	0.058 (4)
H21	0.9758	0.7046	1.237	0.07*
C22	1.0002 (9)	0.6211 (19)	1.1465 (9)	0.056 (4)
H22	1.033	0.5494	1.1774	0.067*
C23	0.8732 (15)	0.914 (3)	1.1757 (14)	0.101 (8)
H23A	0.8893	0.8872	1.2309	0.151*
H23B	0.8193	0.9012	1.148	0.151*
H23C	0.8857	1.014	1.1723	0.151*
C24	1.1542 (18)	0.266 (2)	0.9967 (17)	0.096 (8)
H24	1.1477	0.2289	1.0406	0.116*

C25	1.2003 (19)	0.189 (2)	0.9673 (16)	0.117 (11)
H25A	1.2247	0.105	0.9933	0.14*
C26	1.2093 (11)	0.2337 (17)	0.9045 (12)	0.064 (5)
C27	1.174 (2)	0.355 (4)	0.8725 (18)	0.165 (18)
H27	1.1786	0.3922	0.8272	0.096 (8)*
C28	1.133 (2)	0.427 (4)	0.904 (2)	0.064 (5)
H28	1.1107	0.5146	0.8802	0.225*
C29	1.2598 (13)	0.156 (2)	0.8728 (15)	0.091 (7)
H29A	1.2554	0.201	0.8238	0.137*
H29B	1.2446	0.0561	0.8628	0.137*
H29C	1.3115	0.1613	0.9116	0.137*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0643 (12)	0.1029 (15)	0.0706 (12)	−0.0122 (10)	0.0342 (9)	0.0016 (10)
Br2	0.0633 (12)	0.1009 (15)	0.0707 (12)	−0.0110 (10)	0.0341 (9)	0.0014 (10)
Zn	0.0447 (9)	0.0470 (10)	0.0406 (8)	−0.0113 (8)	0.0177 (7)	−0.0003 (7)
Ni	0.0399 (8)	0.0403 (10)	0.0443 (8)	−0.0041 (8)	0.0215 (6)	−0.0002 (8)
O1	0.035 (5)	0.043 (5)	0.037 (5)	0.000 (4)	0.008 (4)	0.003 (4)
O2	0.048 (6)	0.054 (6)	0.034 (5)	−0.008 (5)	0.017 (4)	0.008 (4)
N1	0.040 (7)	0.057 (7)	0.071 (9)	−0.018 (6)	0.034 (7)	−0.019 (7)
N2	0.064 (8)	0.032 (6)	0.075 (9)	−0.005 (6)	0.046 (8)	0.007 (6)
N3	0.037 (6)	0.048 (7)	0.058 (7)	−0.004 (5)	0.029 (5)	0.000 (6)
N4	0.043 (6)	0.045 (7)	0.068 (8)	−0.008 (6)	0.030 (6)	−0.005 (6)
C1	0.059 (9)	0.035 (8)	0.052 (9)	0.011 (7)	0.035 (8)	0.001 (6)
C2	0.073 (11)	0.055 (9)	0.045 (8)	0.005 (8)	0.022 (8)	0.005 (7)
C3	0.091 (13)	0.067 (11)	0.071 (11)	0.017 (11)	0.034 (11)	0.033 (10)
C4	0.075 (12)	0.074 (12)	0.033 (8)	0.024 (10)	0.002 (8)	0.010 (8)
C5	0.057 (11)	0.076 (12)	0.057 (10)	0.016 (9)	0.021 (8)	−0.013 (9)
C6	0.034 (7)	0.049 (8)	0.049 (8)	0.012 (6)	0.010 (6)	−0.008 (7)
C7	0.039 (8)	0.062 (9)	0.040 (8)	0.003 (7)	0.009 (6)	−0.014 (7)
C8	0.042 (9)	0.088 (13)	0.075 (11)	−0.024 (9)	0.017 (8)	0.001 (10)
C9	0.062 (11)	0.050 (10)	0.123 (17)	−0.031 (9)	0.049 (11)	−0.028 (10)
C10	0.068 (12)	0.071 (12)	0.091 (14)	−0.019 (10)	0.034 (11)	0.000 (11)
C11	0.079 (11)	0.033 (7)	0.068 (10)	0.006 (7)	0.049 (9)	0.011 (7)
C12	0.043 (8)	0.048 (8)	0.040 (7)	0.011 (7)	0.018 (6)	0.007 (6)
C13	0.074 (11)	0.052 (9)	0.069 (10)	0.033 (9)	0.042 (9)	0.033 (9)
C14	0.063 (11)	0.071 (11)	0.067 (11)	0.021 (9)	0.032 (9)	0.011 (9)
C15	0.045 (8)	0.089 (13)	0.045 (8)	0.011 (9)	0.005 (7)	0.004 (8)
C16	0.057 (9)	0.048 (9)	0.053 (8)	0.020 (7)	0.024 (8)	0.012 (7)
C17	0.044 (8)	0.055 (9)	0.029 (7)	0.026 (7)	0.016 (6)	0.011 (6)
C18	0.042 (8)	0.060 (9)	0.056 (9)	0.007 (7)	0.018 (7)	0.011 (7)
C19	0.060 (10)	0.051 (9)	0.085 (12)	0.020 (8)	0.044 (9)	0.008 (8)
C20	0.082 (13)	0.042 (9)	0.096 (13)	0.001 (9)	0.061 (11)	−0.003 (9)
C21	0.081 (12)	0.060 (10)	0.055 (9)	0.002 (9)	0.049 (9)	0.002 (8)
C22	0.050 (9)	0.069 (11)	0.053 (9)	0.007 (8)	0.026 (7)	0.012 (8)
C23	0.13 (2)	0.084 (15)	0.116 (18)	0.015 (14)	0.083 (17)	−0.027 (13)

C24	0.15 (2)	0.059 (12)	0.13 (2)	0.031 (12)	0.112 (19)	0.030 (11)
C25	0.21 (3)	0.063 (13)	0.14 (2)	0.067 (17)	0.13 (2)	0.033 (13)
C26	0.063 (11)	0.050 (9)	0.096 (13)	0.007 (8)	0.049 (10)	−0.007 (9)
C27	0.152 (2)	0.059 (12)	0.131 (2)	0.030 (12)	0.112 (19)	0.031 (11)
C28	0.065 (11)	0.051 (9)	0.096 (13)	0.007 (8)	0.049 (10)	−0.007 (9)
C29	0.084 (14)	0.079 (13)	0.127 (19)	0.001 (11)	0.060 (14)	−0.030 (13)

Geometric parameters (Å, °)

Zn—Br1	2.400 (10)	C10—H10A	0.97
Zn—Br2	2.372 (3)	C10—H10B	0.97
Zn—O1	1.992 (9)	C11—H11	0.93
Zn—O2	1.979 (10)	C12—C13	1.37 (2)
Ni—O1	2.060 (10)	C12—C11	1.44 (2)
Ni—O2	2.000 (10)	C13—C14	1.37 (3)
Ni—N1	2.054 (14)	C13—H13	0.93
Ni—N2	2.063 (12)	C14—H14	0.93
Ni—N3	2.180 (12)	C15—C14	1.34 (3)
Ni—N4	2.243 (13)	C15—H15	0.93
O1—C1	1.283 (18)	C16—C15	1.42 (2)
O2—C17	1.355 (16)	C16—H16	0.93
N1—C8	1.47 (2)	C17—C16	1.35 (2)
N2—C10	1.46 (2)	C17—C12	1.40 (2)
N2—C11	1.27 (2)	C18—C19	1.35 (2)
N3—C18	1.341 (19)	C18—H18	0.93
N3—C22	1.321 (19)	C19—H19	0.93
N4—C24	1.29 (2)	C20—C19	1.35 (2)
N4—C28	1.29 (3)	C20—C23	1.57 (2)
C1—C2	1.40 (2)	C21—C20	1.38 (3)
C1—C6	1.42 (2)	C21—H21	0.93
C2—H2	0.93	C22—C21	1.41 (2)
C3—C2	1.45 (2)	C22—H22	0.93
C3—H3	0.93	C23—H23A	0.96
C4—C3	1.39 (3)	C23—H23B	0.96
C4—H4	0.93	C23—H23C	0.96
C5—C4	1.32 (3)	C24—C25	1.41 (3)
C5—H5	0.93	C24—H24	0.93
C6—C5	1.44 (2)	C25—H25A	0.93
C7—N1	1.25 (2)	C26—C25	1.30 (3)
C7—C6	1.45 (2)	C26—C27	1.31 (3)
C7—H7	0.93	C26—C29	1.51 (2)
C8—H8A	0.97	C27—C28	1.35 (3)
C8—H8B	0.97	C27—H27	0.93
C9—C8	1.50 (3)	C28—H28	0.93
C9—H9A	0.97	C29—H29A	0.96
C9—H9B	0.97	C29—H29B	0.96
C9—C10	1.53 (3)	C29—H29C	0.96
O2—Zn—O1	81.7 (4)	H9A—C9—H9B	107.6
O2—Zn—Br2	115.7 (3)	N2—C10—C9	114.9 (15)

O1—Zn—Br2	120.2 (3)	N2—C10—H10A	108.5
O2—Zn—Br1	114.2 (4)	C9—C10—H10A	108.5
O1—Zn—Br1	123.3 (4)	N2—C10—H10B	108.5
Br2—Zn—Br1	101.6 (3)	C9—C10—H10B	108.5
O2—Ni—N1	169.1 (5)	H10A—C10—H10B	107.5
O2—Ni—O1	79.5 (4)	N2—C11—C12	130.3 (14)
N1—Ni—O1	89.6 (4)	N2—C11—H11	114.9
O2—Ni—N2	90.6 (5)	C12—C11—H11	114.9
N1—Ni—N2	100.3 (6)	C13—C12—C17	117.2 (15)
O1—Ni—N2	170.1 (5)	C13—C12—C11	118.7 (15)
O2—Ni—N3	89.1 (5)	C17—C12—C11	124.2 (13)
N1—Ni—N3	92.1 (5)	C14—C13—C12	125.3 (16)
O1—Ni—N3	90.6 (4)	C14—C13—H13	117.4
N2—Ni—N3	90.0 (5)	C12—C13—H13	117.4
O2—Ni—N4	89.8 (5)	C15—C14—C13	115.3 (16)
N1—Ni—N4	88.9 (5)	C15—C14—H14	122.4
O1—Ni—N4	88.5 (4)	C13—C14—H14	122.4
N2—Ni—N4	90.8 (5)	C14—C15—C16	123.7 (17)
N3—Ni—N4	178.7 (5)	C14—C15—H15	118.1
C1—O1—Zn	133.3 (10)	C16—C15—H15	118.1
C1—O1—Ni	128.2 (9)	C17—C16—C15	117.8 (16)
Zn—O1—Ni	98.2 (4)	C17—C16—H16	121.1
C17—O2—Zn	129.3 (10)	C15—C16—H16	121.1
C17—O2—Ni	128.4 (10)	C16—C17—O2	117.0 (14)
Zn—O2—Ni	100.6 (4)	C16—C17—C12	120.6 (13)
C7—N1—C8	118.2 (14)	O2—C17—C12	122.4 (14)
C7—N1—Ni	126.4 (11)	N3—C18—C19	122.1 (16)
C8—N1—Ni	115.3 (11)	N3—C18—H18	118.9
C11—N2—C10	117.6 (14)	C19—C18—H18	118.9
C11—N2—Ni	122.7 (11)	C18—C19—C20	122.3 (16)
C10—N2—Ni	119.7 (12)	C18—C19—H19	118.8
C22—N3—C18	117.5 (14)	C20—C19—H19	118.8
C22—N3—Ni	122.4 (10)	C19—C20—C21	117.0 (15)
C18—N3—Ni	119.7 (10)	C19—C20—C23	124.5 (17)
C28—N4—C24	113.8 (17)	C21—C20—C23	118.5 (17)
C28—N4—Ni	124.6 (13)	C20—C21—C22	118.5 (15)
C24—N4—Ni	121.5 (13)	C20—C21—H21	120.7
O1—C1—C2	117.8 (14)	C22—C21—H21	120.7
O1—C1—C6	123.0 (14)	N3—C22—C21	122.5 (15)
C2—C1—C6	119.2 (14)	N3—C22—H22	118.8
C1—C2—C3	120.8 (17)	C21—C22—H22	118.8
C1—C2—H2	119.6	C20—C23—H23A	109.5
C3—C2—H2	119.6	C20—C23—H23B	109.5
C4—C3—C2	117.8 (17)	H23A—C23—H23B	109.5
C4—C3—H3	121.1	C20—C23—H23C	109.5
C2—C3—H3	121.1	H23A—C23—H23C	109.5
C5—C4—C3	121.3 (16)	H23B—C23—H23C	109.5
C5—C4—H4	119.4	N4—C24—C25	123 (2)
C3—C4—H4	119.4	N4—C24—H24	118.7

C4—C5—C6	123.7 (16)	C25—C24—H24	118.7
C4—C5—H5	118.2	C26—C25—C24	121.2 (19)
C6—C5—H5	118.2	C26—C25—H25A	119.4
C1—C6—C5	117.1 (15)	C24—C25—H25A	119.4
C1—C6—C7	125.9 (14)	C25—C26—C27	115.5 (17)
C5—C6—C7	116.8 (14)	C25—C26—C29	122.5 (18)
N1—C7—C6	126.1 (14)	C27—C26—C29	122 (2)
N1—C7—H7	116.9	C26—C27—C28	121 (2)
C6—C7—H7	116.9	C26—C27—H27	119.5
N1—C8—C9	115.1 (14)	C28—C27—H27	119.5
N1—C8—H8A	108.5	N4—C28—C27	126 (2)
C9—C8—H8A	108.5	N4—C28—H28	116.0
N1—C8—H8B	108.5	C27—C28—H28	117.2
C9—C8—H8B	108.5	C26—C29—H29A	109.5
H8A—C8—H8B	107.5	C26—C29—H29B	109.5
C8—C9—C10	114.3 (16)	H29A—C29—H29B	109.5
C8—C9—H9A	108.7	C26—C29—H29C	109.5
C10—C9—H9A	108.7	H29A—C29—H29C	109.5
C8—C9—H9B	108.7	H29B—C29—H29C	109.5
C10—C9—H9B	108.7		
O2—Zn—O1—C1	173.2 (13)	Zn—O1—C1—C2	3(2)
Br2—Zn—O1—C1	58.2 (13)	Ni—O1—C1—C2	174.3 (10)
Br1—Zn—O1—C1	−73.2 (13)	Zn—O1—C1—C6	−175.4 (10)
O2—Zn—O1—Ni	0.1 (5)	Ni—O1—C1—C6	−4(2)
Br2—Zn—O1—Ni	−114.8 (3)	Zn—O2—C17—C16	9.8 (19)
Br1—Zn—O1—Ni	113.7 (4)	Ni—O2—C17—C16	172.0 (10)
O1—Zn—O2—C17	165.8 (12)	Zn—O2—C17—C12	−171.8 (10)
Br2—Zn—O2—C17	−74.7 (12)	Ni—O2—C17—C12	−10 (2)
Br1—Zn—O2—C17	42.9 (13)	C7—N1—C8—C9	−138.9 (17)
O1—Zn—O2—Ni	−0.1 (5)	Ni—N1—C8—C9	39 (2)
Br2—Zn—O2—Ni	119.5 (3)	C11—N2—C10—C9	162.5 (17)
Br1—Zn—O2—Ni	−123.0 (5)	Ni—N2—C10—C9	−20 (2)
O2—Ni—O1—C1	−173.7 (12)	C10—N2—C11—C12	−179.6 (17)
N1—Ni—O1—C1	7.3 (12)	Ni—N2—C11—C12	3(2)
N3—Ni—O1—C1	−84.8 (12)	C22—N3—C18—C19	−1(2)
N4—Ni—O1—C1	96.2 (12)	Ni—N3—C18—C19	−172.9 (13)
O2—Ni—O1—Zn	−0.1 (5)	C18—N3—C22—C21	−1(2)
N1—Ni—O1—Zn	−179.1 (5)	Ni—N3—C22—C21	170.8 (12)
N3—Ni—O1—Zn	88.8 (5)	C28—N4—C24—C25	1(4)
N4—Ni—O1—Zn	−90.2 (5)	Ni—N4—C24—C25	−176 (2)
N1—Ni—O2—C17	−161 (2)	C24—N4—C28—C27	2(6)
O1—Ni—O2—C17	−165.9 (12)	Ni—N4—C28—C27	178 (4)
N2—Ni—O2—C17	13.3 (12)	O1—C1—C2—C3	−178.2 (15)
N3—Ni—O2—C17	103.3 (11)	C6—C1—C2—C3	0(2)
N4—Ni—O2—C17	−77.5 (12)	O1—C1—C6—C5	179.5 (13)
N1—Ni—O2—Zn	5(3)	C2—C1—C6—C5	1(2)
O1—Ni—O2—Zn	0.1 (5)	O1—C1—C6—C7	−5(2)
N2—Ni—O2—Zn	179.4 (5)	C2—C1—C6—C7	176.8 (14)
N3—Ni—O2—Zn	−90.6 (5)	C4—C3—C2—C1	0(3)

N4—Ni—O2—Zn	88.6 (5)	C5—C4—C3—C2	−2(3)
O2—Ni—N1—C7	−10 (4)	C6—C5—C4—C3	4(3)
O1—Ni—N1—C7	−4.2 (13)	C1—C6—C5—C4	−3(2)
N2—Ni—N1—C7	176.7 (13)	C7—C6—C5—C4	−179.2 (16)
N3—Ni—N1—C7	86.3 (13)	N1—C7—C6—C1	8(3)
N4—Ni—N1—C7	−92.7 (13)	N1—C7—C6—C5	−176.2 (15)
O2—Ni—N1—C8	173 (2)	C6—C7—N1—C8	175.4 (15)
O1—Ni—N1—C8	178.4 (12)	C6—C7—N1—Ni	−2(2)
N2—Ni—N1—C8	−0.6 (12)	C10—C9—C8—N1	−78 (2)
N3—Ni—N1—C8	−91.0 (12)	C8—C9—C10—N2	66 (2)
N4—Ni—N1—C8	89.9 (12)	C13—C12—C11—N2	−174.7 (16)
O2—Ni—N2—C11	−9.6 (13)	C17—C12—C11—N2	5(3)
N1—Ni—N2—C11	169.2 (13)	C17—C12—C13—C14	1(2)
N3—Ni—N2—C11	−98.7 (13)	C11—C12—C13—C14	−178.7 (16)
N4—Ni—N2—C11	80.2 (13)	C12—C13—C14—C15	2(3)
O2—Ni—N2—C10	173.0 (14)	C16—C15—C14—C13	−3(3)
N1—Ni—N2—C10	−8.2 (14)	C17—C16—C15—C14	1(2)
N3—Ni—N2—C10	83.9 (14)	C16—C17—C12—C13	−4(2)
N4—Ni—N2—C10	−97.2 (14)	O2—C17—C12—C13	178.2 (13)
O2—Ni—N3—C22	128.7 (12)	C16—C17—C12—C11	176.2 (14)
N1—Ni—N3—C22	−40.5 (12)	O2—C17—C12—C11	−2(2)
O1—Ni—N3—C22	49.1 (12)	O2—C17—C16—C15	−178.8 (14)
N2—Ni—N3—C22	−140.8 (12)	C12—C17—C16—C15	3(2)
O2—Ni—N3—C18	−59.6 (11)	N3—C18—C19—C20	1(3)
N1—Ni—N3—C18	131.3 (11)	C21—C20—C19—C18	0(3)
O1—Ni—N3—C18	−139.1 (11)	C23—C20—C19—C18	−179.5 (19)
N2—Ni—N3—C18	31.0 (12)	C22—C21—C20—C19	−1(3)
O2—Ni—N4—C28	79 (3)	C22—C21—C20—C23	177.8 (18)
N1—Ni—N4—C28	−112 (3)	N3—C22—C21—C20	2(3)
O1—Ni—N4—C28	159 (3)	N4—C24—C25—C26	−2(5)
N2—Ni—N4—C28	−11 (3)	C27—C26—C25—C24	2(5)
O2—Ni—N4—C24	−105.0 (19)	C29—C26—C25—C24	178 (3)
N1—Ni—N4—C24	64 (2)	C25—C26—C27—C28	0(6)
O1—Ni—N4—C24	−25.5 (19)	C29—C26—C27—C28	−176 (4)
N2—Ni—N4—C24	164.4 (19)	C26—C27—C28—N4	−2(8)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···Br2^{i}	0.93	2.93	3.78 (2)	153
C23—H23A···Br1^{ii}	0.96	2.91	3.79 (3)	153
C24—H24···O1	0.93	2.54	3.09 (4)	118
C28—H28···N2	0.93	2.60	3.18 (4)	121

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

Fig. 1

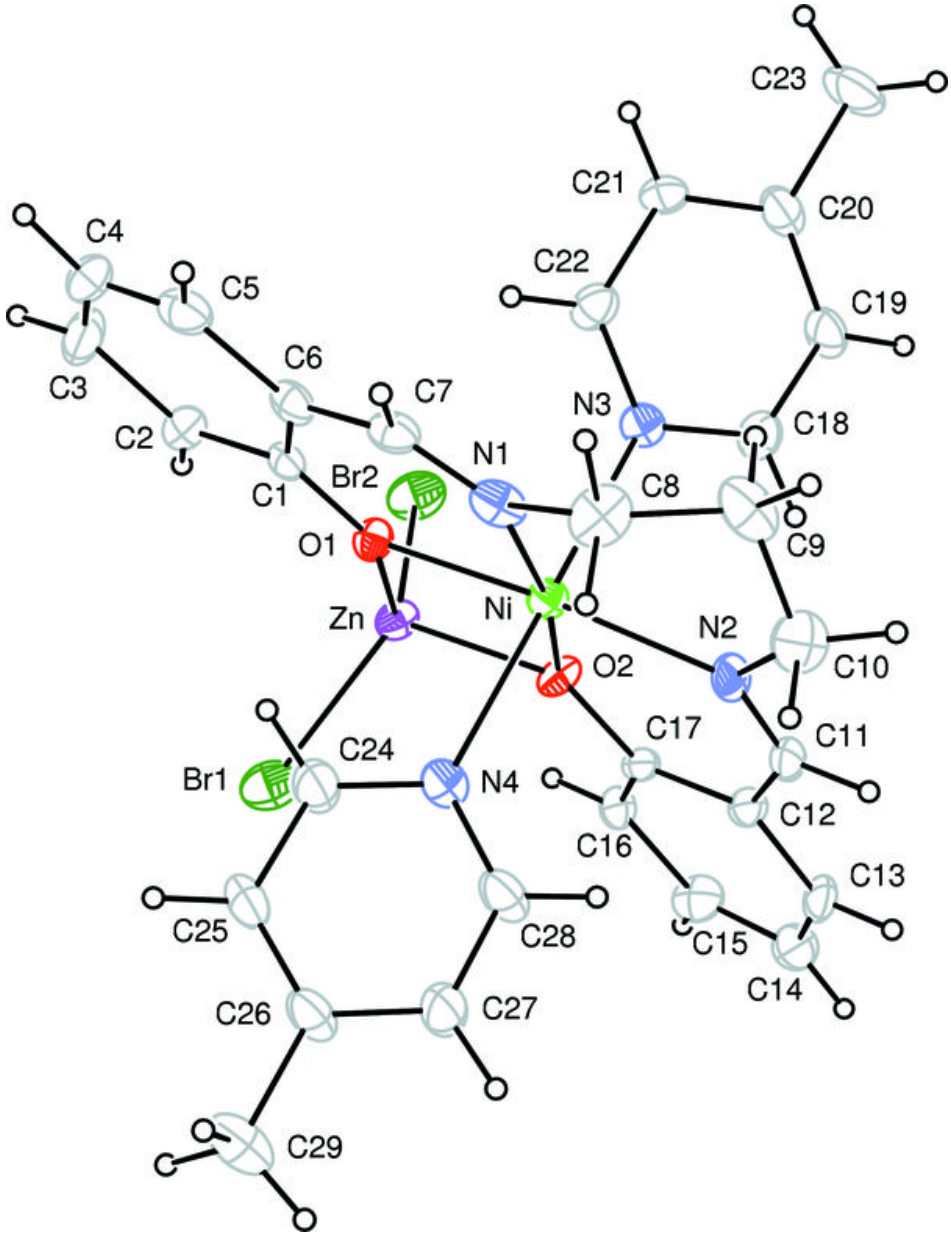
C23
C21
C20
C4
C22
C5
C19
C6
C3
C7
N3
C18
C2
N1
Br2
C8
C1
C9
O1
Ni
Zn
N2
O2
C10
C17
C11
C24
Br1
N4
C12
C16
C13
C25
C28
C15
C14
C26
C27
C29

Fig. 2