{[*μ*-Bis(salicylidene)-1,3-propanediaminato]-bis(3,5-dimethylpyridine)-nickel(II)}dibromozinc(II)

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The title compound, [NiZnBr$_2$(C$_{17}$H$_{16}$N$_2$O$_2$)(C$_7$H$_9$N)$_2$], is a double oxygen-bridged heterometal complex based on a Schiff base ligand. The Ni atom has an irregular octahedral environment involving two bridging O and two N atoms from a SALPD^{2-} [N,N'-bis(salicylidene)-1,3-propanediaminate] ligand in the equatorial plane and two N atoms from two 3,5-dimethylpyridine molecules in the axial positions.

Comment

Double oxygen-bridged dinuclear homo- or heterometal complexes based on Schiff base ligands are of interest, because they have subnormal magnetic moments, due to the super-exchange mechanism over the O atoms (Kato *et al.*, 1964; Butcher & Sinn, 1975; Kato & Muto, 1988). We previously reported several members in the family of double oxygen-bridged dinuclear metal complexes, which involve oxygen-bridged metal atoms Cu, Ni, Zn and Hg, different Schiff base ligands and halogen atoms Cl, Br and I, such as [Cu$_2$(C$_{11}$H$_{10}$ClNO$_2$)$_2$] (Tahir *et al.*, 1996), [Cu$_2$(C$_{12}$H$_{13}$NO$_2$)$_2$] (Ülkü *et al.*, 1998), [CuZnCl$_2$(C$_{17}$H$_{16}$N$_2$O$_2$)] (Tatar *et al.*, 1999), [CuZnI$_2$(C$_{17}$H$_{16}$N$_2$O$_2$)(C$_6$H$_7$N)] (Ercan *et al.*, 1999), [CuHgBr$_2$(C$_{17}$H$_{16}$N$_2$O$_2$) (Kaynak *et al.*, 1999), [NiZnI$_2$-(C$_{17}$H$_{16}$N$_2$O$_2$)(C$_7$H$_9$N)$_2$] (Arıcı *et al.*, 1999). The title compound, [NiZnBr$_2$(C$_{17}$H$_{16}$N$_2$O$_2$)(C$_7$H$_9$N)$_2$], (I), reported here, turned out to be isomorphous with the very last of these compounds. At the appropriate step in the preparation, if ZnBr$_2$ is used instead of ZnI$_2$, one obtains compound (I). The coordination around the central metal atoms in the double oxygen-bridged dinuclear heterometal complexes of the type cited above is square-planar, square-pyramidal or octahedral, depending on the ligands. The terminal metal atom has a tetrahedral coordination in all cases and the title compound is no exception.
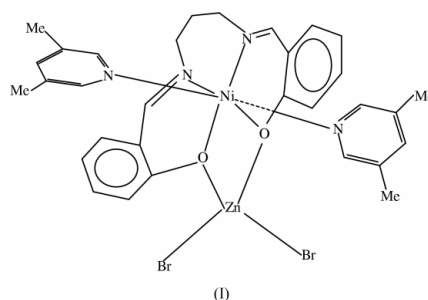
(I)

The Ni atom has an irregular octahedral environment involving two bridging O and two N atoms from the SALPD^{2-} ligand in the equatorial plane [SALPD is N,N'-bis(salicyl-
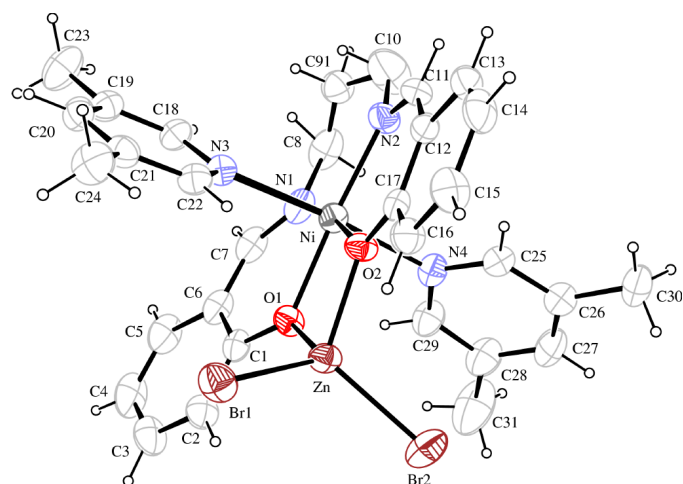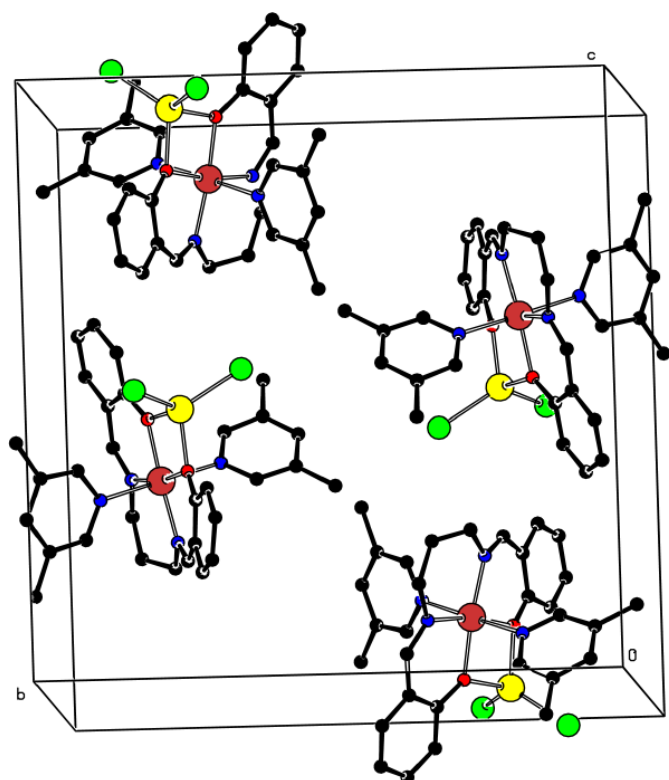
Figure 1
ORTEP drawing (Johnson, 1965) of the asymmetric unit of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 35% probability level.

idene)-1,3-propanediaminate]. Atoms N3 and N4 from the two 3,5-dimethylpyridine molecules occupy the apical positions of the irregular octahedron. The Ni—O distances [2.026 (2) and 2.028 (3) Å], as well as the Ni—N distances [2.020 (3) and 2.027 (3) Å] in the equatorial plane, are equal within experimental error. The Ni—N3 [2.268 (3) Å] and Ni—N4 [2.162 (3) Å] distances have values slightly different from each other and they are both longer than the Ni—N bond lengths in the equatorial plane. The bond angles around the Ni atom range from 79.32 (10) (O1—Ni—O2) to 98.90 (15)° (N1—Ni—N2). When one considers the steric limitation in the propanediamine chelate ring and the bridging plane, the deviations of these values from 90° is understandable. The Ni atom is only 0.0072 (6) Å out of the equatorial plane. The coordination around the Zn atom is irregular tetrahedral, involving two bridging O atoms and two terminal Br atoms. The minimum and maximum bond-angle values are 80.68 (10) (O1—Zn—O2) and 118.24 (3)° (Br1—Zn—Br2), respectively. The Zn—O [1.984 (2)–2.012 (3) Å] and Zn—Br [2.3657 (7)–2.3391 (7) Å] distances have different values. Similar structural parameters are also observed in the isomorphous compound [NiZnI$_2$(C$_{17}$H$_{16}$N$_2$O$_2$)(C$_7$H$_9$N)$_2$] (Arıcı *et al.*, 1999). In (I), the closest intermolecular contact is between atoms C5 and Br1 of neighbouring molecules, with a $D \cdots A$ distance of 3.755 (6) Å (Fig. 2).

Experimental

N,N'-Bis(salicylidene)-1,3-propanediamine (1.410 g, 0.005 mol) was dissolved in hot ethanol (50 ml). A solution of NiCl$_2$.6H$_2$O (1.185 g, 9.005 mol) in hot water (30 ml) and ammonia (20%, 10 ml) were added to this solution. The mixture was set aside for 2–3 h. The precipitated light-green complex was filtered and dried at 413 K. This complex (0.338 g, 0.001 mol) was dissolved in hot dioxane (50 ml). First, 3,5-dimethylpyridine was added to this mixture and then ZnBr$_2$ (0.226 g, 0.001 mol) in hot methanol. The resulting mixture was set aside for 2 d. Precipitated crystals were filtered and dried in air.

Figure 2
A view of the unit cell of (I) (*PLATON*; Spek, 2000). H atoms have been omitted for clarity.

Crystal data

[NiZnBr$_2$(C$_{17}$H$_{16}$N$_2$O$_2$)(C$_7$H$_9$N)$_2$]	$D_x = 1.595$ Mg m^{-3}
$M_r = 778.50$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 23
$a = 9.2033$ (8) Å	reflections
$b = 18.8786$ (13) Å	$\theta = 10.7$–18.0°
$c = 19.1011$ (15) Å	$\mu = 3.82$ mm^{-1}
$\beta = 102.358$ (8)°	$T = 295$ K
$V = 3241.8$ (5) Å^3	Prism, purple
$Z = 4$	$0.30 \times 0.20 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.019$
$\omega/2\theta$ scans	$\theta_{max} = 25.6°$
Absorption correction: ψ scan (*MolEN*; Fair, 1990)	$h = -11 \rightarrow 0$
	$k = 0 \rightarrow 22$
$T_{min} = 0.416$, $T_{max} = 0.564$	$l = -22 \rightarrow 23$
6102 measured reflections	3 standard reflections
5746 independent reflections	frequency: 120 min
3651 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.034$	independent and constrained
$wR(F^2) = 0.101$	refinement
$S = 0.93$	$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2]$
5746 reflections	where $P = (F_o^2 + 2F_c^2)/3$
421 parameters	$(\Delta/\sigma)_{max} = 0.003$
	$\Delta\rho_{max} = 0.53$ e Å^{-3}
	$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—Ni	3.0757 (7)	Ni—O2	2.026 (2)
Br1—Zn	2.3657 (7)	Ni—N4	2.162 (3)
Br2—Zn	2.3391 (7)	Ni—N3	2.268 (3)
Zn—O1	1.984 (2)	C8—C91	1.367 (11)
Zn—O2	2.012 (3)	C8—C92	1.578 (13)
Ni—N1	2.020 (3)	C10—C92	1.314 (13)
Ni—N2	2.027 (3)	C10—C91	1.522 (13)
Ni—O1	2.028 (3)		
O1—Zn—O2	80.68 (10)	Br2—Zn—Br1	118.24 (3)
O1—Zn—Br2	115.61 (8)	N1—Ni—N2	98.90 (15)
O2—Zn—Br2	113.62 (8)	N1—Ni—O1	91.46 (13)
O1—Zn—Br1	112.23 (8)	O1—Ni—O2	79.32 (10)
O2—Zn—Br1	110.53 (8)		

Atom C9 of the propanediamine moiety is disordered. To prevent abnormal bond lengths in the chelate ring, geometrical restraints were applied to the neighbouring atomic distances. The H atoms of the two components of the disordered atom C9 were located in difference maps. Atom C9 components, together with the respective H atoms, were refined isotropically for a few cycles. The occupation factor converged at 0.5. The H atoms of C8 and C10 in the chelate ring were found in difference maps and were refined isotropically. All other H atoms were placed geometrically in fixed positions and their displacement parameters were refined isotropically.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993); data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *PARST* (Nardelli, 1995).

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