metal-organic papers

{[μ-N,N'-Bis(salicylidene)-1,3-propanediaminato]-(N,N-dimethylformamide)(methanol)nickel(II)}-dibromozinc(II)

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In the crystals structure of the title compound, [ZnNiBr$_2$(C$_{17}$H$_{16}$N$_2$O$_2$)(C$_3$H$_7$NO)(CH$_4$O)], there is a heterodinuclear nickel(II)–zinc(II) complex molecule, with the Ni^{2+} and Zn^{2+} ions bridged by the phenolic O atoms of the Schiff base N,N'-bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminate (SALPD^{2-}, C$_{17}$H$_{16}$N$_2$O$_2$) ligand. The coordination geometry around the Ni^{2+} ion is irregular octahedral, involving two O and two N donors of the SALPD^{2-} ligand in the equatorial plane, and O atoms of dimethylformamide and methanol in the apical positions. The Zn^{2+} ion has a distorted tetrahedral coordination.

Comment

Zinc is of essential importance in several biological processes and nickel often exhibits interesting magnetic properties. In this study, as described in the *Experimental* section, ZnBr$_2$ was added to the complex of [N,N'-bis(salicylidene)-1,3-propanediamine]nickel(II) in MeOH to form a heterodinuclear complex. In general, MeOH forms weak coordination bonds. The coordinated MeOH evaporates easily on mild heating, but in the title complex the coordinated MeOH is thermally stable and only leaves the structure at 383 K, as a result of the stabilizing influence of the short Ni—O4 bond, 2.178 (6) Å.

(I)
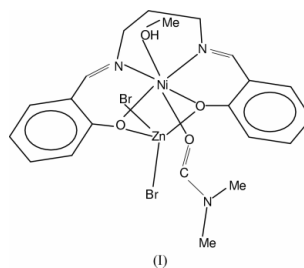
This distance implies a strong Ni—O coordination and the resulting molecular structure includes one MeOH and one dmf solvent group coordinated to the nickel(II) at the apical positions to complete the six-coordination. This metal ion is coordinated in the four equatorial positions by the two N and phenoxy–O donors of the SALPD^{2-} ligand. The distances between Ni and the apical donors with donors O3 [2.122 (6) Å, dmf] and O4 [2.178 (6) Å, MeOH] are significantly longer than the average bond distance between Ni and the equatorial donors (2.026 Å). The Ni atom is displaced 0.064 (1) Å out of the least-squares plane defined by atoms O1, O2, N1 and N2, in the direction of the dmf ligand. The greatest deviation of bond angles from those of ideal octahedral geometry is found for O1—Ni—O2 78.2 (2)° and N1—Ni—N2 98.9 (3)°. All other bond angles are close to their ideal 90 and 180° values (Table 1).
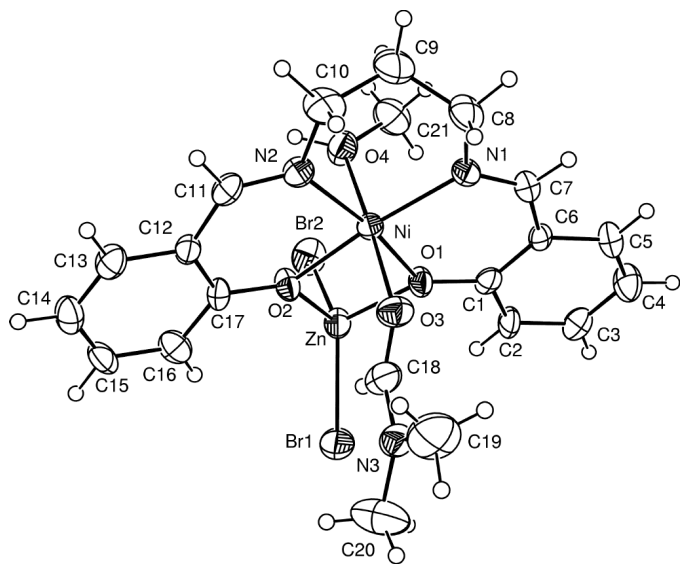
Figure 1
The molecular structure and atomic numbering scheme of (I) (40% probability displacement ellipsoids) (Farrugia, 1997).

Figure 2
Packing diagram of complex (I) (Spek, 2000).

In the title complex, (I), the Zn^{2+} ion is surrounded tetrahedrally by two terminal bromides and two bridging O atoms. The Zn—O and Zn—Br bond distances are 1.995 (6)–1.996 (6) and 2.3356 (16)–2.3634 (15) Å, respectively. The Br1—Zn—Br2 and O1—Zn—O2 angles are 117.95 (6) and 79.8 (2)°, respectively, and these two planes are almost perpendicular to each other; the dihedral angle is 89.2 (3)°. The coordination environments of the metal ions are common ones, *viz.* octahedral for nickel(II) and tetrahedral for zinc(II) (Sogo *et al.*, 1988; Greenwood & Earnshaw, 1994; Atakol *et al.*, 1999, and references therein; Arıcı *et al.*, 2001).

The bridging unit is not completely planar. The planes through atoms O1—Zn—O2 and O1—Ni—O2 subtend a dihedral angle of 11.1 (3)°. The molecule has an approximate boat conformation, excluding the solvent groups. The dihedral angle between the planes of the two moieties O1/C1–C8/N1 and O2/C10–C17/N2 is 10.01 (14)°. The distance between the two metal ions is 3.0917 (15) Å. There are two intramolecular hydrogen bonds, C18—H18···O2 and O4—H4A···Br2 (Table 2). Fig. 2 gives a perspective view of the crystal packing.

Experimental

N,N'-Bis(salicylidene)-1,3-propanediamine (1.400 g, 5 mmol) was dissolved in 50 ml hot EtOH. Then 20% ammonia (10 ml) and 20 ml of a hot aqueous solution of $NiCl_2.6H_2O$ (1.185 g, 5 mmol) were added to this solution. The mixture was set aside in air for 2 h and the light-green mononuclear nickel(II) complex which formed was filtered off and dried in an oven at 423 K. This complex (0.339 g, 1 mmol) was dissolved in 20 ml dmf at boiling temperature. A solution of 0.225 g (1 mmol) anhydrous $ZnBr_2$ in 50 ml hot MeOH was added dropwise. The resulting mixture was set aside for 2 d and after this period the light-blue crystals which formed were filtered off and dried in air. Elemental analysis found for $C_{21}H_{27}Br_2N_3NiO_4Zn$: Ni
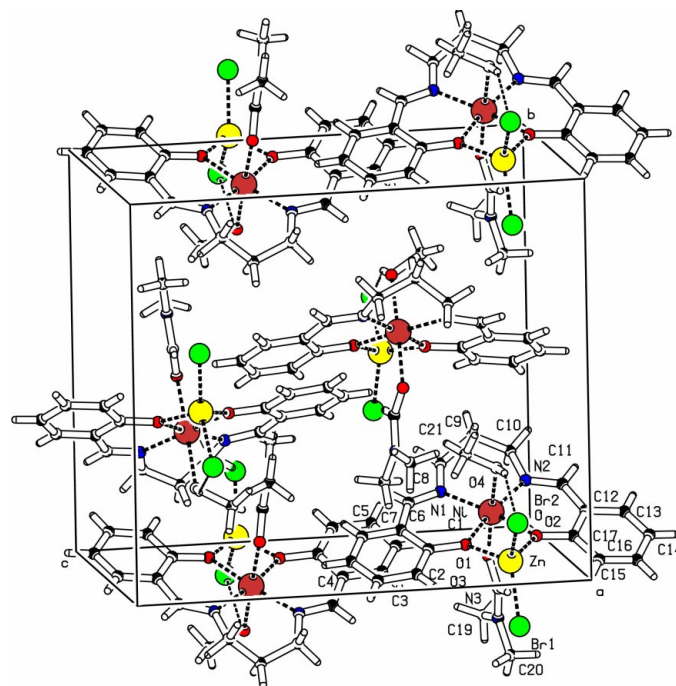
8.49, Zn 9.68, Br 23.86, N 6.29%; calculated: Ni 8.93, Zn 9.33, Br 24.27, N 6.38%. Selected IR data (cm^{-1}): ν(C—H) [aromatic] 3051–3080, ν(C—H) [aliphatic] 2953–2880; ν(O—H) [MeOH] 3465, ν(C=O) [dmf] 1651, ν(C=N) 1625.

Crystal data

[ZnNiBr2(C17H16N2O2)-(C3H7NO)(CH4O)]	$D_x = 1.793$ Mg m^{-3}
$M_r = 669.34$	Mo $K\alpha$ radiation
Orthorhombic, $P2_12_12_1$	Cell parameters from 25 reflections
$a = 10.5304$ (12) Å	$\theta = 10.2$–18.2°
$b = 14.4184$ (11) Å	$\mu = 4.98$ mm^{-1}
$c = 16.3327$ (13) Å	$T = 295$ K
$V = 2479.8$ (4) Å^3	Prism, light blue
$Z = 4$	$0.25 \times 0.20 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.064$
$\omega/2\theta$ scans	$\theta_{max} = 26.3°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 13$
	$k = 0 \rightarrow 17$
$T_{min} = 0.315$, $T_{max} = 0.474$	$l = 0 \rightarrow 20$
2791 measured reflections	3 standard reflections
2784 independent reflections	frequency: 120 min
1862 reflections with $I > 2\sigma(I)$	intensity decay: 2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.079$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.50$ e Å^{-3}
2784 reflections	$\Delta\rho_{min} = -0.61$ e Å^{-3}
291 parameters	Absolute structure: (Flack, 1983), 73 Friedel pairs
H-atom parameters constrained	Flack parameter = 0.53 (3)

Table 1
Selected geometric parameters (Å, °).

Ni—Zn	3.0917 (15)	Ni—O2	2.031 (6)
Br1—Zn	2.3356 (16)	Ni—O3	2.122 (6)
Br2—Zn	2.3634 (15)	Ni—O4	2.178 (6)
N1—Ni	2.028 (7)	O1—Zn	1.996 (6)
N2—Ni	2.017 (8)	O2—Zn	1.995 (6)
Ni—O1	2.027 (6)		
C7—N1—Ni	124.1 (7)	O2—Ni—O4	85.0 (3)
C8—N1—Ni	118.1 (6)	O3—Ni—O4	177.8 (3)
C11—N2—Ni	123.9 (7)	C1—O1—Zn	130.6 (6)
C10—N2—Ni	121.1 (6)	C1—O1—Ni	128.5 (6)
N2—Ni—O1	169.0 (3)	Zn—O1—Ni	100.5 (3)
N2—Ni—N1	98.9 (3)	C17—O2—Zn	131.9 (6)
O1—Ni—N1	91.2 (3)	C17—O2—Ni	127.7 (6)
N2—Ni—O2	91.4 (3)	Zn—O2—Ni	100.3 (2)
O1—Ni—O2	78.2 (2)	C18—O3—Ni	121.6 (7)
N1—Ni—O2	169.1 (3)	C21—O4—Ni	124.1 (6)
N2—Ni—O3	92.4 (3)	O2—Zn—O1	79.8 (2)
O1—Ni—O3	91.9 (3)	O2—Zn—Br1	116.4 (2)
N1—Ni—O3	90.1 (3)	O1—Zn—Br1	116.26 (19)
O2—Ni—O3	92.9 (3)	O2—Zn—Br2	109.2 (2)
N2—Ni—O4	87.4 (3)	O1—Zn—Br2	111.20 (19)
O1—Ni—O4	88.0 (3)	Br1—Zn—Br2	117.95 (6)
N1—Ni—O4	92.1 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···Br2	0.99	2.68	3.572 (6)	150
C18—H18···O2	0.93	2.56	3.120 (13)	119

The achiral molecule of the title compound crystallizes in a chiral space group. The Flack parameter of 0.53 (3) suggests that the crystal is an inversion twin. The H atoms, except H4A, were positioned geometrically with U_{eq}(H) = 1.2U_{eq}(C), and a riding model was used during the refinement process. H4A, in the methanol ligand, was located in a difference map, and its position was fixed.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997) and *PLATON*2000 (Spek, 2000); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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