{Bis(N,N-dimethylformamide)[μ-N,N'-bis(salicylidene)-1,3-propane-diaminato]nickel(II)}dibromozinc(II)[1]

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The title compound, $[NiZnBr_2(C_3H_7NO)_2(C_{17}H_{16}N_2O_2)]$, is a heterodinuclear nickel complex. The Ni atom has an irregular octahedral environment involving two O and two N atoms from the bis(salicylidene)-1,3-propanediaminate ligand in the equatorial plane, and two O atoms from the dimethylformamide groups. The Zn—O—Ni, O—Zn—O, Ni—O—Zn and O—Ni—O angles in the bridged plane are 100.1 (2), 79.9 (2), 100.4 (2) and 78.89 (17)°, respectively. The Ni···Zn distance is 3.0738 (19) Å.

Comment

N,N'-Bis(salicylidene)-1,3-propanediamine is quite an interesting ligand, and has appeared in the coordination chemistry literature for 50 years. The complexes formed between this ligand and first row transition metals tend toward μ-bridging in non-aqueous media with Lewis acids. Consequently, di-, tri- and even polynuclear complexes are formed.

At present, the magnetic properties of homo- and hetero-polynuclear compounds are not clearly understood, but these properties are currently under investigation (Meenakumari *et al.*, 1993; Tuna *et al.*, 1999).

Nickel often exhibits interesting magnetic properties, and zinc has biological importance and is an essential element for living beings. In this study, $ZnBr_2$ was added to the square-planar complex of N,N'-bis(salicylidene)-1,3-propanediamine and nickel(II) (Drew *et al.*, 1985) to form a heterodinuclear complex. In a previous study, we prepared a similar Ni–Zn complex *via* the reaction of [N,N'-bis(salicylidene)-1,3-propanediaminato]nickel(II) as a Lewis acid with 3,5-dimethylpyridine and ZnI_2, and the resulting molecular struc-

ture was reported (Arıcı *et al.*, 1999). This previous dinuclear complex included two 3,5-dimethylpyridine molecules coordinated to the nickel(II) at the axial position to complete the octahedral coordination. The present structure, (I), is very similar to the aforesaid complex, except that no pyridine derivatives are added and the six-coordination of Ni[II] is completed by dimethylformamide solvent (DMF) molecules.

(I)
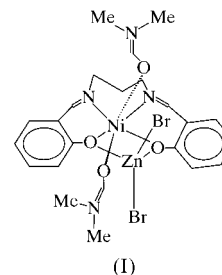
As can be seen in Fig. 1, the coordination environments of the metal atoms are common ones, *i.e.* octahedral for Ni[II] and tetrahedral for Zn[II], even though the Ni[II] starting material was a square-planar complex (Sogo *et al.*, 1988; Greenwood & Earnshow, 1994). The transformation is aided by the Lewis basicity of the Zn[II] bromide, such that electron density is drawn away from the phenolic O atoms. The reduced electron density at the Ni[II] center thus promotes axial coordination of solvent molecules such as 3,5-dimethylpyridine in the previous case or the DMF solvent in the present one. In each case, the structure includes one octahedron and one tetrahedron which share one edge.

The distances from the Ni atom to N1 and N2 are essentially the same as those in the 3,5-dimethylpyridine complex (within 1σ), but the Ni—O1 and Ni—O2 distances [2.016 (5) and
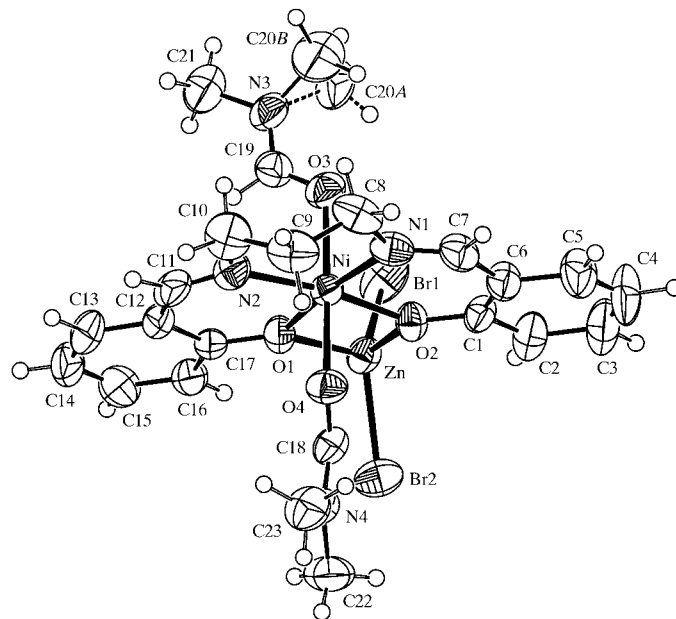

Figure 1
*PLATON*99 (Spek, 1999) drawing of the asymmetric unit of the title compound. The disordered C20 atom with suffix *A* has an occupancy of 0.41 (8) and that with suffix *B* has an occupancy of 0.59 (8). The displacement ellipsoids are drawn at the 50% probability level.

[1] Systematic name: dibromo-2κ²Br-bis(N,N-dimethylformamido-1κO)-μ-{2,2'-[1,3-propanediylbis(nitrilomethylidene)]diphenolato}-1κ⁴O,N,N',O':2κ²O,O'-nickel(II)zinc(II).

2.010 (5) Å] are significantly shorter than the corresponding distances in the 3,5-dimethylpyridine complex [2.039 (3) and 2.030 (3) Å], probably due to the difference in the halide bonded to the Zn atom. The coordination around the Ni and Zn atoms are quite distorted from ideal octahedral and ideal tetrahedral geometries due to the constraints imposed by the chelating ligands. The Ni—O(axial) distances are 2.128 (5) and 2.137 (5) Å. The distance between the two metals is 3.0738 (19) Å, which is shorter than in some similar complexes (Ercan *et al.*, 1998).

The complex is stable up to 423 K (the approximate boiling point of *N*,*N*-dimethylformamide). Thermogravimetric analysis results indicate a loss of dimethylformamide at this temperature, followed by irregular decomposition with increasing temperature.

The average Ni—O, Ni—N and Zn—Br bond lengths are 2.07 (3), 2.023 (4) and 2.35 (1) Å, respectively, which are in agreement with values reported previously for Ni^{II} complexes (Ercan *et al.*, 1998). Atom Ni is 0.0188 (3) Å out of the least-squares plane defined by O1, O2, N1 and N2. The dihedral angle between the planes of the two chelating moieties (O2/C1/C6/C7/N1 and O1/C17/C12/C11/N2) is 3.2 (3)°. Atom C20 is disordered; the atom with suffix *A* has occupancy 0.41 (8).

All the chelate rings around Ni, except for one, are planar. The Ni/N1/C8/C9/C10/N2 ring is in a half-chair conformation. The Ni/O1/Zn/O2 ring is planar within 0.05 Å, as it is in similar complexes.

Experimental

To a solution of *N*,*N*′-bis(salicylidene)-1,3-propanediamine (0.840 g, 3 mmol) in hot ethanol (50 ml), ammonia solution (10 ml) was added and the mixture was heated to boiling. A solution of $NiBr_2 \cdot 6H_2O$ (0.715 g, 3 mmol) in hot water (20 ml) was added, and the resulting mixture was left to stand in air. After 2 h, the light-blue Ni complex was filtered and dried at 423 K for 3 h. This complex (0.339 g, 1 mmol) was dissolved in hot DMF (10 mmol) and dioxane (30 mmol). $ZnBr_2$ (0.225 g, 1 mmol) in hot methanol (10 ml) was added dropwise. The resulting mixture was set aside for 3 d and the light-blue crystals which formed were filtered off and dried in air.

Crystal data

[NiZnBr2(C3H7NO)2(C17H16N2O2)]
$M_r = 710.39$
Monoclinic, *Cc*
$a = 10.518$ (3) Å
$b = 15.180$ (8) Å
$c = 17.618$ (6) Å
$\beta = 98.85$ (2)°
$V = 2779.5$ (19) Å^3
$Z = 4$

$D_x = 1.698$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.78–12.69°$
$\mu = 4.450$ mm^{-1}
$T = 295$ K
Prism, light blue
$0.45 \times 0.35 \times 0.18$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{min} = 0.138$, $T_{max} = 0.459$
3265 measured reflections
3181 independent reflections (plus 84 Friedel-related reflections)

2965 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.45°$
$h = -13 \rightarrow 13$
$k = -20 \rightarrow 19$
$l = -23 \rightarrow 22$
3 standard reflections
  frequency: 120 min
  intensity decay: 1.79%

Table 1
Selected geometric parameters (Å, °).

Ni—Zn	3.0738 (19)	Ni—O2	2.010 (5)
Br1—Zn	2.3412 (18)	Ni—O3	2.128 (5)
Br2—Zn	2.3628 (16)	Ni—O4	2.137 (5)
Zn—O1	1.993 (5)	Ni—N1	2.025 (6)
Zn—O2	1.991 (4)	Ni—N2	2.020 (7)
Ni—O1	2.016 (5)		
Br1—Zn—Br2	118.01 (5)	O2—Ni—O3	91.3 (2)
Br1—Zn—O1	116.41 (15)	O2—Ni—O4	91.22 (19)
Br1—Zn—O2	111.45 (15)	O2—Ni—N1	90.2 (2)
Br2—Zn—O1	111.73 (14)	O2—Ni—N2	169.4 (2)
Br2—Zn—O2	113.38 (14)	O3—Ni—O4	176.7 (2)
O1—Zn—O2	79.9 (2)	O3—Ni—N1	89.5 (2)
O1—Ni—O2	78.89 (17)	O3—Ni—N2	91.6 (2)
O1—Ni—O3	89.78 (19)	O4—Ni—N1	88.4 (2)
O1—Ni—O4	92.81 (19)	O4—Ni—N2	86.4 (2)
O1—Ni—N1	169.0 (2)	N1—Ni—N2	100.0 (3)
O1—Ni—N2	90.9 (2)		

Refinement

Refinement on F^2
$R(F) = 0.039$
$wR(F^2) = 0.108$
$S = 1.03$
3265 reflections
329 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0884P)^2 + 1.4211P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0026 (3)
Absolute structure: Flack (1983)
Flack parameter = −0.022 (15)

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*99 (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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