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A new Ni–Zn heterodinuclear complex: [μ_2-bis(salicylidene)propane-1,3-diaminato]dichlorobis(*N*,*N*-dimethylformamide)nickel(II)zinc(II)

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The title compound, [$NiZn(C_{17}H_{16}N_2O_2)Cl_2(C_3H_7NO)_2$], is a new heterodinuclear Ni^{II}–Zn^{II} complex. X-ray crystallographic analysis shows that the nickel(II) ion is in a distorted O_4N_2 octahedral environment, while the zinc(II) ion is in a distorted O_2Cl_2 tetrahedral environment.

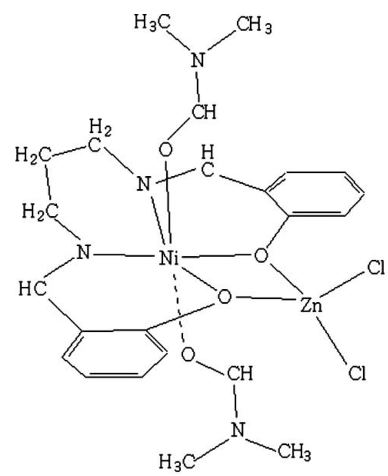
Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.036
wR factor = 0.100
Data-to-parameter ratio = 8.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

N,*N*′-Bis(salicylidene)propane-1,3-diamine (H_2L) has a strong tendency to form polynuclear complexes (Fukuhara *et al.*, 1990; Gerli *et al.*, 1991; Atakol *et al.*, 1999; Ercan *et al.*, 1999). There are many references in the literature to multinuclear complexes involving L^{2-}.



(I)

The mononuclear nickel(II) complex of H_2L, NiL, reacts with zinc halides in non-aqueous polar solvents to form heterodinuclear complexes (Ercan *et al.*, 1999; Atakol *et al.*, 1999; Arıcı *et al.*, 1999, 2001; Tatar, 2002; Ülkü *et al.*, 2002; Tatar *et al.*, 2002; Elmali & Elerman, 2003; Atakol *et al.*, 2003).

In this study, zinc(II) forms a μ_2-bridge with the phenolate O atoms of NiL. The Ni^{II} atom is coordinated by two dimethylformamide (DMF) solvent molecules, and two N and two O donor atoms of the ligand *L*, to form a distorted octahedral coordination sphere. Previously, we prepared a smilar Ni–Zn complex *via* the reaction of H_2L–nickel(II) as a Lewis acid with 3,5-dimethylpyridine and ZnI_2, and the resulting molecular structure has been reported (Arıcı *et al.*, 1999). The Ni–ZnI_2 heterodinuclear complex included two 3,5-dimethylpyridine molecules coordinated to the nickel(II) in axial positions to complete the octahedral coordination.

As can be seen from Fig. 1, the nickel(II) ion is in a distorted octahedral coordination sphere, while the zinc(II) ion is in a distorted tetrahedral sphere. The zinc(II) ion is coordinated by the phenolate O atoms of the ligand and two halogen atoms. As can be seen from the bond angles in Table 1, the donor atoms form a distorted tetrahedron about Zn. The Ni—N distances are longer, and are in an octahedral coordination rather than a square-pyramidal coordination (Atakol *et al.*, 2003).

The structure of another previously determined Ni–$ZnBr_2$ heterodinuclear complex is very similar to that of the title Ni–ZnI_2 dinuclear complex, with the six-coordination of nickel(II) also being completed by DMF solvent molecules (Arıcı *et al.*, 2001). The two structures have a common coordination environment for the metal atoms, *i.e.* octahedral for Ni^{II} and tetrahedral for Zn^{II}. The Ni—N and Ni—O distances are approximately the same [Ni—N1 = 2.025 (6) Å, Ni—N2 = 2.020 (7) Å, Ni—O1 = 2.016 (5) Å and Ni—O2 = 2.010 (5) Å (Arici *et al.*, 2001); Ni—N1 = 2.032 (4) Å, Ni—N2 = 2.017 (4) Å, Ni—O1 = 2.020 (3) Å and Ni—O2 = 2.013 (3) Å in (I)]. The Ni—O(axial) distances are 2.143 (3) and 2.141 (3) Å in (I), longer than in the isomorphous Ni—$ZnBr_2$ complex [2.128 (5) and 2.137 (5) Å]. The distance between the two metal atoms is 3.0862 (7) Å, in agreement with values reported previously for Ni^{II} complexes. The Flack (1983) parameter is 0.04 (3), thus the absolute configuration is determined reliably. The six-membered Ni/N1/C8–C10/N2 chelate ring is in a flattened-boat conformation and atoms Ni and C9 are displaced from their respective planes by 0.0115 (5) and −0.7245 (6) Å.

Experimental

2,2′-Dimethyl-*N*,*N*′-bis(salicylidene)propane-1,3-diamine (1.410 g, 5 mmol) was dissolved in hot ethanol (50 ml). To this solution were added 20% ammonia solution (10 ml) and a solution of $NiCl_2 \cdot 6H_2O$ (1.119 g, 5 mmol) in hot water (20 ml). The resulting mixture was set aside for 2 h, and the light-green nickel complex which formed was filtered off and dried in an oven at 400 K for 3 h. The nickel complex (0.240 g, 1 mmol) was dissolved in hot dimethylformamide (30 ml). A solution of non-aqueous $ZnCl_2$ (1 mmol, 0.136 g) in hot dimethylformamide (20 ml) was added slowly to this solution. The resulting mixture was set aside for 4–5 d. The crystals which formed were filtered off and dried in air.

Crystal data

[NiZn($C_{17}H_{16}N_2O_2$)Cl_2(C_3H_7NO)$_2$]	D_x = 1.506 Mg m^{-3}
M_r = 621.53	Mo *Kα* radiation
Monoclinic, *Cc*	Cell parameters from 25 reflections
a = 10.4862 (3) Å	*θ* = 2.4–26.3°
b = 15.1938 (2) Å	*μ* = 1.79 mm^{-1}
c = 17.4233 (3) Å	*T* = 299 (2) K
β = 99.010 (2)°	Prism, dark green
V = 2741.72 (10) Å^3	0.18 × 0.15 × 0.13 mm
Z = 4	

Data collection

Enraf–Nonius diffractometer	R_{int} = 0.052
ω/2*θ* scans	θ_{max} = 26.3°
Absorption correction: *ψ* scan (Fair, 1990)	*h* = −13 → 12
T_{min} = 0.732, T_{max} = 0.792	*k* = 0 → 18
2999 measured reflections	*l* = 0 → 21
2886 independent reflections	3 standard reflections frequency: 120 min
2747 reflections with $I > 2\sigma(I)$	intensity decay: 0.1%

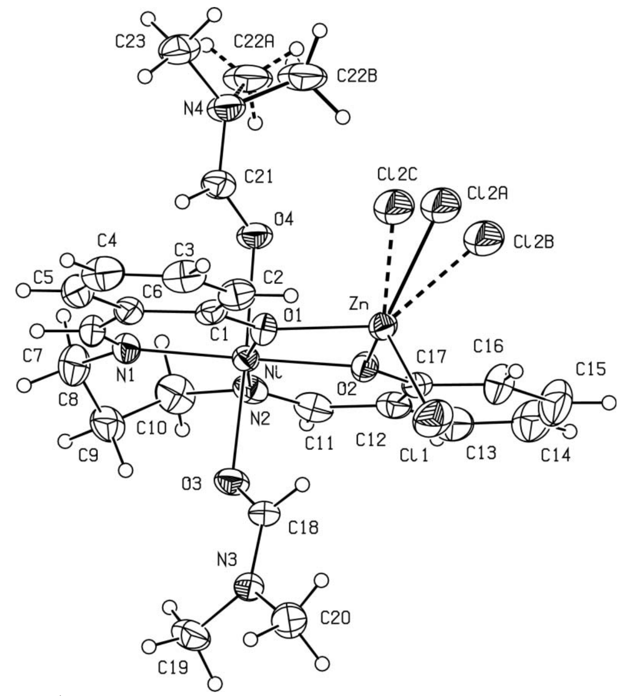


Figure 1
PLATON (Spek, 2003) drawing of (I), showing the atom-numbering scheme. The disordered atoms C22*A* and Cl2*A* have occupancies of 0.568 (16) and 0.707 (6), respectively. Displacement ellipsoids are drawn at the 30% probability level.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0718P)^2 + 2.3115P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.036	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.100	$(\Delta/\sigma)_{max}$ = 0.052
S = 1.06	$\Delta\rho_{max}$ = 0.75 e Å^{-3}
2886 reflections	$\Delta\rho_{min}$ = −0.62 e Å^{-3}
335 parameters	Absolute structure: Flack (1983), 88 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.04 (3)

Table 1
Selected geometric parameters (Å, °) for (I).

Ni—Zn	3.0862 (7)	Ni—O2	2.013 (3)
Zn—O2	1.996 (3)	Ni—N1	2.032 (4)
Zn—O1	2.010 (3)	Ni—O1	2.020 (3)
Zn—Cl1	2.2345 (16)	Ni—O3	2.143 (3)
Zn—Cl2*A*	2.252 (3)	Ni—O4	2.141 (3)
Ni—N2	2.017 (4)		
O2—Zn—O1	79.69 (13)	N2—Ni—O3	88.56 (15)
O2—Zn—Cl1	112.63 (11)	O2—Ni—O3	91.68 (13)
O1—Zn—Cl1	111.50 (10)	N1—Ni—O3	86.86 (15)
O2—Zn—Cl2*A*	113.60 (14)	O1—Ni—O3	92.09 (13)
O1—Zn—Cl2*A*	117.28 (13)	N2—Ni—O4	89.83 (14)
Cl1—Zn—Cl2*A*	116.67 (10)	O2—Ni—O4	90.70 (13)
N2—Ni—O2	90.15 (15)	N1—Ni—O4	91.09 (15)
N2—Ni—N1	100.24 (18)	O1—Ni—O4	89.94 (14)
O2—Ni—N1	169.46 (16)	O3—Ni—O4	177.13 (16)
N2—Ni—O1	169.17 (14)	Zn—O1—Ni	99.95 (14)
O2—Ni—O1	79.02 (12)	Zn—O2—Ni	100.67 (14)
N1—Ni—O1	90.59 (16)		

H atoms were positioned geometrically (C—H = 0.93–0.97 Å). The H atoms of the disordered atoms C22*A* and C22*B* were located in a difference synthesis and then refined as riding, with site-occupancy factors of 0.568 (16) and 0.432 (16), respectively; the site-occupancy factors were 0.707 (6), 0.149 (4) and 0.145 (5) for Cl2*A*/*B*/*C*, respectively. All H atoms were refined using a riding model, with $U_{eq}(H) = 1.2U_{eq}(C)$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993); cell refinement: *CAD-4 EXPRESS*; data reduction: *CAD-4 EXPRESS*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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References

Arıcı, C., Ercan, F., Atakol, O., Akay, A. & Ulku, D. (1999). *Acta Cryst.* C**55**, 928–930.

Arıcı, C., Svoboda, I., Sari, M., Atakol, O. & Fuess, H. (2001). *Acta Cryst.* C**57**, 31–32.

Atakol, O., Ercan, F., Arıcı, C., Fuess, H. & Svoboda, I. (1999). *Acta Cryst.* C**55**, 2023–2026.

Atakol, O., Nazir, H., Arici, C., Durmus, S., Svoboda, I. & Fuess, H. (2003). *Inorg. Chim. Acta*, **342**, 295–300.

Elmali, A. & Elerman, Y. (2003). *Z. Naturforsch. Teil B*, **58**, 539–542.

Enraf–Nonius (1993). *CAD-4 EXPRESS*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ercan, F., Arıcı, C., Akay, A., Atakol, O. & Ülkü, D. (1999). *Acta Cryst.* C**55**, 925–928.

Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Fukuhara, C., Tsuneyoshi, K., Matsumoto, N., Kida, S., Mikuriya, M. & Mori, M. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3473–3479.

Gerli, A., Hagen, K. S. & Marzilli, L. (1991). *Inorg. Chem.* **30**, 4673–4676.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Tatar, L. (2002). *Acta Cryst.* E**58**, m231–m233.

Tatar, L., Atakol, O. & Arici, C. (2002). *Acta Cryst.* E**58**, m154–m156.

Ülkü, D., Kaynak, F. B. & Atakol, O. (2002). *Acta Cryst.* E**58**, m251–m253.