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Key indicators

Single-crystal X-ray study

$T = 299$ K

Mean $\sigma(\text{C}-\text{C}) = 0.009$ 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>.

A new Ni–Zn heterodinuclear complex: $[\mu_2\text{-bis}(\text{salicylidene})\text{propane-1,3-diaminato}]\text{-dichlorobis}(N,N\text{-dimethylformamide})\text{nickel(II)-zinc(II)}$

The title compound, $[\text{NiZn}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)\text{Cl}_2(\text{C}_3\text{H}_7\text{NO})_2]$, is a new heterodinuclear $\text{Ni}^{\text{II}}\text{-Zn}^{\text{II}}$ 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.

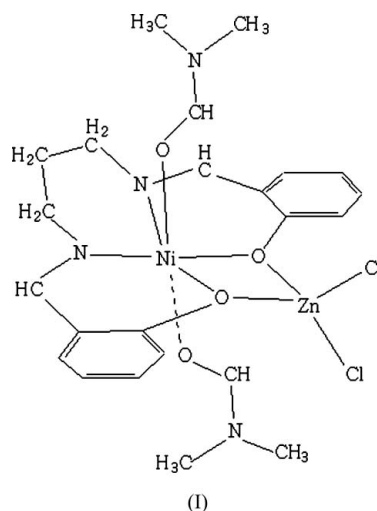
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Comment

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-} .



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 similar 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 (Arici *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–ZnBr₂ heterodinuclear complex is very similar to that of the title Ni–ZnI₂ dinuclear complex, with the six-coordination of nickel(II) also being completed by DMF solvent molecules (Arici *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–ZnBr₂ 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 NiCl₂·6H₂O (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 ZnCl₂ (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 ₂ O ₂)Cl ₂ (C ₃ H ₇ NO) ₂]	$D_x = 1.506 \text{ Mg m}^{-3}$
$M_r = 621.53$	Mo $K\alpha$ radiation
Monoclinic, Cc	Cell parameters from 25 reflections
$a = 10.4862$ (3) Å	$\theta = 2.4\text{--}26.3^\circ$
$b = 15.1938$ (2) Å	$\mu = 1.79 \text{ mm}^{-1}$
$c = 17.4233$ (3) Å	$T = 299$ (2) K
$\beta = 99.010$ (2)°	Prism, dark green
$V = 2741.72$ (10) Å ³	$0.18 \times 0.15 \times 0.13 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius diffractometer	$R_{\text{int}} = 0.052$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 26.3^\circ$
Absorption correction: ψ scan (Fair, 1990)	$h = -13 \rightarrow 12$
$T_{\text{min}} = 0.732$, $T_{\text{max}} = 0.792$	$k = 0 \rightarrow 18$
2999 measured reflections	$l = 0 \rightarrow 21$
2886 independent reflections	3 standard reflections
2747 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 0.1%

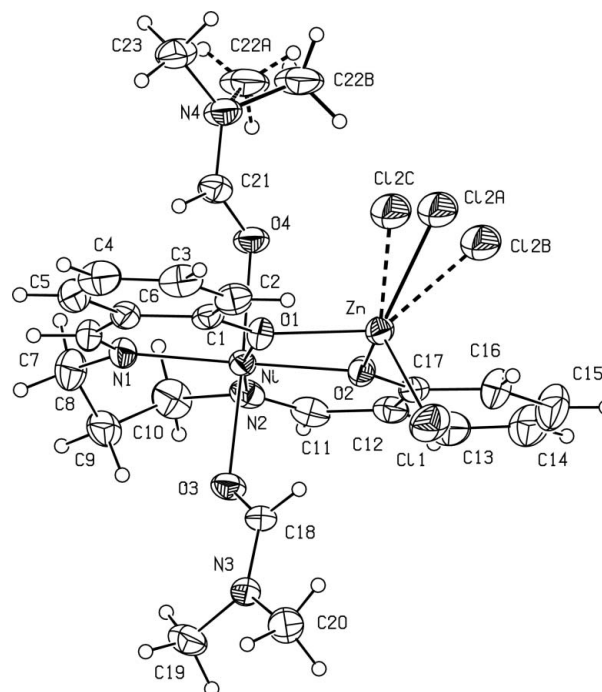


Figure 1
PLATON (Spek, 2003) drawing of (I), showing the atom-numbering scheme. The disordered atoms C22A and C12A have occupancies of 0.568 (16) and 0.707 (6), respectively. Displacement ellipsoids are drawn at the 30% probability level.

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 $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\text{max}} = 0.052$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.75 \text{ e \AA}^{-3}$
2886 reflections	$\Delta\rho_{\text{min}} = -0.62 \text{ e \AA}^{-3}$
335 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	88 Friedel pairs
	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–Cl2A	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–Cl2A	113.60 (14)	O1–Ni–O3	92.09 (13)
O1–Zn–Cl2A	117.28 (13)	N2–Ni–O4	89.83 (14)
Cl1–Zn–Cl2A	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 C22A and C22B 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 $Cl2A/B/C$, 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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