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{[μ -Bis(salicylidene)-1,3-propanediaminato]bis(3,5-dimethylpyridine)-nickel(II)} \ddagger diiodozinc(II) \dagger

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Abstract

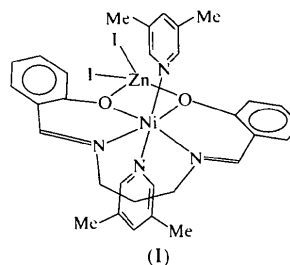
The structure of the title compound, [NiZnI₂(C₁₇H₁₆N₂O₂)(C₇H₉N)₂], consists of doubly oxygen-bridged heteronuclear dimeric complexes. The compound is of interest because of the magnetic superexchange interactions that occur between doubly oxygen-bridged metal ions. The Ni atom has an irregular octahedral environment involving two O and two N atoms from the bis(salicylidene)-1,3-propanediaminate ligand in the equatorial plane and the N atoms from the two 3,5-dimethylpyridine groups in the apical positions. The coordination around the Zn atom is distorted tetrahedral,

\ddagger Systematic name: bis(3,5-dimethylpyridine)-1 κ^2 N-diiodo-2 κ^2 I- μ -{2,2'-[1,3-propanediylbis(nitriolomethylidene)]diphenolato}-1 κ^1 O,N,N',O':2 κ^2 O,O'-nickel(II)zinc(II).

with an average Zn—O distance of 2.001 (2) Å and an average Zn—I distance of 2.5499 (5) Å. In the bridged plane, the Ni—O1—Zn, O1—Zn—O2, Zn—O2—Ni and O2—Ni—O1 angles are 98.82 (9), 81.2 (1), 99.8 (1) and 79.6 (1)°, respectively. The Ni···Zn distance is 3.0753 (7) Å.

Comment

The syntheses and structures of oxygen-bridged binuclear and trinuclear linear homo- or heterometal complexes based on Schiff base ligands, such as [Cu₂(C₁₁H₁₀ClNO₂)₂] (Tahir *et al.*, 1996), [Cu₂(C₁₄H₁₁NO₂)₂] (Ülkü, Ercan, Atakol, Ercan & Gencer, 1997), [Cd{(CH₃CO₂)(SALPD)Ni[(CH₃)₂CHNO]}₂] (Ülkü, Tahir *et al.*, 1997), [Ni₃(SALPD)₂(CH₃CO₂)₂{(CH₃)₂SO}₂] (Ülkü, Ercan, Atakol & Dinçer, 1997), [Cu₂(C₁₂H₁₃NO₂)₂] (Atakol *et al.*, 1997), [Cu₂(C₁₂H₁₃NO₂)₂] (Ülkü *et al.*, 1998) and [CuNi₂(NO₂)₂(SALPD)₂{(CH₃)₂CHNO}₂].2(CH₃)₂CHNO (Tahir *et al.*, 1998) [SALPD is *N,N'*-bis(salicylidene)-1,3-propanediaminate], have been the subject of considerable interest in this laboratory due to the magnetic superexchange interactions which occur between their bridged metal ions. Structural details of doubly oxygen-bridged homonuclear dimeric copper(II) complexes have been reported previously (Kato *et al.*, 1964; Barclay & Hoskins, 1965; Butcher & Sinn, 1976; Kato & Muto, 1988). We describe here the structure of a new heteronuclear dimeric complex, [NiZnI₂(SALPD)-(C₇H₉N)₂], (I).



The magnetic properties of (I) are currently under investigation. Magnetic superexchange interactions depend on the immediate environment of the bridge, as well as on the ligand arrangement about the metal atoms. The coordination around the nickel ion in the title hetero-dinuclear complex is an irregular octahedron involving two bridging O and two N atoms from the SALPD²⁻ ligand in the equatorial plane. In the axial positions of this irregular octahedron lie atoms N3 and N4 from the two 3,5-dimethylpyridine groups. The bond angles around the central Ni ion are in the range 79.6 (1) (O1—Ni—O2) to 98.7 (1)° (N1—Ni—N2). The Ni atom is located −0.0087 (5) Å from the coordination plane (O1, O2, N1, N2). This coordination plane and the bridging plane around the Ni atom (Ni, O1, Zn, O2)

have a dihedral angle of $3.5(9)^\circ$ between them. For dimeric homonuclear structures, there are reports in the literature that this dihedral angle, as well as the bridging angle, influence the magnetic properties of the systems (Kato *et al.*, 1964).

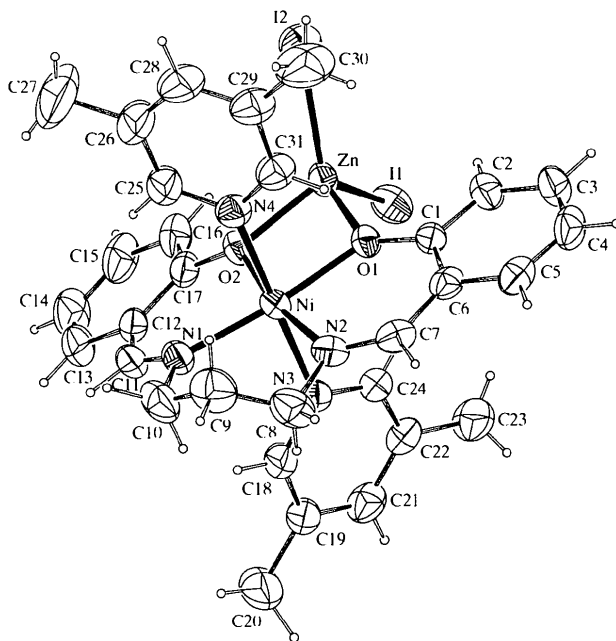


Fig. 1. PLATON (Spek, 1998) drawing of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

The Ni...Zn distance in (I) [$3.0753(7) \text{ \AA}$] is too long for a direct interaction. The six-membered Ni—N2—C8—C9—C10—N1 chelate ring has a boat conformation. The distances of the two *para*-positioned boat atoms, Ni and C9, from the least-squares plane defined by atoms N1, C10, C8 and N2 are $-0.0936(5)$ and $-0.665(5) \text{ \AA}$, respectively. The 3,5-dimethylpyridine groups make dihedral angles of $92.50(8)$ and $100.2(1)^\circ$ with the coordination plane (O1, O2, N1, N2). A comparison of the dihedral angle (κ) between the bridging plane and the coordination plane around the Ni atom, along with the related distance ranges and the bridging angle (φ), are given in Table 2 for the five dimeric metal complexes studied recently in this laboratory. The bond lengths and angles within the ligands show no unusual values.

Experimental

A solution of bis-*N,N'*-salicylidene-1,3-propanediamine (0.565 g, 2 mmol) in hot ethanol (75 ml) was added to ammonia (30 ml) and the mixture was heated to boiling point. A solution of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ (0.475 g, 2 mmol) in hot water (30 ml)

was then added, and the resulting mixture was set aside. After 2 h, the light-green nickel complex was filtered off, then dried at 413 K for 4 h. This complex (0.338 g, 1 mmol) was dissolved in hot dioxane (80 ml). Next, 3,5-dimethylpyridine (0.7 ml) was added to this complex and finally ZnI_2 (0.330 g, 1 mmol) was added in hot methanol (10 ml). The resulting mixture was set aside for 4 d and the light-purple crystals which formed were filtered off and dried in air.

Crystal data

$[\text{NiZnI}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2) \cdot (\text{C}_7\text{H}_9\text{N})_2]$

$M_r = 872.53$

Monoclinic

$P2_1/c$

$a = 9.4282(11) \text{ \AA}$

$b = 18.7170(12) \text{ \AA}$

$c = 19.6325(12) \text{ \AA}$

$\beta = 103.000(2)^\circ$

$V = 3375.7(5) \text{ \AA}^3$

$Z = 4$

$D_x = 1.7167 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 9.97\text{--}18.02^\circ$

$\mu = 3.130 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Prismatic

$0.30 \times 0.20 \times 0.15 \text{ mm}$

Light purple

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

empirical *via* ψ scans

(Fair, 1990)

$T_{\min} = 0.557$, $T_{\max} = 0.625$

6333 measured reflections

5561 independent reflections

4461 reflections with

$I > 3\sigma(I)$

$R_{\text{int}} = 0.014$

$\theta_{\text{max}} = 25.44^\circ$

$h = -11 \rightarrow 0$

$k = -22 \rightarrow 0$

$l = -22 \rightarrow 22$

3 standard reflections

frequency: 120 min

intensity decay: -4%

(corrected)

Refinement

Refinement on F

$R = 0.025$

$wR = 0.033$

$S = 0.98$

4461 reflections

370 parameters

H atoms: see below

$w = 1/[\sigma^2(F) + (0.02F)^2$

$+ 0.15]$, except $w = 0$

if $F^2 < \text{cutoff} \times \sigma F^2$,

where cutoff = 3.0

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.607 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.161 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

I1—Zn	2.5583 (6)	Ni—N1	2.022 (3)
I2—Zn	2.5414 (5)	Ni—N2	2.019 (3)
Zn—O1	2.010 (2)	Ni—N3	2.261 (3)
Zn—O2	1.991 (2)	Ni—N4	2.170 (3)
Ni—O1	2.039 (3)	N1—C11	1.274 (5)
Ni—O2	2.031 (3)	N2—C7	1.276 (5)
I1—Zn—I2	116.94 (2)	O2—Ni—N1	91.6 (1)
I1—Zn—O1	110.65 (7)	O2—Ni—N2	169.6 (1)
I1—Zn—O2	112.72 (7)	O2—Ni—N3	89.3 (1)
I2—Zn—O1	114.10 (7)	O2—Ni—N4	86.3 (1)
I2—Zn—O2	115.96 (8)	N1—Ni—N2	98.7 (1)
O1—Zn—O2	81.2 (1)	N1—Ni—N3	88.6 (1)
O1—Ni—O2	79.6 (1)	N1—Ni—N4	91.0 (1)

O1—Ni—N1	171.2 (1)	N2—Ni—N3	89.6 (1)
O1—Ni—N2	90.1 (1)	N2—Ni—N4	94.8 (1)
O1—Ni—N3	91.7 (1)	N3—Ni—N4	175.6 (1)
O1—Ni—N4	88.0 (1)		

Table 2. Structural data and bridging (φ) and dihedral (κ) angles ($^{\circ}$) for five homo- or hetero-dinuclear complexes

Complex	Bridging M(Cu,Ni)—O	M(Cu,Ni)··· M(Cu,Zn)	φ	κ
(I)	2.030 (3)–2.039 (2)	3.0753 (7)	98.8 (1)–99.7 (1)	3.5 (9)
(II)	1.941 (5)–1.950 (4)	2.994 (2)	100.6 (2)	5 (1)
(III)	1.930 (1)–1.982 (9)	3.073 (2)	103.5 (4)	11.3 (8)
(IV)	1.885 (3)–1.976 (3)	3.021 (2)	102.8 (1)	2.9 (9)– 8.0 (3)
(V)	1.938 (3)–1.995 (3)	3.047 (6)	103.4 (1)	12.7 (2)

Notes: (I) present work; (II) Tahir *et al.* (1996); (III) Ülkü, Ercan, Atakol, Ercan & Gencer (1997); (IV) Atakol *et al.* (1997); and (V) Ülkü *et al.* (1998).

H atoms bonded to C atoms were placed geometrically 0.95 Å from their parent atoms. H-atom displacement parameters were fixed as $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$ and a riding model was used for all H atoms.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1993). Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: MolEN. Program(s) used to refine structure: MolEN. Molecular graphics: PLATON (Spek, 1998). Software used to prepare material for publication: MolEN.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1045). Services for accessing these data are described at the back of the journal.

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{[μ -Bis(salicylidene)-1,3-propanediaminato]copper(II)}diiodozinc(II)†

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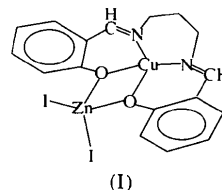
Abstract

The title compound, [CuZnI₂(C₁₇H₁₆N₂O₂)], is a doubly oxygen-bridged hetero-dinuclear complex, with the Cu^{II} ion in a distorted square-planar environment involving two O and two N atoms from the bis(salicylidene)-1,3-propanediaminate (SALPD²⁻) ligand. The Cu···Zn distance is 3.0933 (7) Å. The coordination sphere around the Zn centre is a distorted tetrahedron comprising two bridging O atoms and two terminal iodides.

Comment

The present work is an extension of our structural studies of doubly oxygen-bridged dimeric homo- or heteronuclear metal complexes, of which [Cu₂L₂] [L is 4-(2-hydroxybenzylimino)-2-hydroxy-2-pentene (Ülkü *et al.*, 1998)] and structures referenced therein are recent examples.

Structures with double oxygen bridges are of interest because they have unusual magnetic moments due to the superexchange interactions over the O atoms. Similar dimeric complexes have been investigated previously (Kato *et al.*, 1964; Barclay & Hoskins, 1965; Butcher & Sinn, 1976; Kato & Muto, 1988; Albada *et al.*, 1995).



The copper(II) centre in (I) has a distorted square-planar environment and is coordinated by the two N [Cu—N1 1.963 (7) and Cu—N2 1.969 (6) Å] and two O [Cu—O1 1.939 (5) and Cu—O2 1.949 (5) Å] atoms of the SALPD²⁻ ligand [SALPD is *N,N'*-bis-

† Systematic name: diiodo-2 κ^2 - μ -{2,2'-[1,3-propanediy]bis(nitrilomethylidene)diphenolato}-1 κ^4 O,*N,N',O'*;2 κ^2 O,*O'*-copper(II)zinc(II).