$[NiZnI_2(C_{17}H_{16}N_2O_2)(C_7H_9N)_2]$

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* $(\text{Å}, °)$ *for five homo- or hetero-dinuclear complexes*

Complex	Bridging $M(Cu,Ni)$—O	$M(Cu,Ni)\cdots$ $M(Cu,Zn)$	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 $U_{iso}(H) = 1.3U_{eq}(C)$ 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*.

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-propane-diaminato]copper(II)}diiodozinc(II)†

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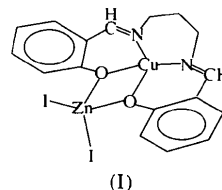
Abstract

The title compound, $[CuZnI_2(C_{17}H_{16}N_2O_2)]$, 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 ($SALPD^{2-}$) ligand. The $Cu\cdots Zn$ 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 $[Cu_2L_2]$ [L is 4-(2-hydroxybenzylimino)-2-hydroxy-2-pentene (Ülku *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).

(I)

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 $SALPD^{2-}$ ligand [SALPD is N,N'-bis-

† Systematic name: diiodo-2$\kappa^2 I$-μ-{2,2'-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato}-1$\kappa^4 O,N,N',O'$;2$\kappa^2 O,O'$-copper(II)zinc(II).

(salicylidene)-1,3-propanediaminate], which form the basal plane (Fig. 1). The O1—Cu—N2 [169.9 (2)°] and O2—Cu—N1 [169.4 (2)°] angles deviate from linearity by approximately 10°. The bridging angles O1—Cu—O2, Cu—O1—Zn, O1—Zn—O2 and Zn—O2—Cu are 78.1 (2), 103.3 (2), 75.4 (2) and 103.1 (2)°, respectively. The Cu—O—Zn—O bridging plane and the O—N—N—O coordination plane around the Cu^{II} atom make a dihedral angle of 1.9 (3)°, smaller than the value of 11.4 (4)° obtained from another investigation (Ercan *et al.*, 1999). The Cu^{II} atom is located 0.0173 (9) Å out of the least-squares O—N—N—O plane. The Cu···Zn distance of 3.0933 (7) Å is long for a direct interaction and is approximately equal to that obtained from other investigations (Ercan *et al.*, 1999; Arıcı *et al.*, 1999). The SALPD^{2-} ligand is not planar; the Cu—N1—C8—C9—C10—N2 chelate ring has a boat conformation. The distances of the diagonally opposite Cu and C9 atoms from the plane defined by the remaining ring atoms are −0.0154 (9) and −0.684 (10) Å, respectively. There are weak intermolecular contacts between the Cu^{II} centre, and the C13 and C14 atoms of a neighbouring dimer, with distances of 3.360 (8) [Cu···C13^i; symmetry code: (i) −x, 1 − y, 1 − z] and 3.217 (9) Å (Cu···C14^i). The coordination around the Zn^{II} centre is distorted tetrahedral involving two bridging O atoms and two terminal iodides. The bond angles range from 75.4 (2)° for O1—Zn—O2 to 119.77 (4)° for I1—Zn—I2. A comparison of the dihedral angles (κ) between the bridging plane and the coordination plane around the Cu atom, together with the related distance ranges and bridging angles (φ), can be found in Table 2 for the seven dimeric metal complexes studied recently in this laboratory. The geometric details are comparable with those reported for our previous dimeric and trimeric

structures. The magnetic properties of these compounds are currently under investigation.

Experimental

To a solution of N,N'-bis(salicylidene)-1,3-propanediamine (0.282 g, 1 mmol) in hot ethanol (50 ml), ammonia solution (10 ml) was added and the mixture heated to boiling. A solution of $CuCl_2 \cdot 2H_2O$ (0.170 g, 1 mmol) in hot methanol (20 ml) was added and the resulting mixture set aside. After 3 h, the resulting copper complex was filtered off and dried at 353 K. This complex (0.343 g, 1 mmol) was dissolved in hot dioxane (50 ml) and ZnI_2 (0.320 g, 1 mmol) in hot methanol (20 ml) was added. The resulting mixture was set aside for 4 d and the green crystals which formed were filtered off and dried in air.

Crystal data

$[CuZnI_2(C_{17}H_{16}N_2O_2)]$	Mo $K\alpha$ radiation
$M_r = 663.05$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 13.8200\,(10)$ Å	$\theta = 10.15\text{--}18.08°$
$b = 9.3728\,(11)$ Å	$\mu = 5.41$ mm^{-1}
$c = 15.3080\,(12)$ Å	$T = 295$ K
$\beta = 92.144\,(2)°$	Monoclinic prismatic
$V = 1981.5\,(3)$ Å^3	$0.25 \times 0.15 \times 0.10$ mm
$Z = 4$	Green
$D_x = 2.222$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	2616 reflections with $I > \sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.028$
Absorption correction: empirical *via* ψ scans (Fair, 1990)	$\theta_{max} = 25.22°$
	$h = -16 \rightarrow 0$
	$k = -11 \rightarrow 0$
$T_{min} = 0.371$, $T_{max} = 0.582$	$l = -18 \rightarrow 17$
3895 measured reflections	3 standard reflections
3577 independent reflections	frequency: 120 min
	random variation: 2%

Refinement

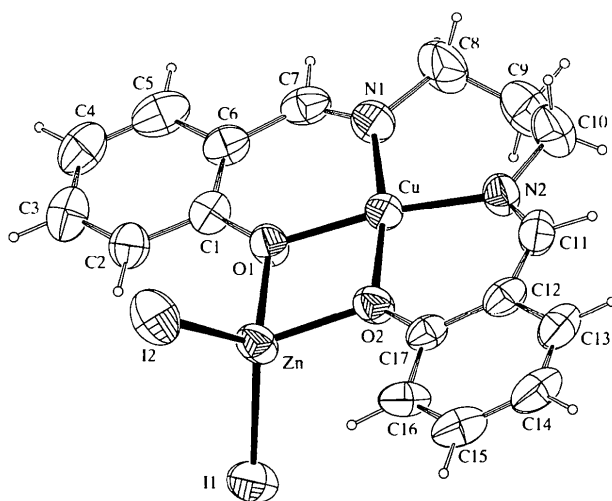|	
Refinement on F	$(\Delta/\sigma)_{max} < 0.001$
$R = 0.040$	$\Delta\rho_{max} = 1.19$ e Å^{-3}
$wR = 0.044$	$\Delta\rho_{min} = -0.25$ e Å^{-3}
$S = 0.98$	Extinction correction: none
2616 reflections	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
226 parameters	
H atoms: see below	
$w = 1/[\sigma F^2 + (0.02F)^2 + 0.25]$, except $w = 0$ if $F^2 < $ cutoff $\times \sigma F^2$, where cutoff is 1.0	

Fig. 1. *PLATON* (Spek, 1998) drawing of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii.

Table 1. *Selected geometric parameters (Å, °)*

Cu—Zn	3.0933 (7)	O2—C17	1.334 (8)
I1—Zn	2.541 (1)	N1—C7	1.28 (1)
I2—Zn	2.538 (1)	N1—C8	1.47 (1)
Zn—O1	2.006 (5)	N2—C10	1.48 (1)

Zn—O2	2.000 (5)	N2—C11	1.28 (1)
Cu—O1	1.939 (5)	C6—C7	1.44 (1)
Cu—O2	1.949 (5)	C8—C9	1.49 (1)
Cu—N1	1.963 (7)	C9—C10	1.49 (1)
Cu—N2	1.969 (6)	C11—C12	1.43 (1)
O1—C1	1.330 (8)		
I1—Zn—I2	119.77 (4)	Zn—O1—C1	125.8 (4)
I1—Zn—O1	113.9 (1)	Cu—O1—C1	130.9 (5)
I1—Zn—O2	111.8 (1)	Zn—O2—Cu	103.1 (2)
I2—Zn—O1	111.5 (1)	Zn—O2—C17	126.7 (4)
I2—Zn—O2	116.3 (1)	Cu—O2—C17	130.0 (4)
O1—Zn—O2	75.4 (2)	Cu—N1—C7	124.2 (5)
O1—Cu—O2	78.1 (2)	Cu—N1—C8	120.8 (6)
O1—Cu—N1	91.2 (2)	C7—N1—C8	115.0 (7)
O1—Cu—N2	169.9 (2)	Cu—N2—C10	122.0 (5)
O2—Cu—N1	169.4 (2)	Cu—N2—C11	123.2 (5)
O2—Cu—N2	91.8 (2)	C10—N2—C11	114.6 (7)
N1—Cu—N2	98.7 (3)	O1—C1—C2	120.0 (7)
Zn—O1—Cu	103.3 (2)	O1—C1—C6	121.2 (6)

Table 2. *Structural data and bridging (φ) and dihedral (κ) angles (Å, °) for seven homo- and hetero-dinuclear metal complexes*

Complex	Bridging M(Cu,Ni)—O	M(Cu,Ni)··· M(Cu,Zn)	φ	κ
(I)	1.941 (5)–1.950 (4)	2.994 (2)	100.6 (2)	5 (1)
(II)	1.930 (1)–1.982 (9)	3.073 (2)	103.5 (4)	11.3 (8)
(III)	1.885 (3)–1.976 (3)	3.021 (2)	102.8 (1)	2.9 (9)– 8.0 (3)
(IV)	1.938 (3)–1.955 (3)	3.047 (6)	103.4 (1)	12.7 (2)
(V)	1.973 (3)–1.974 (2)	3.1013 (7)	102.5 (1)–102.7 (1)	11.4 (4)
(VI)	2.030 (3)–2.039 (2)	3.0753 (7)	98.8 (1)–99.7 (1)	3.5 (9)
(VII)	1.939 (5)–1.949 (5)	3.0933 (7)	103.1 (2)–103.3 (2)	1.9 (3)

Notes: (I) is [Cu₂(C₁₁H₁₀ClNO₂)₂] (Tahir *et al.*, 1996), (II) is [Cu₂(C₁₄H₁₁NO₂)₂] (Ülkü *et al.*, 1997), (III) is [Cu₂(C₁₂H₁₃NO₂)₂] (Atakol *et al.*, 1997), (IV) is [Cu₂(C₁₂H₁₃NO₂)₂] (Ülkü *et al.*, 1998), (V) is [Cu{Zn(C₂₃H₂₁I₂N₃O₂)}] (Ercan *et al.*, 1999), (VI) is [Ni{Zn(C₃₁H₃₄I₂N₄O₂)}] (Arıcı *et al.*, 1999) and (VII) is [Cu{Zn(C₁₇H₁₆I₂N₂O₂)}] (this work).

The H81, H82, H91, H92, H101 and H102 atoms were taken from difference maps, while other H atoms were placed geometrically 0.95 Å from their parent C atoms. A riding model was then used for all H atoms [$U_{iso}(H) = 1.3U_{eq}(C)$]. The highest peak in the final ΔF synthesis was located 0.87 Å from the I2 atom.

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1298). Services for accessing these data are described at the back of the journal.

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Bromotricarbonyl(3,3′-dimethylene-2,2′-biquinoline)rhenium(I)

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Abstract

The mononuclear title compound, bromotricarbonyl(6,7-dihydro-13,14-diazapentaphene-*N,N′*)rhenium(I), [ReBr(C₂₀H₁₄N₂)(CO)₃], presents a rhenium environment with a slightly distorted octahedral geometry: Re—C 1.905 (9), 1.909 (8) and 1.927 (6), Re—N 2.187 (6) and 2.201 (6), and Re—Br 2.6295 (12) Å.

Comment

In the last two decades, a number of structural and co-ordination chemistry studies on transition metal complexes with polypyridinic ligands have been published (Guerrero *et al.*, 1998, and references therein), the interest being driven both by their interesting photophys-