

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Co1—O9	2.066 (3)	P1—O2	1.522 (3)
Co1—O10	2.068 (3)	P1—O3	1.528 (3)
Co1—O11	2.102 (3)	P1—O4	1.519 (3)
Co2—O12	2.061 (3)	N1—C1	1.491 (6)
Co2—O13	2.101 (3)	N2—C2	1.469 (6)
Co2—O14	2.056 (3)	C1—C2	1.499 (7)
P1—O1	1.605 (3)		
O9—Co1—O9 <sup>i</sup>	180	O1—P1—O3	104.4 (2)
O9—Co1—O10	89.4 (1)	O1—P1—O4	107.8 (2)
O9—Co1—O10 <sup>i</sup>	90.6 (1)	O2—P1—O3	112.2 (2)
O10—Co1—O11	91.9 (1)	O2—P1—O4	113.0 (2)
O10—Co1—O11 <sup>i</sup>	88.1 (1)	O3—P1—O4	112.1 (2)
O1—P1—O2	106.7 (2)		

Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
O9—H11...O4 <sup>i</sup>	0.94	1.78	2.690 (4)	162.2
O9—H12...O8 <sup>ii</sup>	0.92	1.86	2.728 (4)	155.9
O10—H13...O7 <sup>iii</sup>	1.01	1.70	2.714 (4)	177.2
O10—H14...O8 <sup>iii</sup>	0.96	1.75	2.702 (4)	172.5
O11—H15...O2 <sup>iii</sup>	0.89	1.82	2.708 (4)	176.1
O11—H16...O4 <sup>ii</sup>	0.95	1.92	2.868 (4)	173.2
O12—H17...O6 <sup>i</sup>	0.87	1.92	2.742 (4)	157.4
O12—H18...O3	0.90	1.80	2.697 (4)	175.1
O13—H19...O2	1.08	1.68	2.754 (4)	173.1
O13—H20...O3 <sup>iv</sup>	0.89	1.89	2.753 (4)	161.0
O14—H21...O6 <sup>iii</sup>	0.97	1.79	2.707 (4)	157.7
O14—H22...O7 <sup>iii</sup>	0.99	1.74	2.725 (4)	172.0
N1—H2...O4 <sup>i</sup>	0.95	1.92	2.859 (4)	170.0
N1—H3...O6 <sup>i</sup>	0.95	1.86	2.764 (5)	158.8
N2—H8...O7 <sup>iv</sup>	0.95	1.76	2.694 (5)	168.9
N2—H9...O2	0.95	1.94	2.867 (5)	163.0
N2—H10...O5	0.95	2.03	2.943 (5)	161.2

Symmetry codes: (i)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (ii)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iv)  $1 + x, y, z$ .

The H atoms in the  $[\text{enH}_2]^{2+}$  cation were calculated and included in the structural model and those in the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cation were found in difference Fourier maps. All H atoms were fixed.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1997). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1152). Services for accessing these data are described at the back of the journal.

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## { $[\mu$ -Bis(salicylidene)-1,3-propanediaminato]-copper(II)}dichlorozinc(II)†

LEYLA TATAR,<sup>a</sup> ORHAN ATAKOL,<sup>b</sup> DİNÇER ÜLKÜ<sup>a</sup> AND MECİT AKSU<sup>b</sup>

<sup>a</sup>Department of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey, and <sup>b</sup>Department of Chemistry, Ankara University, Ankara, Turkey. E-mail: tatar@lidy.cc.hun.edu.tr

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## Abstract

The title compound,  $[\text{CuZnCl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)]$ , is a double oxygen-bridged hetero-dinuclear complex. The  $\text{Cu}^{2+}$  atom has a distorted square-planar environment involving the two O and two N atoms from the bis(salicylidene)-1,3-propanediaminate ( $\text{SALPD}^{2-}$ ) ligand. The average Cu—O distance is 1.940 (3)  $\text{\AA}$  and the average Cu—N distance is 1.966 (3)  $\text{\AA}$ . The coordination around the  $\text{Zn}^{2+}$  atom is distorted tetrahedral, with average Zn—O and Zn—Cl distances of 2.007 (3) and 2.208 (1)  $\text{\AA}$ , respectively. In the bridging plane, the Zn—O1—Cu, Zn—O2—Cu, O1—Zn—O2 and O1—Cu—O2 angles are 102.4 (1), 102.3 (1), 75.0 (1) and 78.1 (1)  $^\circ$ , respectively.

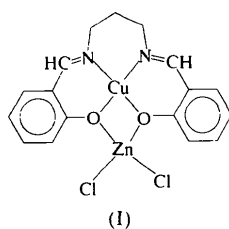
## Comment

Zinc is an essential trace element for all living organisms, especially during development and growth. Therefore, new zinc compounds are the subject of interest in bioinorganic chemistry research (Bertini *et al.*, 1994; Lippard & Berg, 1994).

In the present work, a complex, (I), containing  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions was prepared, and the crystal structure of this new hetero-dinuclear complex determined. Similar hetero-dinuclear complexes have been reported in the

† Systematic name: dichloro- $2\kappa^2\text{Cl}$ - $\mu$ -{2,2'-[1,3-propanediylbis(nitrilomethylidene)]diphenolato}- $1\kappa^4\text{O,N,N',O'}$ : $2\kappa^2\text{O,O'}$ -copper(II)zinc(II).

literature (Kato *et al.*, 1964; Butcher & Sinn, 1976; Aminabhavi *et al.*, 1986).



It is frequently observed that copper complexes have a tendency to dimerize (Kato & Muto, 1988). Dimeric metal complexes with double oxygen bridges also show magnetic superexchange interactions (Ülkü *et al.*, 1998, and references therein). Magnetic superexchange interactions depend on the immediate environment of the bridge, as well as on the ligand arrangement about the metal atoms. The title compound is a product of the reaction between zinc(II) chloride, which is a Lewis acid, and another copper(II)-containing complex (Lewis base). The Cu<sup>II</sup> atom has a distorted square-planar environment, coordinated by the two N [Cu—N1 1.960 (3) and Cu—N2 1.971 (3) Å] and two O atoms [Cu—O1 1.942 (3) and Cu—O2 1.938 (3) Å] of the SALPD<sup>2-</sup> ligand (Fig. 1). The Cu atom is located 0.0207 (5) Å from the coordination plane. The bond angles O1—Cu—N2 [169.9 (1)°] and O2—Cu—N1 [168.3 (1)°] deviate by approximately 11° from linearity.

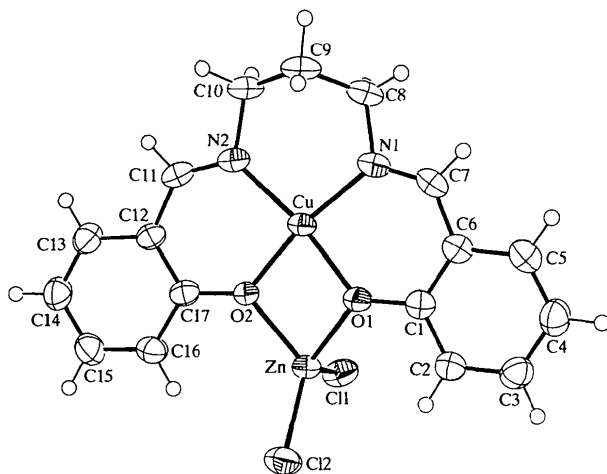


Fig. 1. ORTEP-3 (Farrugia, 1997) drawing of [Cu{Zn(C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>)}] with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

The Zn<sup>II</sup> atom has a distorted tetrahedral coordination, which is common for zinc(II) and copper(II) complexes (Greenwood & Earnshaw, 1994). The Cu...Zn

distance [3.0757 (6) Å] is long for a direct interaction. The bridging plane (Cu—O1—Zn—O2) and the coordination plane (O1—O2—N1—N2) around the Cu atom form a dihedral angle of 8.6 (5)° with respect to one another. The Cu—O1—Cu—O2 bridging plane in the corresponding copper complexes (Butcher & Sinn, 1976; Atakol *et al.*, 1997) is planar. The bridging plane (Cu—O1—Zn—O2) in the title compound is not planar. The dihedral angle between the O1—Cu—O2 and O1—Zn—O2 planes is 14.0 (4)°. The bond lengths and angles of the ligand show no unusual values. Coordination bond lengths (Cu—O, Cu—N, Zn—O and Zn—Cl) are comparable with those reported previously (Butcher & Sinn, 1976; Atakol *et al.*, 1997, 1999; Ülkü *et al.*, 1998; Uhlenbrock *et al.*, 1996; Zelenák *et al.*, 1996).

## Experimental

The title compound was prepared in two steps. Bis(salicylidene)-1,3-diaminopropane (1.410 g, 0.005 mol) was dissolved in hot ethanol (50 ml), and ammonia solution (20%, 10 ml) was added with stirring. A solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.850 g, 0.005 mol) in hot water (30 ml) was then added and the resulting solution set aside. After 24 h, crystals of C<sub>17</sub>H<sub>16</sub>CuN<sub>2</sub>O<sub>2</sub> were filtered off and dried in an oven at 353 K. The crystals obtained (0.344 g, 0.001 mol) were dissolved in 1,4-dioxane (60.0 ml) and heated to boiling point. To this solution, ZnCl<sub>2</sub> (0.136 g, 0.001 mol) in methanol (10 ml) was added and the resulting solution set aside for 24 h. The crystals which formed were filtered off and dried in air. Elemental analysis for C<sub>17</sub>H<sub>16</sub>Cl<sub>2</sub>CuN<sub>2</sub>O<sub>2</sub>Zn: calculated Cu 13.24, Zn 13.62, N 5.83, Cl 14.77%; observed Cu 13.19, Zn 13.79, N 5.49, Cl 14.63%.

## Crystal data

[CuZnCl<sub>2</sub>(C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>)]  
*M<sub>r</sub>* = 480.158  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 11.6166 (9) Å  
*b* = 8.2634 (8) Å  
*c* = 18.2929 (18) Å  
 $\beta$  = 98.856 (7)°  
*V* = 1734.9 (3) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.8382 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 11.24–18.11°  
 $\mu$  = 2.929 mm<sup>-1</sup>  
*T* = 295 K  
 Prismatic  
 0.175 × 0.125 × 0.125 mm  
 Green

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: empirical *via*  $\psi$  scans (Fair, 1990)  
 $T_{\min}$  = 0.657,  $T_{\max}$  = 0.690  
 4622 measured reflections  
 4492 independent reflections

2442 reflections with  $I > 3\sigma(I)$   
 $R_{\text{int}}$  = 0.019  
 $\theta_{\text{max}}$  = 28.52°  
 $h = -15 \rightarrow 15$   
 $k = 0 \rightarrow 10$   
 $l = 0 \rightarrow 24$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 0.035%

**Refinement**

Refinement on $F$	$(\Delta/\sigma)_{\max} < 0.001$
$R = 0.031$	$\Delta\rho_{\max} = 0.343 \text{ e } \text{Å}^{-3}$
$wR = 0.038$	$\Delta\rho_{\min} = -0.240 \text{ e } \text{Å}^{-3}$
$S = 0.99$	Extinction correction: none
2442 reflections	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
226 parameters	
H atoms: see below	
$w = 1/[\sigma^2(F^2) + (0.020F)^2 + 0.075]$	

Table 1. Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ )

Zn—Cu	3.0757 (6)	Cu—N2	1.971 (3)
Zn—Cl1	2.208 (1)	O1—C1	1.339 (5)
Zn—Cl2	2.208 (1)	O2—C17	1.333 (5)
Zn—O1	2.004 (3)	N1—C7	1.286 (5)
Zn—O2	2.010 (3)	N1—C8	1.477 (5)
Cu—O1	1.942 (3)	N2—C10	1.497 (5)
Cu—O2	1.938 (3)	N2—C11	1.282 (6)
Cu—N1	1.960 (3)		
Cl1—Zn—Cl2	116.46 (5)	O1—Cu—N1	91.2 (1)
Cl1—Zn—O1	108.6 (1)	O1—Cu—N2	169.9 (1)
Cl1—Zn—O2	112.6 (1)	O2—Cu—N1	168.3 (1)
Cl2—Zn—O1	119.54 (9)	O2—Cu—N2	92.2 (1)
Cl2—Zn—O2	117.82 (9)	N1—Cu—N2	98.7 (1)
O1—Zn—O2	75.0 (1)	Zn—O1—Cu	102.4 (1)
O1—Cu—O2	78.1 (1)	Zn—O2—Cu	102.3 (1)

Ring H atoms were placed geometrically 0.95 Å from their parent atoms, while the other H atoms were taken from a difference map. For all H atoms, a riding model was used with  $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$ .

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP-3* (Farrugia, 1997). 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: SK1278). Services for accessing these data are described at the back of the journal.

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**{[ $\mu$ -Bis(salicylidene)-1,3-propanediaminato](3-methylpyridine)copper(II)-diiodozinc(II)} $\dagger$**

FILIZ ERCAN,<sup>a</sup> CENGİZ ARICI,<sup>a</sup> ABDÜLKADIR AKAY,<sup>b</sup> ORHAN ATAKOL<sup>b</sup> AND DİNÇER ÜLKÜ<sup>a</sup>

<sup>a</sup>Department of Physics Engineering, Hacettepe University, Beytepe 06532, Ankara, Turkey, and <sup>b</sup>Department of Chemistry, Ankara University, Tandogan 06100, Ankara, Turkey. E-mail: dulku@eti.cc.hun.edu.tr

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**Abstract**

The title complex,  $[\text{CuZnI}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)(\text{C}_6\text{H}_7\text{N})]$ , consists of a doubly oxygen-bridged heteronuclear dimeric complex. The Cu atom has a distorted square-pyramidal environment involving two O atoms and two N atoms of the bis(salicylidene)-1,3-propanediaminate ( $\text{SALPD}^{2-}$ ) ligand, and an N atom of the 3-methylpyridine group. The Cu—O distances in the coordination plane are 1.973 (3) and 1.974 (2) Å, and the average Cu—N distance is 2.088 (4) Å. In the bridging plane, the Cu—O—Zn, O—Zn—O, Zn—O—Cu and O—Cu—O angles are 102.5 (1), 76.7 (1), 102.7 (1) and 77.9 (1) $^\circ$ , respectively. The dihedral angle between the coordination plane around the Cu atom and the 3-methylpyridine group is 88.4 (1) $^\circ$ . The Cu—Zn distance is 3.1013 (7) Å.

**Comment**

Binuclear and trinuclear metal complexes based on Schiff base ligands are of interest because of the magnetic superexchange interactions between the bridged metal ions. These polynuclear complexes have been the subject of considerable interest in our laboratory,

$\dagger$  Alternative name: diiodo- $2\kappa^2I$ -(3-methylpyridine- $1\kappa N$ )- $\mu$ -{ $2,2'$ -[1,3-propanediylbis(nitriomethylidyne)]diphenolato}- $1\kappa^4O, N, N', O'$ : $2\kappa^2-O, O'$ -copper(II)zinc(II).